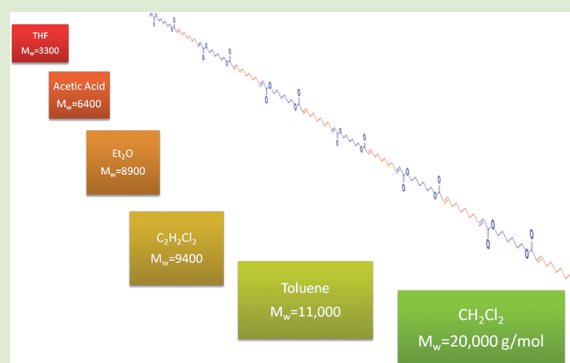# Solvent Effects in Alternating ADMET Polymerization

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ABSTRACT: Alternating AB copolymers were synthesized by exploiting the selectivity of the metathesis reaction between α,ω-dienes and α,ω-diacrylates. Unlike standard acyclic diene metathesis (ADMET) polymerizations, the copolymerization of dienes and diacrylates does not require high vacuum conditions. This work utilizes this unique characteristic to explore the effect of various solvents on ADMET polymerization. We found significant variation in the efficacy of the solvents we screened, with CH_2Cl_2 yielding the highest molecular weight polymer. Additionally, the performance of Grubbs second generation catalyst was compared with Hoveyda–Grubbs second generation catalyst in different solvents, revealing a stark difference in the molecular weight of the resulting polymers in CH_2Cl_2 but a relatively minor difference in the final molecular weight from polymerizations in acetic acid.

Here we report the effect of solvent choice on alternating acyclic diene metathesis (ADMET) polymerization. Our results are illustrated in Figure 1. Metathesis polymerization is
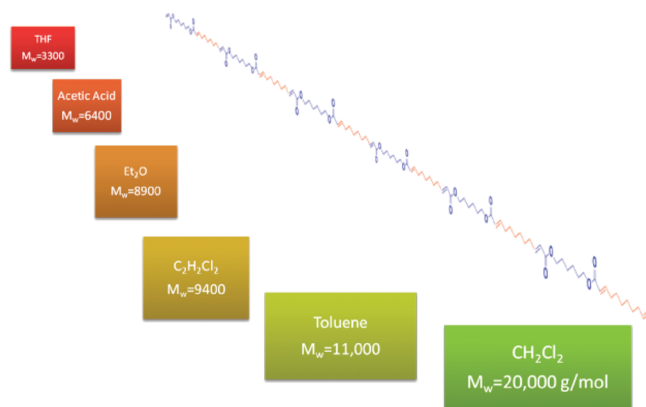

Figure 1. Illustration of solvent effect on molecular weight.

one of the most active areas of research in polymer chemistry. The past several years have seen the development of a wide variety of polymers synthesized with ruthenium-based catalysts, resulting in numerous publications.[1] The synthesis of AB-alternating copolymers is a common motif in polymer chemistry, but one that has been, historically, undeveloped in metathesis chemistry. This changed with the report of ring-opening insertion metathesis polymerization (ROIMP) by Grubbs and co-workers,[2] which demonstrated that, following a relatively fast ROMP reaction of a cylcoalkene monomer, a gradual incorporation of α,ω-diacrylates into the double bonds of the polymer produces a new alternating AB-copolymer with remarkably high degrees of alternation. The same concept has

also been applied to ADMET polymerizations using α,ω-dienes and α,ω-diacrylates[3] and in making block and star copolymers.[4] Analogous with ROIMP, a conventional ADMET polymerization produces an unsaturated polymer (or oligomer) scaffold into which the diacrylates are gradually incorporated. Because of these mechanistic characteristics, certain conditions required for ADMET polymerizations become unnecessary. In a typical ADMET polymerization, the driving force of the reaction is the removal of ethylene. This prevents the otherwise thermodynamically mandated depolymerization by ethenolysis. However, when a relatively electron-rich (type 1) olefin is coupled with one that is relatively electron-deficient (type 2), the reaction is irreversible under typical metathesis conditions.[5] Consequently, the alternating copolymer is not susceptible to depolymerization caused by the presence of ethylene. This allows the high vacuum conditions, requisite in standard ADMET polymerizations, to be forgone.

Because high-vacuum conditions are not required, there is greater flexibility in choosing the solvent for this polymerization. Most ADMET reactions are done neat or with high-boiling solvents. Although this approach has been successful, there is a consensus that dichloromethane is the best solvent for metathesis reactions with Grubbs-type catalysts. However, with a boiling point around 40 °C, dichloromethane is unsuitable as a solvent under low-pressure conditions.

While an impressive array of metathesis catalysts (**1**−**4** in Figure 2 being commonly used examples) have been developed, ADMET chemistry has largely relied on first generation Grubbs' catalyst (**1**). Although it is far from the most active
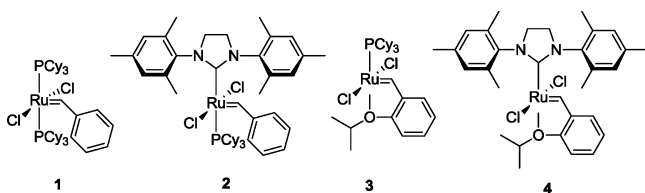
Figure 2. Common metathesis catalysts.

metathesis catalyst, it has two distinct advantages: (1) it is relatively stable, making it easy to handle and (2) it does not catalyze olefin isomerization unlike later generations of Grubbs and Hoveyda−Grubbs-type catalysts that include the *N*-heterocyclic carbine ligand (**2** and **4**) under standard ADMET conditions.[6] Abbas et al. has shown that, among several catalysts screened, Hoveyda−Grubbs second generation catalyst (**4**) was the most active toward the cross-metathesis of terminal olefins with acrylates.[7] Herein we investigate the effect of various solvents on the copolymerization of 1,9-decadiene and 1,6-diol diacrylate (Figure 3).
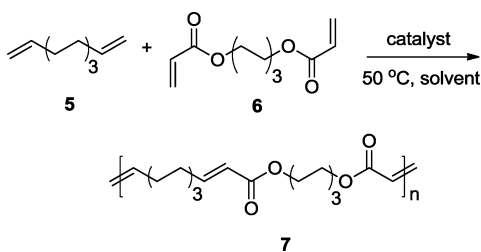

Figure 3. Polymerization reaction.

To establish a baseline of the efficacy of standard ADMET conditions on the diene−diacrylate polymerization system, the polymerization was conducted without solvent, using **4**, under high vacuum (Table 1, entry *g*). After 1 h, the reaction mixture

Table 1. Solvent Effects Using Catalyst 4[a]

entry	solvent	M_w (g/mol)	PDI	% alternation[b]
a	CH_2Cl_2	20000	1.87	>98
b	toluene	11000	1.67	98
c	$C_2H_4Cl_2$	9400	1.70	95
d	Et_2O	8900	1.82	94
e	DCB[c]	7600	1.81	97
f	acetic acid	6400	1.56	95
g	none	4800	1.76	97
h	THF	3300	1.57	84

[a]1 mol % catalyst, 2.55 M monomer solution, 50 °C, 6 h. [b]Determined by ^{1}H NMR. [c]1,2-Dichlorobenzene.

had become too viscous to continue stirring, and after 2 h, it had completely solidified. The reaction was exposed to air after 6 h, and the molecular weight of the solid was determined (M_w = 4800 g/mol). Thus, solvation is necessary to achieve higher molecular weights.

Because vacuum conditions do not affect this polymerization, we were able to screen a diverse set of solvents (Table 1) using **4** and running the polymerization for 6 h. In all cases, conversion was high (95−99%). All solvents tested increased the molecular weight of the polymer compared to the bulk reaction, with the exception of THF. This inhibitory effect may be due to the solvent binding to the active site of the catalyst,

consequently limiting its reactivity.[8] We found that dichloromethane significantly increased the final molecular weight of the polymer. Potentially, this result may be generalized to other metathesis reactions.

An increase in viscosity was observed in the polymerization in dichloromethane, which was not observed in the other solvents. We believe this is because the molecular weight achieved in the other solvents was not high enough to significantly affect the viscosity, unlike the higher molecular weight achieved in dichloromethane. Because most of the polymerizations did not achieve high molecular weight, we believe viscosity was not a significant factor in this study.

Although solvent effects undoubtedly play a role in metathesis reactions, they have been the focus of a relatively few number of publications.[9] Broadly speaking, the effect of the solvent can be subdivided into three categories: (1) the effect of the solvent on the rate of catalyst initiation, (2) its effect on the rate of reaction of the active catalyst species and the substrate(s), and (3) the rate of catalyst deactivation. Grubbs and co-workers showed that, for **1** and **2**, the rate of catalyst initiation is roughly proportional to the dielectric constant of the reaction medium.[10] However, in this work there appears to be no correlation between the dielectric constant of the reaction medium and the molecular weight of the final polymer. This may be because, in the case of **1** and **2**, the rate limiting step is the dissociation of the phosphine ligand. This is not the case with Hoveyda-type catalysts at high olefin concentration.[11]

More likely, however, is that the lifetime activity of the catalyst, that is, the combination of the rate of the productive metathesis reaction and the rate of catalyst deactivation, in a given solvent, dominates the molecular weight of the polymer over the rate of catalyst activation. Adjiman et al. investigated the effects of several solvents on ring-closing metathesis (RCM) with **2** and determined that, in their model, the rate of catalyst deactivation in dichloromethane is essentially zero, whereas solvating with acetic acid produces a much higher rate of productive metathesis, but also a higher rate of catalyst deactivation.[9] Our results appear to indicate that the catalyst lifetime is then the dominant factor in ADMET polymerization.

A comparison of catalysts in CH_2Cl_2, the most common solvent for metathesis, 1,2-dichlorobenzene, a high-boiling solvent used for ADMET reactions, and acetic acid revealed remarkable differences in the performance of catalyst **2** compared to catalyst **4** (Table 2; catalyst **3** gave only the

Table 2. Catalyst Comparison in a Variety of Solvents[a]

entry	catalyst	solvent	M_w (g/mol)	PDI	% alternation[b]
i	**2**	CH_2Cl_2	8000	1.72	96
j	**4**	CH_2Cl_2	20000	1.87	99
k	**2**	acetic acid	5400	1.56	93
l	**4**	acetic acid	6400	1.56	95
m	**2**	DCB	4600	1.50	84
n	**4**	DCB	7600	1.81	97

[a]1 mol % catalyst, 2.55 M monomer solution, 50 °C, 6 h. [b]Determined by ^{1}H NMR.

homopolymer of **5** and was, therefore, not included in the comparison). In dichloromethane, the molecular weight is more than doubled with **4** compared with **2** (Table 2, entries *i* and *j*). Interestingly, the polymerizations performed in acetic acid yielded polymers of comparable molecular weight, a stark contrast to the differences observed in other solvents. This may

be due to the extremely fast initiation rate of catalyst **2** and relatively low rate of the reverse reaction in acetic acid.[9] The differences in molecular weight are likely related to the differences in the kinetic profile of the two catalysts. The initiation rate constant of **2** has been shown to be independent of olefin concentration over a wide range of concentrations.[12] The initiation mechanism for the Grubbs–Hoveyda-type catalyst, however, has been the source of much discussion in the literature.[11,13] Unlike the phosphine-containing catalysts, there is no saturation behavior observed for **4**. In fact, at high olefin concentration (as is typical in ADMET polymerizations), the rate-limiting step seems to occur later in the olefin metathesis reaction sequence.[11] Given these considerations, it is plausible that the ability of a given solvent to promote the initial dissociation of the phosphine ligand of **2** and to inhibit a deactivating reassociation event is crucial. Catalysts that have an isopropoxystyrene bidentate ligand instead of a phosphine initiate at a slower rate but propagate at a faster rate than their phosphine containing analogues.[14] In solvents that mitigate the effect of free phosphine in solution on the active catalyst species and speed the initial dissociation, the rates of reaction with **2** and **4** become similar, as appears to be the case with acetic acid.

In conclusion, this investigation of solvent effects in metathesis polymerization demonstrates the profound variations between solvents in terms of their efficacy. The choice of solvent can either magnify or mitigate the factors that differentiate the catalytic activity of **2** and **4**, leading to very different outcomes. While the rate of catalytic turnover is of primary importance, the rate of catalyst deactivation plays a significant role in the achievement of high molecular weight polymers.

■ EXPERIMENTAL METHODS

Materials and measurements: All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. Anhydrous solvents were obtained from an anhydrous solvent system and subsequently sparged with argon for 2 h immediately prior to use. All ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR were referenced to residual signals from CDCl$_3$ (^{1}H 7.25 ppm and ^{13}C 77.00 ppm). Gel permeation chromatography (GPC) was performed at 40 °C using a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector and two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length) using HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min.

Polymerizations: A Schlenk flask was charged with 0.276 g (2 mmol) 1,9-decadiene (50 equiv) and 0.452 g (2 mmol) 1,6-diol diacrylate (50 equiv) under argon. A 0.75 mL aliquot of solvent was added, resulting in a 2.55 M monomer solution. A 1 equiv aliquot of catalyst was added, and the solution was stirred at 50 °C for 6 h. Afterward, approximately 200 μL of ethyl vinyl ether was added. The solution was precipitated into cold methanol and dried under vacuum.

The 11 polymers made all displayed similar spectra. Characteristic spectra peaks are given below.

^{1}H NMR (300 MHz, CDCl$_3$): δ 6.97–6.92 (m, 2H, OCCH=C*H*, 5.81 (d, 2H, OCC*H*=CH), 4.12 (t, 4H, O–C*H$_2$*), 2.19 (m, 4H, C*H$_2$*-CH=CH), 1.67 (m, 4H, C*H$_2$*-CH$_2$O), 1.5–1.3 (m, 12H, C*H$_2$*).

^{13}C NMR (75 MHz, CDCl$_3$): δ 166.8 (2C, C=O), 149.3 (2C, OCCH=CH), 121.3 (2C, OCCH=CH), 64.1 (2C, OCO-CH$_2$), 32.1 (2C, CH$_2$–CH=CH), 28.9, 28.6, 27.9 (6C, CH$_2$), 25.6 (2C, OCH$_2$–CH$_2$).

FT-IR (KBr): 2929–2857 (s, ν_{CH}), 1717 (s, $\nu_{C=O}$), 1653 (m), 1467 (m), 1393 (w), 1305 (m), 1262 (s), 1212 (m), 1184 (s), 1137 (m), 1062 (m), 983 (m), 852 (w), 714 (w).

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Notes
The authors declare no competing financial interest.

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