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Mechanical Force for the Transformation of Aziridine into Imine

Sangmin Jung, and Hyo Jae Yoon*

Abstract: Force-selective mechanochemical reactions may be important for applications in polymer mechanochemistry, yet it is difficult to achieve such reactions. This paper reports that *cis*-N-phthalimidoaziridine incorporated into a macromolecular backbone undergoes migration of N-phthalimido group to afford imine under mechanochemical condition and not thermal one. The imine is further hydrolyzed by water bifurcating into amine and aldehyde. These structural transformations are confirmed by ^{1}H NMR and FT-IR spectroscopic analyses. Computational simulations are conducted for the aziridine mechanophore to propose the mechanism of reaction and define the substrate scope of reaction.

Polymer mechanochemistry permits access to mechanochemical activation of latent catalysts,[1] stress-sensing,[2] materials transfer,[3] drug release,[4] changes in optical and electrical properties,[5] and degradation of polymer.[6] It also provides the ability to steer chemical reactions toward routes that are forbidden under traditional photochemical and thermal conditions.[7] The utility and application scope of polymer mechanochemistry depend on covalent mechanophores designed to facilitate chemical transformations upon exposure to external force.[8] Mechanochemical reactions that have been reported thus far can be categorized as follows: i) retro-[2+2],[9] [4+2],[10] and [4+4] cycloadditions,[11] ii) 2π,[7a, 7b, 12] 4π,[7c, 13] and 6π electrocyclic ring opening reactions,[14] iii) homolytic reactions[15] and iv) heterolytic reactions.[16]

As summarized in Table S1, many mechanophores respond to both thermal and photochemical stimuli, yet the reaction routes differ from each other. Such a universal sensitivity of mechanophore makes it difficult to couple orthogonally mechanochemical reactions with other reactions that proceed under traditional thermal and photochemical conditions. A handful of studies have reported on mechanical force-selective activation of mechanophores (Table S2).

Here we show force-selective migration in N-phthalimidoaziridine incorporated into an aliphatic macromolecular backbone (Scheme 1). A pulling force along the backbone transduced by ultrasonication activates the aziridine ring structure and induces migration of N-phthalimido group, yielding the corresponding imine. Once the reaction is coupled with the scenario of hydrolytic cleavage in ambient conditions, the polymer backbone bifurcates into amine and aldehyde. These sequential reactions are verified by chemical structure analysis of polymers using ^{1}H NMR and FT-IR spectroscopies. Computational simulations are employed to understand the mechanism and the substrate scope of our mechanochemical reaction.

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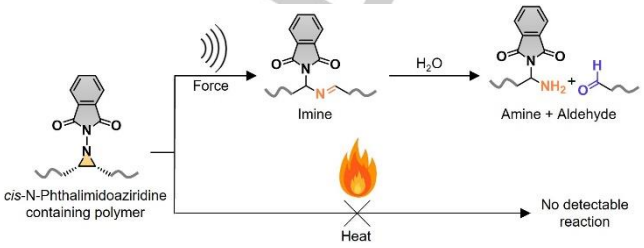

Scheme 1. Mechanical force selective transformation of N-phthalimidoaziridine into imine.

Our group has recently probed the potential of aziridine for a mechanophore.[7a] The trivalency of nitrogen atom allows one to fine-tune reactivity of aziridine.[17] To design force-sensitive and thermal-insensitive aziridine mechanophore, we focused on aziridine with N-phthalimido moiety. Under thermal condition, N-phthalimidoaziridine with C-aryl substituents undergoes 1,2-migration of N-phthalimido group to afford an imine.[18] When aryl group is substituted on the aziridine carbon, the azomethine ylide intermediate formed under thermal conditions can be stabilized.[18b] We hypothesized that, if the stabilizing aryl substituents are replaced with alkyl ones, the aziridine are inactive under thermal conditions.

We synthesized the polymer containing *cis*-N-phthalimidoaziridine (**P** in Figure 1A). An enantiopure eight-membered cyclic monomer containing *cis*-N-phthalimidoaziridine (**M** in Figure 1A) was prepared from *cis*,*cis*-1,5-cyclobutadiene in one step. The desired chemical structure and stereochemistry were confirmed by ^{1}H and ^{13}C NMR spectroscopies and high-resolution mass spectrometry (HRMS). The proton resonance of aziridine's carbon at δ = 2.62 ppm was indicative of formation of the desired aziridine ring (Figure 1B). Entropically driven ring opening metathesis polymerization (ED-ROMP) of compound **M** and *cis*-cyclooctene at 1:1 molar ratio in the presence of Grubbs 2nd generation catalyst yielded *cis*-N-phthalimidoaziridine embedded copolymer (**P**). ^{1}H NMR analysis indicated that the molar ratio of monomers was reflected into the polymer chain structure. The proton resonance of the aziridine carbon in the copolymer **P** was observed at δ = 2.59 ppm (Figure 1B), consistent with that of monomer **M** and indicative of the retention of aziridine ring structure after the polymerization. Figure 1C shows the size exclusion chromatography (SEC) trace of copolymer **P**; the number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) were revealed to be 81.3 kDa, 487.7 kDa, and 6.0, respectively. The Supporting Information contains detailed synthetic procedures and analytical data.

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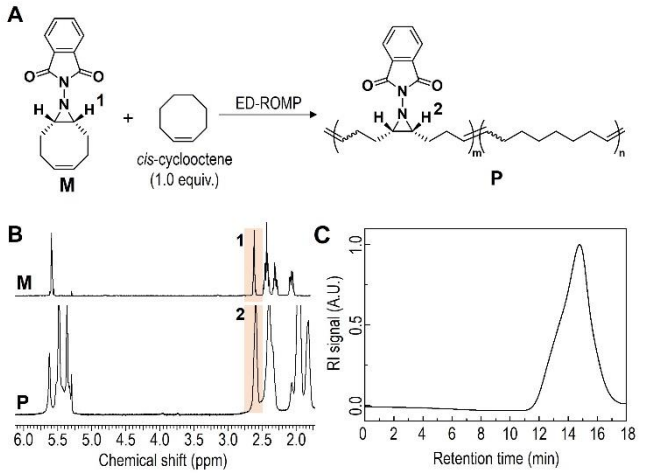

Figure 1. A) Synthesis of *cis*-N-phthalimidoaziridine embedded copolymer (**P**) from 8-membered cyclic monomer (**M**) through ED-ROMP. B) Comparison of ^{1}H NMR spectra for monomer **M** and polymer **P**. C) Size exclusion chromatography (SEC) trace of **P**.

For mechanochemical experiments, ultrasound (20 kHz, 30 % amplitude; pulse sequence: 1 sec on / 1 sec off; power intensity: 10.26 W/cm^2) was applied to the copolymer **P** dissolved in anhydrous THF at 4-8 °C under N_2 atmosphere for 2 h. ^{1}H NMR analysis revealed the appearance of new proton resonances at δ = 7.79, 7.40 and 7.33 ppm (**d**-**f** in Figure 2C). To confirm the formation of imine, ^{1}H NMR spectrum of **P1** was compared with that of model imine compound (**Model 4**): the **f** peak was consistent with the imine proton at δ = 7.79 ppm, indicative of imine formation (Figure 2C, D). Additional new peaks were detected at δ = 9.76, 7.85, 7.76, and 5.24 ppm (orange squares in Figure 2C), which were attributed to the formation of aldehyde and amine species resulting from unexpected decomposition of imine via hydrolysis with adventitious water. To evaluate the thermal stability of copolymer **P**, its toluene solution was refluxed for 24 h (**P2** in Figure 2A). There was no detectable change in ^{1}H NMR (Figure 2E) and FT-IR (Figure S4C in the Supporting Information) spectra compared to the intact copolymer **P**. This indicates the 1,2-dialkyl-substituted *cis*-N-phthalimidoaziridine is reactive under mechanochemical condition and not thermal condition, within the detection limits of NMR and FT-IR spectroscopies.

The imine resulting from the force-induced migration reaction underwent hydrolytic cleavage, bifurcating into amine and aldehyde (Figure 3A). Upon addition of water (5.0 % v/v) into the THF solution containing the imine product **P1** (1 mg/mL) in ambient conditions, the intensity of proton resonance at δ = 9.76, which corresponded to the aldehyde proton, significantly increased while the intensity of imine proton peak at δ = 7.79 ppm was significantly reduced (**f** in Figure 3C). The ^{1}H NMR spectrum of hydrolytic product **P1'** was further compared with those of model aldehyde and amine compounds (**Model 2** and **3** in Figure 3D and E, respectively). The comparison indicated that the **g**-**j** peaks in **P1'** corresponded to the aldehyde and amine species (Figure 3C-E).

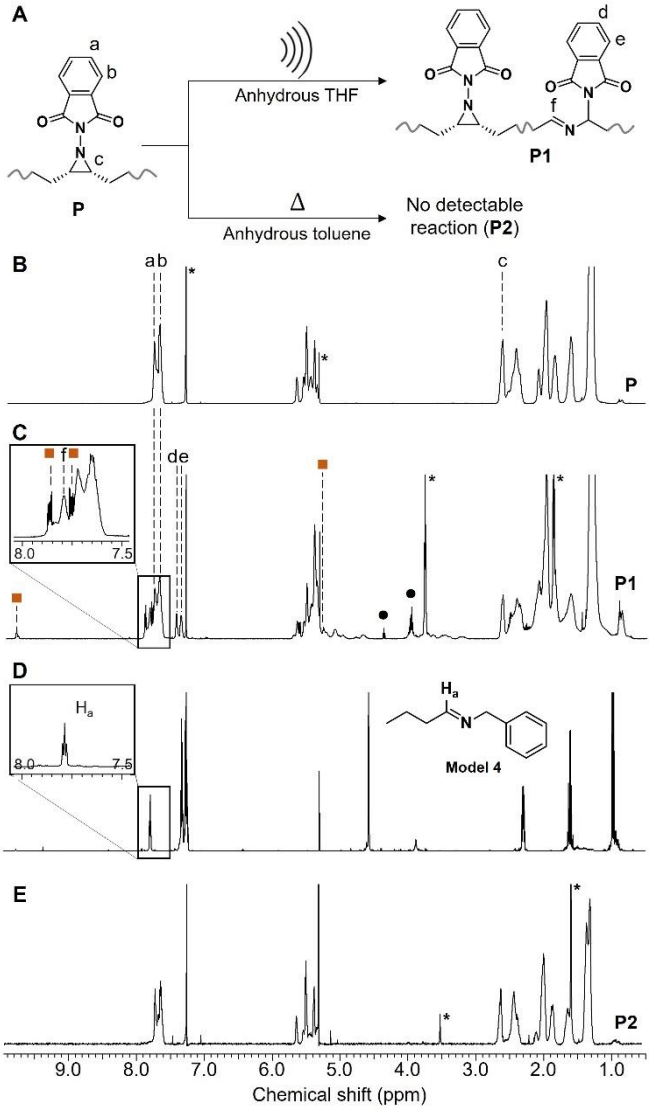

Figure 2. A) Mechanochemical and thermal reactions of **P** to yield products **P1** and **P2**, respectively. B-E) Comparison of ^{1}H NMR spectra for **P**, **P1**, **Model 4**, and **P2**. Asterisk indicates the residual solvent peaks; black circles are attributed to undesirable chain scission of polymer backbone (and/or its reaction with THF solvent) by ultrasonication. Orange squares are peaks of hydrolysis products (see Figure 3 for details).

The amine proton was difficult to observe in ^{1}H NMR spectroscopic analysis. The occurrence of amine was confirmed through FT-IR spectroscopy (Figure 3F). The absorption peaks at 3210, 1710, 1375 and 1310 cm^{-1} were attributed to –NH_2, phthalimido group's C=O, aziridine's C-N, and the C-N bond of migrated phthalimido group, respectively (①-④ in Figure 3F). Molecular weight analysis before and after the hydrolysis revealed reduced M_n by 28.0 % (Figure S9A). There were no detectable changes in ^{1}H NMR and FT-IR spectra when **P2** was exposed to the same hydrolytic condition (Figure S4B and S4C).

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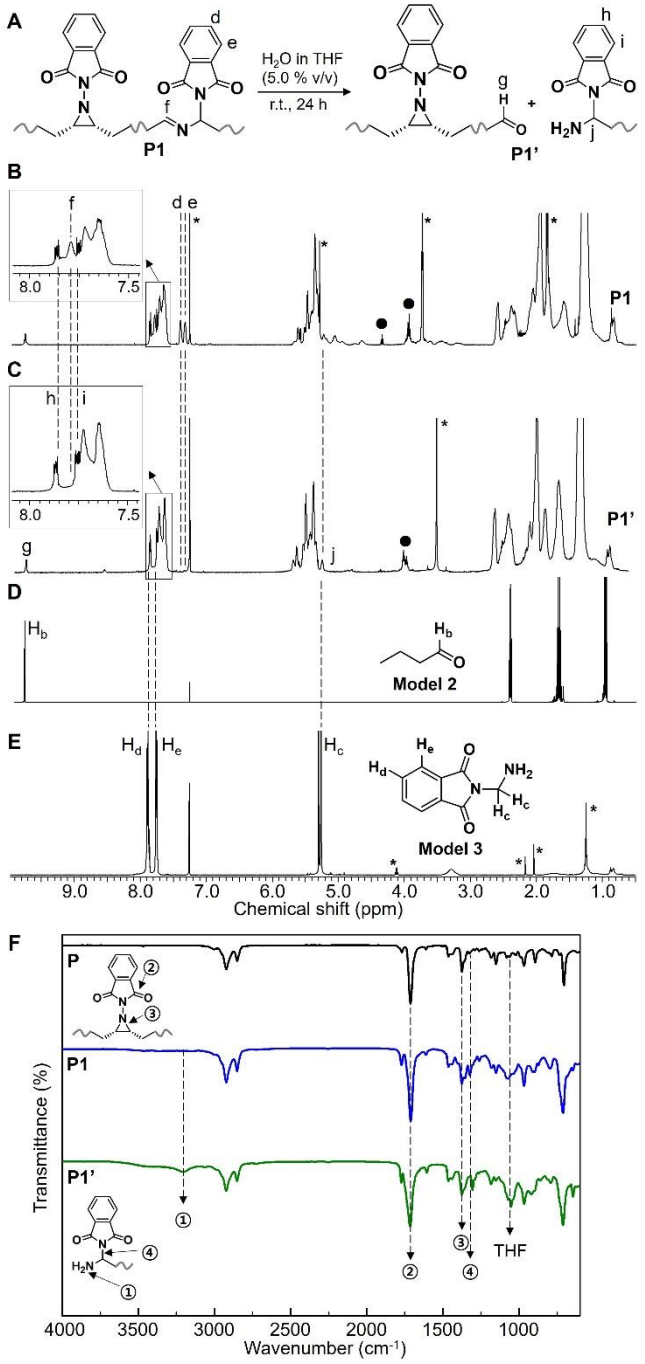

Figure 3. A) Hydrolysis of **P1** into **P1'**. B-E) Comparison of ^{1}H NMR spectra among **P1**, **P1'**, and model compounds (**Model 2** and **3**). F) Comparison of FT-IR spectra among **P**, **P1**, and **P1'**. Asterisk indicates the residual solvent peaks; black circles are attributed to undesirable chain scission of polymer backbone (and/or its reaction with THF solvent) by ultrasonication.

The mechanism of our reaction was further examined by constrained geometries simulate external force (CoGEF) calculation using density functional theory (DFT) at the B3LYP/6-31G* level with the model structure (*cis*-N-phthalimidoaziridine with alkyl side chains; Figure 4A).[19] In simulation, the distance between terminal methyl substituents (*d*, Å) gradually increased. At the initial stage (i-ii region in Figure 4), the increase in Δ*d* (an increase in *d* relative to the intact structure) led to a gradual increase in the relative energy of the system (Figure 4B) and exponential increase in the N−N bond length and aziridine's C-C bond length (Figure 4C). At Δ*d* = 1.50 Å (iii in Figure 4), the C-C bond of aziridine was finally cleaved while the N-N bond was not, suggesting the formation of ylide intermediate. Upon the C-C bond cleavage, the natural atomic charge (NAC) of aziridine's carbons and phthalimido's nitrogen showed sharp decrease and increase (Figure 4D, E), indicative of electron-rich and deficient charge states, respectively. This charge unbalance seems to induce migration of phthalimido group (Figure 4F). Nonetheless, we believe that further experimental and computational studies are needed to clarify the detailed mechanisms of our migration reactions: particularly, whether ylide is indeed formed in our reaction, and, if yes, whether its structure is identical with the one formed under thermal conditions.[18a, 20]

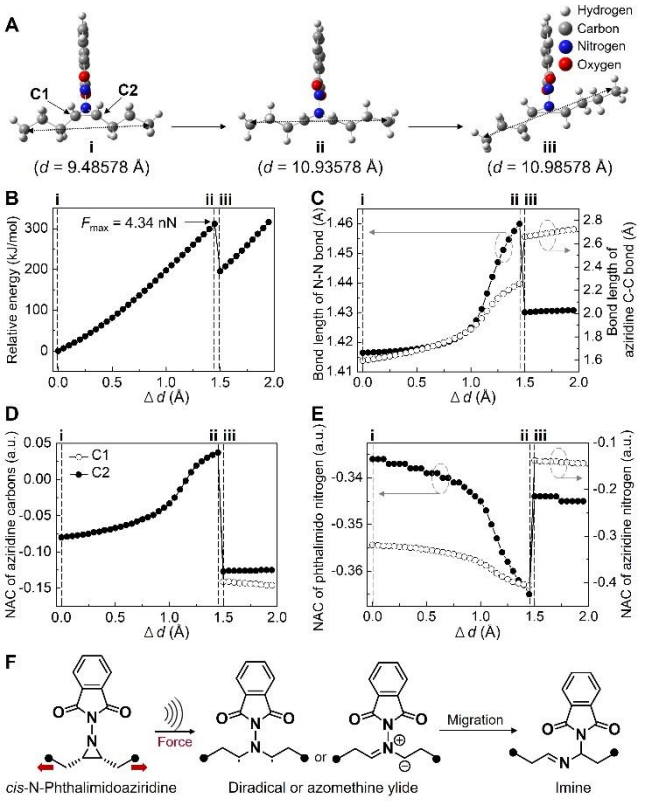

Figure 4. Simulation of tensile stress-induced structural changes in *cis*-N-phthalimidoaziridine. A) Increase in the distance between terminal methyl groups (*d*, Å). B) Plots of relative energy as a function of the change in *d* relative to intact aziridine (Δ*d*, Å). C) Plots of the N-N bond length (filled circle) and aziridine's C-C bond length (open circle). D) Plots of NAC of the aziridine's two carbon atoms. E) Plots of NAC of the phthalimido group's nitrogen (filled circle) and aziridine's nitrogen atoms (open circle). Note that the former bond persist as an artifact in Gaussian after a reaction is predicted to occur. F) Plausible mechanism for structural transformation of N-phthalimidoaziridine into imine.

We reconciled our simulation results with the literature. In our simulation with the *cis*-aziridine, F_{max}—the parameter enabling relative comparison of mechanochemical reactivity between different mechanophores[19b]—was revealed to be 4.34 nN. Recently, theoretical work by Robb[19b] revealed that 2π electrocyclic mechanophores such as aziridine and *gem*-dichlorocyclopropane (*g*DCC) can undergo mechanochemical

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transformation reactions in the range of 3.2 - 5.7 nN. Our calculated F_{max} value fell into the range, proving the mechanochemical activation at the C-C bond of aziridine.

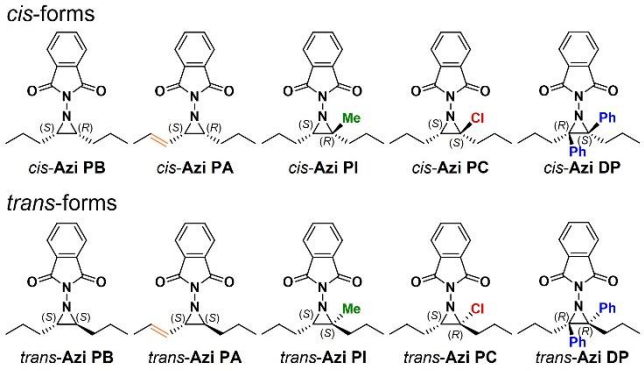

Figure 5. N-Phthalimidoaziridine derivatives that can be derived from widely used synthetic olefinic polymers.

Table 1. CoGEF simulation results for the aziridines presented in Figure 5.

Stereochemistry	Structure	Activation of aziridine C-C bond	F_{max} (nN)
cis	**Azi PB**	O	4.34
	Azi PA	O	2.77
	Azi PI	O	3.70
	Azi PC	O	3.70
	Azi DP	O	2.54
trans	**Azi PB**	O	5.61
	Azi PA	O	6.18
	Azi PI	O	5.45
	Azi PC	O	5.07
	Azi DP	X	-

The substrate scope of our reaction was evaluated by conducting CoGEF calculations over N-phthalimidoaziridine derivatives that can be formed on widely used synthetic olefinic polymers—polybutadiene (**PB**), polyacetylene (**PA**), polyisoprene (**PI**), polychloroprene (**PC**), and diphenyl polyene (**DP**). If aziridine can be introduced into the synthetic polymers through top-down approach and coupled with the repertoire of simple hydrolysis, our migration reaction can be a new mechanochemical gate for developing degradable or activatable polymers. We performed CoGEF simulations over N-phthalimidoaziridine derivatives shown in Figure 5 and obtained F_{max} values. As summarized in Table 1, all the aziridines exhibited higher F_{max} values (by 1.27 – 3.41 nN) in *trans*-isomers than *cis*-isomers, which is consistent with the findings by Craig and Robb.[7c, 19b]The F_{max} values of our aziridines were lower than 5.7 nN, proving their potential as a mechanophore, except the *trans*-**Azi PA** and *trans*-**Azi DP**.

In the simulation, *trans*-**Azi DP** underwent a bond scission in the C-C bond of alkyl substituent and aziridine carbon, rather than the aziridine's C-C bond, implying its low mechanochemical reactivity. Such a competition between desired and undesired covalent bonds has been previously observed in epoxide mechanophores.[7b, 21] It is noteworthy that, due to this reason, the mechanochemical ring opening reaction of epoxide mechanophores cannot be simulated by CoGEF.[19b] Despite the high value of F_{max} (6.18 nN; Table 1), *trans*-**Azi PA** exhibited cleavage of the aziridine's C-C bond, which indicates that the F_{max} value required for the mechanochemical 2π electrocyclic ring opening reactions of three-membered ring mechanophores may have a value greater than what Robb has proposed (5.7 nN).[19b]

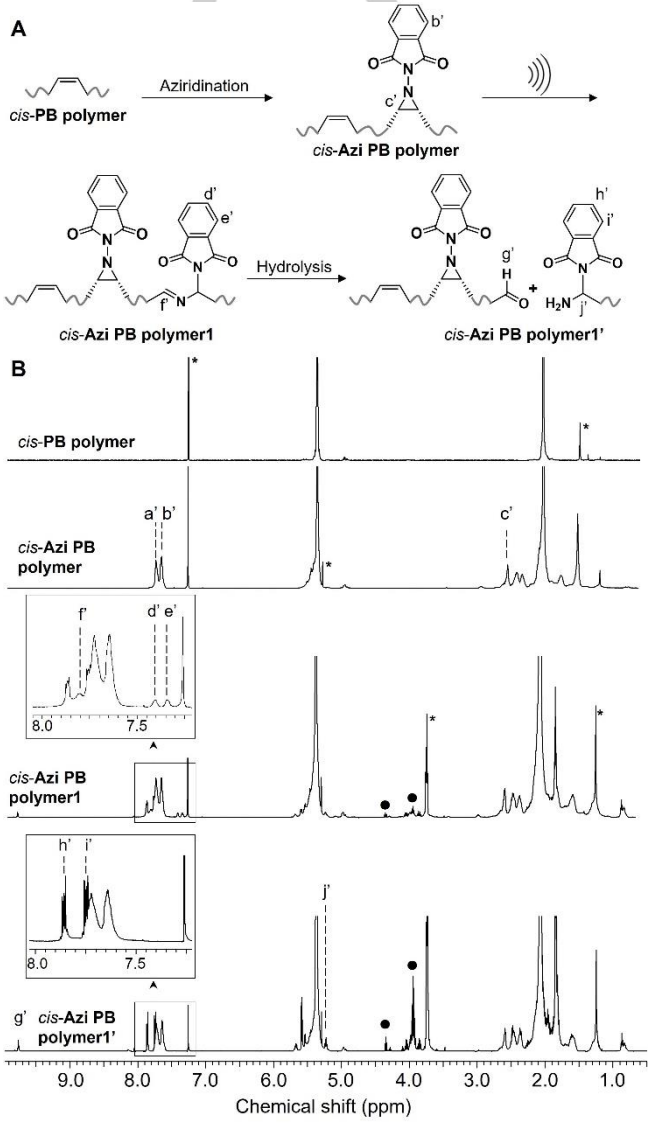

Figure 6. A) Aziridination of *cis*-**PB polymer** and sequential mechanochemical and hydrolysis reactions of *cis*-**Azi PB polymer**. B) The ^{1}H NMR characterization of activated species in *cis*-**Azi PB polymer**. Asterisk indicates the residual solvent peaks; black circles are attributed to undesirable chain scission of polymer backbone (and/or its reaction with THF solvent) by ultrasonication.

To verify the simulation results, *cis*-**PB polymer** (Figure 6) was post-modified to have N-phthalimidoaziridine through oxidative addition of N-aminophthalimide. Force was applied to

the resulting *cis*-**Azi PB polymer** under the same conditions as those of compound **P**. The ^{1}H NMR spectrum showed the imine peak at 7.80 ppm (denoted as **f'** in Figure 6). When *cis*-**Azi PB polymer1** was hydrolyzed, the imine peak (**f'**) disappeared, and peak intensities of protons **j'** and **g'** in amine and aldehyde species were increased (*cis*-**Azi PB polymer1'** in Figure 6B). Each peak shown in Figure 6B was assigned based on the comparison with the model compounds. Molecular weight analysis indicated reduced M_n upon the hydrolysis (Figure S9C).

In summary, we have shown transformation of N-phthalimidoaziridine into imine via 1,2-migration of the N-phthalimido group, triggered by force and not heating. The force activates the bond whose axis is orthogonal to the direction of applied force, similar to the previous results reported by Craig[12, 22] and Boulatov.[23] Our method can be useful, once coupled with hydrolytic bond cleavage, as it enables cleavage of olefinic polymers via mechanochemical gating.

Acknowledgements

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Keywords: aziridines • mechanochemistry • polymers • reaction mechanisms • structure elucidation

[1] a) A. Piermattei, S. Karthikeyan, R. P. Sijbesma, *Nat. Chem.* **2009**, *1*, 133-137; b) K. Wei, Z. C. Gao, H. R. Liu, X. J. Wu, F. Wang, H. X. Xu, *ACS Macro Lett.* **2017**, *6*, 1146-1150; c) S. Y. Wu, T. Wang, H. X. Xu, *ACS Macro Lett.* **2020**, *9*, 1192-1197.

[2] a) E. M. Nofen, A. Dasgupta, N. Zimmer, R. Gunckel, B. Koo, A. Chattopadhyay, L. L. Dai, *Polym. Eng. Sci.* **2017**, *57*, 901-909; b) R. Sandoval-Torrientes, T. R. Carr, G. De Bo, *Macromol. Rapid Commun.* **2021**, *42*, 2000447.

[3] a) Y. Ren, A. A. Banishev, K. S. Suslick, J. S. Moore, D. D. Dlottt, *J. Am. Chem. Soc.* **2017**, *139*, 3974-3977; b) M. Di Giannantonio, M. A. Ayer, E. Verde-Sesto, M. Lattuada, C. Weder, K. M. Fromm, *Angew. Chem. Int. Edit.* **2018**, *57*, 11445-11450.

[4] a) X. R. Hu, T. Zeng, C. C. Husic, M. J. Robb, *J. Am. Chem. Soc.* **2019**, *141*, 15018-15023; b) S. D. Huo, P. K. Zhao, Z. Y. Shi, M. C. Zou, X. T. Yang, E. Warszawik, M. Loznik, R. Gostl, A. Herrmann, *Nat. Chem.* **2021**, *13*, 131-139; c) Y. Q. Zhang, J. C. Yu, H. N. Bomba, Y. Zhu, Z. Gu, *Chem. Rev.* **2016**, *116*, 12536-12563.

[5] a) J. H. Yang, M. Horst, J. A. H. Romaniuk, Z. X. Jin, L. Cegelski, Y. Xia, *J. Am. Chem. Soc.* **2019**, *141*, 6479-6483; b) W. Chen, Y. Yuan, Y. L. Chen, *ACS Macro Lett.* **2020**, *9*, 438-442; c) J. Kida, K. Imato, R. Goseki, D. Aoki, M. Morimoto, H. Otsuka, *Nat. Commun.* **2018**, *9*, 3504.

[6] a) T. G. Hsu, J. F. Zhou, H. W. Su, B. R. Schrage, C. J. Ziegler, J. P. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 2100-2104; b) Y. J. Lin, T. B. Kouznetsova, C. C. Chang, S. L. Craig, *Nat. Commun.* **2020**, *11*, 4987; c) Y. J. Lin, T. B. Kouznetsova, S. L. Craig, *J. Am. Chem. Soc.* **2020**, *142*, 2105-2109; d) J. Yang, Y. Xia, *Chem. Sci.* **2021**, 4389-4394.

[7] a) S. M. Jung, H. J. Yoon, *Angew. Chem. Int. Edit.* **2020**, *59*, 4883-4887; b) H. M. Klukovich, Z. S. Kean, A. L. B. Ramirez, J. M. Lenhardt, J. X. Lin, X. Q. Hu, S. L. Craig, *J. Am. Chem. Soc.* **2012**, *134*, 9577-9580; c) J. P. Wang, T. B. Kouznetsova, Z. B. Niu, M. T. Ong, H. Klukovich, A. L. Rheingold, T. J. Martinez, S. L. Craig, *Nat. Chem.* **2015**, *7*, 323-327.

[8] G. Cravotto, E. C. Gaudino, P. Cintas, *Chem. Soc. Rev.* **2013**, *42*, 7521-7534.

[9] a) M. F. Pill, K. Holz, N. Preusske, F. Berger, H. Clausen-Schaumann, U. Luning, M. K. Beyer, *Chem. Eur. J.* **2016**, *22*, 12034-12039; b) J. H. Yang, M. Horst, S. H. Werby, L. Cegelski, N. Z. Burns, Y. Xia, *J. Am. Chem. Soc.* **2020**, *142*, 14619-14626.

[10] a) A. Khanal, F. Long, B. Cao, R. Shahbazian-Yassar, S. Y. Fang, *Chem. Eur. J.* **2016**, *22*, 9760-9767; b) H. Y. Duan, Y. X. Wang, L. J. Wang, Y. Q. Min, X. H. Zhang, B. Y. Du, *Macromolecules* **2017**, *50*, 1353-1361; c) X. R. Hu, M. E. McFadden, R. W. Barber, M. J. Robb, *J. Am. Chem. Soc.* **2018**, *140*, 14073-14077.

[11] a) Y. K. Song, K. H. Lee, W. S. Hong, S. Y. Cho, H. C. Yu, C. M. Chung, *J. Mater. Chem.* **2012**, *22*, 1380-1386; b) D. Y. Wu, L. P. Zhang, L. Z. Wu, B. J. Wang, C. H. Tung, *Tetrahedron Lett.* **2002**, *43*, 1281-1283.

[12] J. M. Lenhardt, A. L. Black, B. A. Beiermann, B. D. Steinberg, F. Rahman, T. Samborski, J. Elsakr, J. S. Moore, N. R. Sottos, S. L. Craig, *J. Mater. Chem.* **2011**, *21*, 8454-8459.

[13] C. R. Hickenboth, J. S. Moore, S. R. White, N. R. Sottos, J. Baudry, S. R. Wilson, *Nature* **2007**, *446*, 423-427.

[14] a) M. E. McFadden, M. J. Robb, *J. Am. Chem. Soc.* **2019**, *141*, 11388-11392; b) B. A. Versaw, M. E. McFadden, C. C. Husic, M. J. Robb, *Chem. Sci.* **2020**, *11*, 4525-4530.

[15] a) J. M. Lenhardt, M. T. Ong, R. Choe, C. R. Evenhuis, T. J. Martinez, S. L. Craig, *Science* **2010**, *329*, 1057-1060; b) T. Sumi, R. Goseki, H. Otsuka, *Chem. Commun.* **2017**, *53*, 11885-11888; c) Z. X. Chen, X. L. Zhu, J. H. Yang, J. A. M. Mercer, N. Z. Burns, T. J. Martinez, Y. Xia, *Nat. Chem.* **2020**, *12*, 302-309.

[16] a) R. Nixon, G. De Bo, *Nat. Chem.* **2020**, *12*, 826-831; b) Z. J. Wang, Z. Y. Ma, Y. Wang, Z. J. Xu, Y. Y. Luo, Y. Wei, X. R. Jia, *Adv. Mater.* **2015**, *27*, 6469-6474.

[17] a) S. Kang, H. K. Moon, H. J. Yoon, *Macromolecules* **2018**, *51*, 4068-4076; b) S. Jung, S. Kang, J. Kuwabara, H. J. Yoon, *Polym. Chem.* **2019**, *10*, 4506-4512; c) H. K. Moon, S. Kang, H. J. Yoon, *Polym. Chem.* **2017**, *8*, 2287-2291; d) H. J. Jang, J. T. Lee, H. J. Yoon, *Polym. Chem.* **2015**, *6*, 3387-3391.

[18] a) A. S. Pankova, M. V. Sorokina, M. A. Kuznetsov, *Tetrahedron Lett.* **2015**, *56*, 5381-5385; b) M. A. Kuznetsov, A. S. Pan'kova, V. V. Voronin, N. A. Vlasenko, *Chem. Heterocycl. Compd.* **2012**, *47*, 1353-1366.

[19] a) M. K. Beyer, *J. Chem. Phys.* **2000**, *112*, 7307-7312; b) I. M. Klein, C. C. Husic, D. P. Kovacs, N. J. Choquette, M. J. Robb, *J. Am. Chem. Soc.* **2020**, *142*, 16364-16381.

[20] H. Person, A. Foucaud, K. Luanglath, C. Fayat, *J. Org. Chem.* **1976**, *41*, 2141-2143.

[21] M. H. Barbee, J. P. Wang, T. Kouznetsova, M. L. Lu, S. L. Craig, *Macromolecules* **2019**, *52*, 6234-6240.

[22] a) J. M. Lenhardt, A. L. Black, S. L. Craig, *J. Am. Chem. Soc.* **2009**, *131*, 10818-10819; b) J. P. Wang, T. B. Kouznetsova, S. L. Craig, *J. Am. Chem. Soc.* **2015**, *137*, 11554-11557.

[23] S. Akbulatov, Y. Tian, Z. Huang, T. J. Kucharski, Q. Z. Yang, R. Boulatov, *Science* **2017**, *357*, 299-303.

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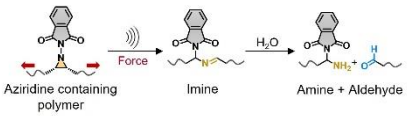

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When *cis*-N-phthalimidoaziridine is incorporated into a macromolecular backbone, it undergoes structural transformation into an imine by mechanical-force-induced 1,2-migration of the N-phthalimido group. The migration occurs under mechanochemical conditions but not thermal conditions. The imine is further hydrolyzed in the presence of water under ambient conditions, resulting in an amine and aldehyde.