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Metathesis Step-Growth Polymerizations in Ionic Liquid

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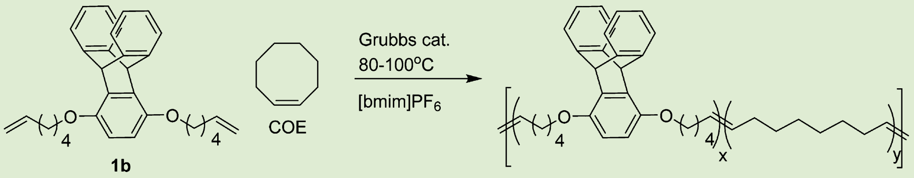
Ⓢ *Supporting Information*



ABSTRACT: Metathesis step-growth polymerizations in ionic liquids (ILs) was explored to take advantage of the high boiling points of ILs, thereby permitting the use of low pressures at high temperatures. Optimization reactions found that high polymers form efficiently using small amounts of catalyst and short reaction times. For example, high molecular weight main-chain triptycene polymers with high triptycene incorporation were synthesized. This new methodology is applicable to various metathesis reactions that require removal of volatile byproducts as a driving force, including acyclic diene metathesis (ADMET).

Ionic liquids (ILs) are an attractive alternative class of solvents[1] with several attractive properties: (1) ILs are nonvolatile, greatly simplifying the separation of volatile organic compounds. (2) ILs are miscible with many metal catalysts, organic compounds, gases and even biomolecules, making most homogeneous catalytic reactions feasible. (3) ILs are also immiscible with many organic solvents, making biphasic or multiphasic reactions possible. (4) Many ILs provide a noncoordinating and non-nucleophilic environment, which is often necessary to maintain high catalytic activity. (5) ILs can also provide a very broad and stable temperature window to conduct reactions, ranging from −80 to 300 °C. (6) Many ILs can be regarded as both organic molecules and salts, with multiple sites available for functionalization. Thus, a wide array of designer ILs can be tailored to given reactions.

Applications of ILs in synthesis have included both organic and inorganic reactions, but rarely have metathesis polymerizations been performed in ILs and, to the best of our knowledge, ADMET polymerizations in ILs have not been studied. A major limitation has been that most polymers are poorly soluble in ILs. Therefore, ILs are normally used in conjunction with a conventional organic solvent to form a biphasic system, in order to simplify purification and immobilization of the metal catalysts in the IL phase. Metathesis reactions in ILs have been briefly surveyed,[2] but little work has been published on their use in metathesis polymerization. Ring-opening metathesis polymerization (ROMP) in ILs was first reported in 2002 by Csihony et al.,[3] but there have been no reports of ADMET polymerizations in ionic liquids. Csihony et al. demonstrated that polymers of high molecular weight could be prepared using either Grubbs first (G1) or second (G2) generation catalysts. We envisioned that high temperature and high vacuum conditions may become feasible in reactions mediated by IL solvents, which have extremely high boiling points and essentially no detectable vapor pressures. We demonstrate herein that ILs are the solvents of choice for making ADMET specialty polymers containing difficult-to-incorporate unconventional molecular structures.

Conventional ADMET chemistry makes use of several methods to produce high molecular weight polymers. The earliest and most widely employed method is ethylene byproduct removal under high vacuum conditions.[4] This technique has proven to be extremely versatile and convenient and impurities in the system are minimized. Although widely used successfully, bulk ADMET polymerizations have several drawbacks. (1) In a bulk system, only liquid monomers can be used effectively. Investigations into solid-state ADMET polymerization have shown to be successful, but reaction times are generally on the order of weeks.[5] (2) Another drawback is increasing viscosity as the polymerization proceeds, which reduces the rate of ethylene removal and slows the reaction. (3) ADMET monomers are largely nonpolar, and nonpolar solvents have been shown to reduce the effectiveness of olefin metathesis catalysts.[6]

Instead of relying on a vacuum system to remove ethylene, higher boiling solvents, such as toluene, can be used to dissolve the monomer and catalyst followed by purging the reaction with an inert atmosphere during the polymerization.[7] This method allows solid monomers to be polymerized, keeps the viscosity low, and provides a solvent that both dissolves and

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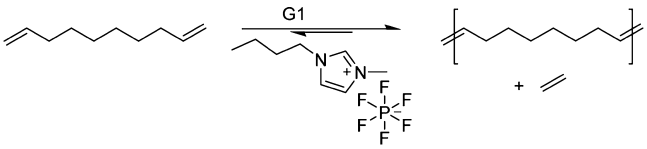
stabilizes the olefin metathesis catalyst. However, this technique has drawbacks: (1) Because the solvent introduces another possible source of impurities to contaminate the reaction, only solvents that have been extensively purified and degassed can be used; (2) Another problem is that because the solvent evaporates due to constant purging, the addition of more solvents risks exposing the reaction to air and other impurities; and (3) As this method does not utilize vacuum conditions, removal of ethylene is not always efficient.

Ethylene removal can be enhanced using a high-boiling solvent.[8] The most common solvent used for this purpose is 1,2-dibromobenzene with a boiling point of 224 °C. The polymerization is then held under a gentle vacuum (ca. 40 Torr) with simultaneous purging with an inert atmosphere. This method benefits from many of the same advantages of the inert atmosphere method described above but also shares many of the same drawbacks. Fortunately, ethylene removal is more efficient under vacuum conditions.

In consideration of the key role of solvent and conditions in ADMET polymerizations, we have undertaken a study of utility of ILs in these processes. Our findings reveal that ILs effectively combine many of the advantages of the previous methods.

Our investigations began with polymerizations of 1,9-decadiene in 1-butyl-3-methyl imidazolium hexafluorophosphate ([bmim]PF_6) as a model system for the optimization of the reaction conditions (Table 1). As 1,9-decadiene is a liquid, use of IL or any solvent is unnecessary, but due to the simple structure and availability, it is an excellent monomer for optimizations studies. The specific IL was selected because the [bmim]$^+$ cation has been proven to yield the best results in ruthenium-catalyzed metathesis reactions and is most readily available in large quantities with the PF_6^- counterion.[6] It is necessary to purify [bmim]PF_6 prior to use to remove components that may inhibit G1. Purification was accomplished by dissolving the IL in dichloromethane and passing the solution through a pad of neutral alumina. Because ILs dissolve gases, [bmim]PF_6 was degassed via freeze pump thawing. The conditions were then optimized for catalyst loading, reaction time, and effects of ionic liquid impurities.

Table 1. Effect of Catalyst Concentration on Molecular Weight of Poly(1,9-decadiene1,9-decadiene)[a]



[G1] (mol %)	M_n (kDa)	M_w (kDa)	PDI
0.25	5.6	8.6	1.6
0.5	18.5	41.8	2.3
1	12.7	26.7	2.1
2	10.7	24.7	2.3
3	12.5	26.7	2.1
4	9.5	22.9	2.4
7	8.8	20.4	2.3
11	8.7	19.2	2.2

[a] G1 = Grubbs 1st generation catalyst. Conditions: 0.25 g 1,9-decadiene in 1.5 mL [bmim]PF_6 at 50 °C for 48 h.

Table 1 details the effect of catalyst loading, using Grubbs first generation catalyst (G1), with 0.5 mol % as the optimum, resulting in a M_n of 18.5 kDa, almost 1.5 times the next highest (12.7 kDa at 1 mol %).

The conditions were subsequently optimized for reaction time, as shown in Table 2. The polymers displayed increasing M_n until about 48 h, when the M_n began to plateau at around 18 kDa. Thus, 48 h was selected as the optimal polymerization time for this system.

Table 2. Molecular Weight of Poly(1,9-decadiene) as a function of reaction time[a]

time (h)	M_n (kDa)	M_w (kDa)	PDI
6	8.7	16.7	1.9
18	10.8	20.6	1.9
24	16.6	33.5	2.0
48	18.4	42.5	2.3
72	15.4	33.5	2.2
96	19.1	35.3	1.9
120	17.6	37.0	2.1
144	19.2	42.0	2.2

[a] Conditions: 0.25 g 1,9-decadiene, 0.5 mol % G1 in 1.5 mL [bmim]PF_6 at 50 °C.

The quality of ionic liquids varies greatly from batch to batch. As described above, purification of the IL was performed before our reaction optimization studies. The common impurities found in [bmim]PF_6 are 1-butyl-3-methyl imidazolium chloride ([bmim]Cl), 1-butyl imidazole, and water.[2] Table 3 demonstrates the effect of these impurities on molecular weight, as well the effect of various additives commonly used to mitigate the negative effects of these impurities.

Table 3. Effects of Impurties and Additives on Molecular Weight of Poly(1,9-decadiene)[a]

series	impurity	additive	M_n (kDa)	M_w (kDa)	PDI
A	control	none	11.9	23.0	1.92
	water	none	15.1	32.9	2.18
	chloride	none	14.0	31.4	2.24
	imidazole	none	0	0	N/A
B	control	PinB	25.4	42.7	1.69
	water	PinB	18.7	37.0	1.98
	chloride	PinB	22.2	42.7	1.93
	imidazole	PinB	0	0	N/A
C	control	H_3PO_4	10.4	22.6	2.18
	water	H_3PO_4	9.7	19.3	1.99
	chloride	H_3PO_4	7.3	12.9	1.78
	imidazole	H_3PO_4	10.0	20.0	2.00

[a] Impurities: chloride =1-butyl-3-methylimidazolium chloride, water = deionized water, and imidazole = 1-methyl imidazole. Additives: PinB = pinacol phenyl borate, H_3PO_4 = phosphoric acid. Conditions: 0.25 g 1,9-decadiene, 0.5 mol % G1, 0.5 mol % impurity, and 20 mol % additive in 1.5 mL [bmim]PF_6 at 50 °C for 48 h.

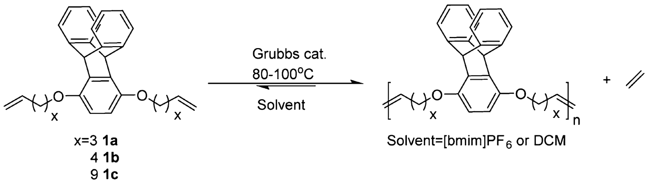
Table 3A examines the effect of impurities on the molecular weight of poly(1,9-decadiene). The control reaction, containing no impurity and no additive, yielded a M_n of 11.9 kDa. Addition of small amounts of both water and [bmim]Cl had no negative effect on molecular weight, but addition of 1-methyl imidazole prevented any polymer from being formed. This was expected, as the inhibiting effect of imidazole on Grubbs catalysts has been well documented for olefin metathesis.[9]

Pinacol phenyl borate (PinB) was used as an additive in an attempt to counter the effect of the imidazole and other impurities on the ADMET polymerization of 1,9-decadiene. Previous work demonstrated that PinB is compatible with olefin metathesis.[10] As a result of its Lewis acid character, PinB was hypothesized possibly to counteract the inhibiting effect of the Lewis basic imidazole impurity. Table 3B demonstrates how the addition of PinB affects the molecular weight. In the control polymerization, containing no impurity, a M_n of 25.4 kDa was obtained. When compared to the control experiment in Table 3A, the addition of PinB results in a doubling of molecular weight. These results are consistent with previous work on the effects of boron-containing Lewis acids of olefin metathesis,[10] but they have not previously been demonstrated in an ADMET polymerization. In spite of this enhancement, the addition of PinB proved ineffective in preventing the inhibition of G1 in experiments with the added imidazole impurity.

H_3PO_4 was also investigated as an additive to neutralize the effect of the imidazole impurity (Table 3C). Work by P'Pool et al.[9] and Aitken et al.[9] has demonstrated that phosphoric acid can be used to counter imidazole impurities. We confirmed this observation; the addition of phosphoric acid allowed the polymerization to occur in the presence of imidazole.

With an understanding and optimization of our IL conditions, we are working to optimize the polymerization of the triptycene acyclic diene **1b**. To begin, we investigated the reaction under traditional ADMET conditions using dichloromethane as the solvent and using an argon purge to remove the ethylene (Scheme 1). Gel permeation chromatography (GPC) analysis indicated an inefficient process resulting in a low recovered yield that is a mixture of low molecular weight oligomers and no detectable high molecular weight components.

Scheme 1. ADMET Polymerization of Triptycene-Containing Monomers



The potential of the IL solvent was tested for ADMET polymerization in $[bmim]PF_6$ of the triptycene-containing monomers shown in Scheme 1. Table 4 demonstrates the effect of temperature on the polymerization of various triptycene monomers (**1a**−**1c**). Monomer **1c** is only partially soluble in the IL at 50 °C and only oligomers were formed. However, with increased temperature, the monomers melt and become miscible with the IL; however, only oligomers formed, presumably due to poor solubility of the polymer after approximately 24 h. The reactions done at high temperature were analyzed via NMR. At 100 °C, no external olefins were observed, indicating either complete conversion or isomerization. Given the low molecular weight obtained by many of the triptycene-containing polymers and the high temperatures involved during the polymerization, isomerization of the olefin the likely cause.

Table 4. Polymerization of Triptycene-Containing Polymers in Ionic Liquids

monomer	*T* (°C)	cat.	M_n (kDa)	M_w (kDa)	PDI	DPn
1c[a]	50	G1	2.5	6.0	2.4	4.4
1c[a]	80	G1	1.8	5.1	2.8	3.2
1c[a]	100	G1	2.2	6.4	2.9	3.9
1a[a]	100	G1	1.5	2.3	1.5	3.8
1a[a]	100	G2	2.1	3.6	1.7	5.3
1b[b]	100	G1	8.7	12.4	1.5	20.5
1b[b]	100	G2	11.5	17.6	1.5	27.1

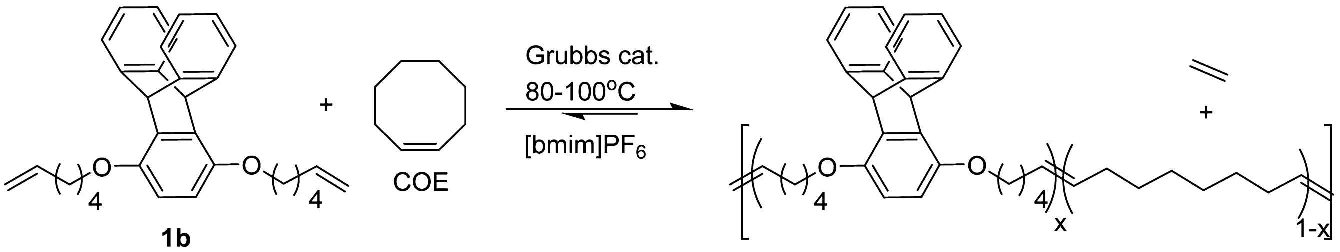
[a] Reaction time, 48 h; catalyst, 0.5 mol %. [b] Reaction time, 7 days; catalyst, 11 mol %; temperature, initially 80 °C, increased to 100 °C after 24 h.

Monomer **1a** was reacted under our optimized IL conditions using Grubbs first (G1) or Grubbs second (G2) generation catalysts. Low molecular weight oligomers were obtained with both catalysts resulting in similar degrees of polymerization as seen with monomer **1c**. Finally, monomer **1b** was polymerized for 7 days with two additions of 5.5 mol % catalyst, G1 or G2. This yielded moderate molecular weight polymers, 8.7 kDa for G1 and 11.5 kDa for G2. Low solubility and long reaction times indicate that the polymerization proceeds even when the polymer is no longer soluble in the IL. The IL still solubilizes the catalyst, low molecular weight oligomers, and swells the polymer, increasing the mobility of the reaction allowing for faster polymerization than in a bulk solid state ADMET polymerization.[5]

To increase the molecular weights of the triptycene polymers, monomer **1b** was copolymerized with *cis*-cyclooctene (**COE**) or norbornene (**NBE**) in $[bmim]PF_6$ under high temperatures, 80−100 °C, and vacuum. The reaction was first run at 80 °C to prevent loss of the volatile COE. Once oligomers were formed, the temperature was increased to 100 °C. Presumably, the reaction occurs via an amended ring-opening insertion metathesis polymerization (ROIMP) mechanism. The original ROIMP employed a cyclic olefin, typically COE, and a diacrylate monomer in a 1:1 ratio to produce an A,B-alternating copolymer.[11] In the modified ROIMP reaction in IL (Table 5), **1b** was employed instead of the diacrylate. Under these conditions, removal of ethylene became the driving force for formation of high molecular weight polymers, which displayed a high degree of incorporation of the triptycene monomer. Presumably the COE segments solubilize the triptycene repeat units, allowing for high molecular weight polymers to be formed. Entry 3 also included norbornene (NBE) as a comonomer to demonstrate the versatility of this polymerization technique.

In conclusion, $[bmim]PF_6$ was studied as a new solvent for metathesis polymerization. High molecular weight polymer has been made with low catalyst loading and relatively short polymerization times. The purity of the IL solvent is important since imidazole impurities can inhibit polymer formation, but phosphoric acid can be used to counter the effect of the imidazole impurity and allow polymerization. Addition of pinacol phenyl borate was shown to increase the molecular weight of ADMET polymers when using G1. Solubility plays an important role in the polymerization, but by increasing the reaction times and catalyst loading, even poorly soluble monomers can be polymerized. This work provides strong evidence that 1-butyl-3-methyl imidazolium hexafluorophosphate is a viable solvent for ADMET and ROIMP polymerization.

Table 5. ROIMP of 1b with *cis*-Cyclooctene



entry (%)	Grubbs cat.	[Ru] (mol %)	**1b**/COE	yield[a]	M_n[b] (kDa)	M_w[b] (kDa)	PDI[b]	*x*/*y*[c]
1	1st gen	2	1:4	72	17.9	30.8	1.72	1:2
2	2nd gen	1	1:5	88	49.9	104.0	2.09	1:3
3	2nd gen	1	1:4:1 NBE[d]	34	27.0	82.2	3.04	1:3[e]

[a] Isolated yield after column chromatography. [b] Determined by GPC vs polystyrene standards. [c] Determined by ^{1}H NMR. [d] One equivalent norbornene (NBE) was added. [e] *y* is the sum of COE and NBE.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, spectra, and GPC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Wasserscheid, P., Welton, T., Eds. In *Ionic Liquids in Synthesis*; Wiley-VCH: New York, 2003. (b) Wasserscheid, P., Welton, T., Eds. In *Ionic Liquids in Synthesis*, 2nd ed.; Wiley-VCH: New York, 2008. (c) Rogers, R. D., Seddon, K. R., Eds. In *Ionic Liquids: Industrial Applications to Green Chemistry*; ACS Symposium Series 818; Oxford University Press: New York, 2002. (d) Rogers, R. D., Seddon, K. R., Eds. In *Ionic Liquids as Green Solvents: Progress and Prospects*; ACS Symposium Series 856; Oxford University Press: New York, 2003. (e) Brazel, C. S., Rogers, R. D., Eds. *Ionic Liquids in Polymer Systems: Solvents, Additives, and Novel Applications*; ACS Symposium Series 913; Oxford University Press: New York, 2005. (f) Malhotra, S. V., Ed. *Ionic Liquids in Organic Synthesis*; ACS Symposium Series 950; Oxford University Press: New York, 2007. (g) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015. (h) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772. (i) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459. (d) Wilkes, J. S. *J. Mol. Catal. A: Chem.* **2004**, *214*, 11. (j) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (k) Olivier-Bourbigou, H.; Magna, L. *J. Mol. Catal. A: Chem.* **2002**, *182–183*, 419. (l) Scammells, P. J.; Scott, J. L.; Singer, R. D. *Aust. J. Chem.* **2005**, *58*, 155. (m) Baker, G. A.; Baker, S. N.; Pandey, S.; Bright, F. V. *Analyst* **2005**, *130*, 800. (n) Ding, J.; Armstrong, D. W. *Chirality* **2005**, *17*, 281. (o) Mehnert, C. P. *Chem.—Eur. J.* **2005**, *11*, 50. (p) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667.

(2) (a) Dyson, P. J.; Geldbach, T. J. *Metal Catalysed Reactions in Ionic Liquids*; Springer: New York, 2005. (b) Stark, A.; Ajam, M.; Green, M.; Raubenheimer, H. G.; Ranwell, A.; Ondruschka, B. *Adv. Synth. Catal.* **2006**, *348*, 1934.

(3) Csihony, S.; Fischmeister, C.; Bruneau, C.; Horváth, I. T.; Dixneuf, P. H. *New J. Chem.* **2002**, *26*, 1670.

(4) Watson, M. D.; Wagener, K. B. *Macromolecules* **2000**, *33*, 8963.

(5) (a) Oakley, G. W.; Lehman, S. E.; Smith, J. a.; Van Gerven, P.; Wagener, K. B. *Macromolecules* **2003**, *36*, 542. (b) Delgado, P. A.; Liu, D. Y.; Kean, Z.; Wagener, K. B. *Macromolecules* **2011**, *44*, 9529–9532.

(6) (a) Schulz, M. D.; Wagener, K. B. *ACS Macro Lett.* **2012**, *1*, 451. (b) Stark, A.; Ajam, M.; Green, M.; Raubenheimer, H. G.; Ranwell, A.; Ondruschka, B. *Adv. Synth. Catal.* **2006**, *348*, 1941. (c) Adjiman, C. S.; Clarke, A. J.; Cooper, G.; Taylor, P. C. *Chem. Commun.* **2008**, 2808.

(7) Leonard, J. K.; Wei, Y.; Wagener, K. B. *Macromolecules* **2012**, *45*, 680.

(8) (a) Weychardt, H.; Plenio, H. *Organometallics* **2008**, *27*, 1479. (b) Sydlik, S. A.; Delgado, P. A.; Inomata, S.; VanVeller, B.; Yang, Y.; Swager, T. M.; Wagener, K. B. *J. Polym. Sci., Part A-1: Polym. Chem.* **2013**, 12.

(9) (a) P'Pool, S. J.; Schanz, H.-J. *J. Am. Chem. Soc.* **2007**, *129*, 14212. (b) Aitken, B. S.; Lee, M.; Hunley, M. T.; Gibson, H. W.; Wagener, K. B. *Macromolecules* **2010**, *43*, 1701.

(10) Simocko, C.; Wagener, K. B. *Organometallics* **2013**, *32*, 2516.

(11) Choi, T.-L.; Rutenberg, I. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3839.