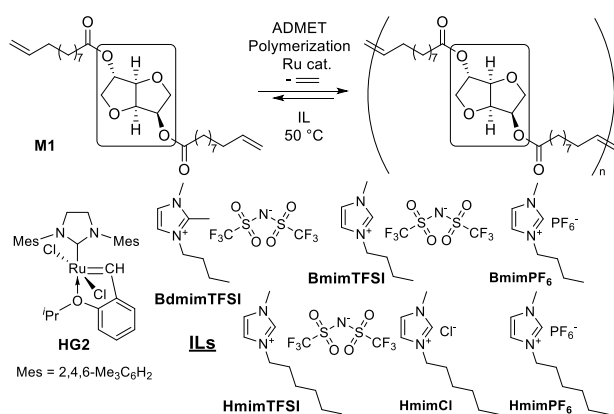


Synthesis of Bio-based Polyesters by Acyclic Diene Metathesis (ADMET) Polymerization in Ionic Liquid

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1. Introduction

Synthesis of bio-based polyesters attracts considerable attention due to utilization of abundant feedstocks as alternative of fossil fuels, as well as tunable mechanical properties and potential biodegradability in the resultant polymers.¹ The acyclic diene metathesis (ADMET) polymerization with Ru catalysts, RuCl₂(IMesH₂)(CH-2-OⁱPr-C₆H₄) (**HG2**) generally gave rather high molecular weight unsaturated polyesters, but repetitive removal of ethylene, accompanied by-product in this condensation polymerization, was prerequisite.²⁻⁴ Unlike organic solvents, use of ionic liquids (ILs) plays an important role as solvent to remove ethylene and dissolve the resultant polymers due to extremely low vapor pressure, high boiling point and the good dissolving ability. We herein present that synthesis of the high molecular weight polymers can be simply achieved by conducting the ADMET polymerization in ILs as solvent (Scheme 1).



Scheme 1

2. Experimental

The ADMET polymerizations of dianhydro-*D*-glucityl bis(undec-10-enoate) (**M1**) by **HG2** catalyst were conducted in ILs *in vacuo*. Molecular weights and molecular weight distributions for the resultant polymers were measured by GPC, and their microstructure was analyzed by ¹H NMR spectra.

3. Results and discussion

The results in ADMET polymerization of **M1** by **HG2** in a series of ILs are summarized in Table 1. It

was found that these polymerizations afforded high molecular weight polymers with unimodal molecular weight distributions. The *M_n* value increased slightly after 6 h and the catalyst was stable under these conditions. Note that the polymerizations conducted in **BmimPF₆** and **HmimTFSI** afforded higher molecular weight polymers than those conducted in the others, suggesting that the *M_n* value was affected by kind of the ILs employed. Various ILs with different alkyl chain length and counter anions were thus employed and more details will be introduced in the symposium.

Table 1. ADMET polymerization of monomer (**M1**) with **HG2** catalyst in ionic liquids (ILs).^a

IL	time / h	yield ^b / %	<i>M_n</i> ^c	<i>M_w</i> / <i>M_n</i> ^c
BmimPF₆	6	87	24700	1.97
BmimPF₆	16	89	32200	1.87
BmimTFSI	6	86	17700	1.79
BmimTFSI	16	93	23000	1.94
BdmimTFSI	6	87	20000	1.73
BdmimTFSI	16	92	23600	1.88
HmimCl	6	84	6100	1.74
HmimCl	16	91	11200	1.65
HmimPF₆	6	87	11600	2.15
HmimPF₆	16	89	19100	1.69
HmimTFSI	6	89	28600	1.76
HmimTFSI	16	93	39200	1.95

^aConditions: HG2 1.0 mol%, monomer 300 mg in IL 0.14 mL (initial M1 conc. 4.64 M), 50 °C *in vacuo*. ^bIsolated yield as MeOH insoluble fraction. ^cGPC data in THF vs polystyrene standards.

References

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