ADMET polymerization in affordable, commercially available, high boiling solvents

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Abstract

Acyclic diene metathesis polymerization is a powerful technique for creating polymers with precise placement of functional groups. However, due to the need to use high vacuum or other methods to remove the volatile ethylene byproduct and drive the reaction forward, traditional solvents are not feasible. Here we demonstrate the use of three cheap, commercially available solvents as a medium for ADMET polymerizations: propylene carbonate, diethyl phthalate, and dioctyl phthalate. We have shown that by using these solvents, we can increase the molecular weights of ADMET-synthesized polyethylene by over 450% as compared to the bulk polymerization as well as reduce polymerization times from 72 h down to 24 and polymerize challenging, solid monomers.

Keywords ADMET · Precision polymers · Scale-up · Plasticizer

1 Introduction

Since its development by Wagener et al., acyclic diene metathesis polymerization (ADMET) has become a valuable tool for the production of polymeric materials with distinctive properties [1–5]. ADMET has the unique capability of synthesizing linear, “precise” polymers, where the functional groups on the polymer backbone are at regular and known intervals [6, 7]. The design of symmetrical diene monomers allows the control of the carbon spaces between functional groups [8, 9]. Additionally, linear polyethylene can be made from monomers such as 1,9-decadiene and 1,5-hexadiene with complete absence of branching [5, 10]. In each of these cases the morphology of the final polymer can be known without ambiguity making this synthetic approach useful for developing a deeper understanding of the structure–property relationships [7, 11, 12]. Some closely studied ADMET polymers have

potential uses in optoelectronics [13–15], ion transport [11, 16], and polymer-based pharmaceuticals [17–19].

Using Schrock’s tungsten centered [20] or Grubb’s 1st [21] and 2nd [22] generation ruthenium centered catalysts, symmetric α,ω -diene monomers can react in a step-growth fashion, creating polyethylene polymers and copolymers [23, 24]. Unlike the more familiar ring-opening metathesis polymerization (ROMP) [25, 26], ADMET is a condensation polymerization, which releases ethylene, and is also equilibrium driven. For the reaction to progress, removal of the ethylene byproduct is essential. ADMET polymerizations also tend to be sluggish since the product is not significantly lower energy than the starting materials. Typically, polymerizations are run for many hours or days under a high vacuum environment or with an inert gas purge for multiple days if high molecular weight polymers are to be made [27]. This makes the use of traditional volatile solvents problematic as they will evaporate

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during the course of the polymerization. Because of this, bulk polymerizations are often done with no solvent when liquid monomers are used, but this cannot be done with solid monomers. Work has been done in solid state ADMET polymerization which has been successful using Grubb's 1st and 2nd generation catalysts, but on long time scales with difficulty achieving high molecular weight [28]. Solvents have also been used with both liquid and solid monomers, but are limited due to a poor selection of solvents that can be used in heated vacuum environments [10, 29]. Solvents must have high boiling points, generally greater than 240 °C so they have a suitably low vapor pressure, as well as be unreactive towards olefin metathesis, and be compatible with the ADMET catalyst. Few common solvents meet these criteria.

Previously, solvents such as 1,2-dichlorobenzene, 3,4-dichlorotoluene, 1,2,4-trichlorobenzene, and 4-chloroanisole have been used by Weyhardt and Plenio [29] for the successful polymerization of high molecular weight ADMET divinylarenes. Specially synthesized solvents, for instance, dibenzyl carbonate, have also been investigated by Sauty et al. [30] and have proven to almost triple the number average molar mass obtained. Simocko et al. used an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆), and reported increased efficiency in the removal of ethylene from the reaction, resulting in higher molecular weight polymer compared to bulk conditions [10]. Although these solvents have proven to be successful in ADMET for various monomers, they are costly, with some requiring custom synthesis and others being difficult to handle.

In this study, we explored solvents that are compatible with a variety of monomers and are affordable, commercially available, relatively safe, high boiling and that could serve as a medium for large batch ADMET reactions (Scheme 1). It should be noted that while the solvents selected here are less toxic than di and trichlorobenzenes and ionic liquids, they could still pose a safety hazard as some phthalates, such as bis(2-ethylhexyl) phthalate, may damage fertility so should be handled with care. Published studies of ADMET polymers typically yield hundreds of mg of polymer or less. While this quantity of polymer is sufficient for small scale structural studies like X-ray and neutron scattering, increasing the scale of ADMET polymerizations is critical to providing enough material for testing

the polymers' conductivity, mechanical properties, and controlled release of bioactive molecules.

2 Materials and methods

2.1 Instrumentation

Nuclear Magnetic Resonance (NMR) spectra were recorded on an Anasazi Eft-90 or a Varian Mercury-400 NMR Spectrometer. Chemical shifts are referenced to residual solvent. Polymer molecular weights were determined by Gel Permeation Chromatography (GPC) versus polystyrene standards (Polysciences, Warrington, PA) using THF as the eluent at a flow rate of 1.0 mL/min in an Agilent series 1100 HPLC system equipped with Waters Styragel HR4 followed by HR4E operated at room temperature, Agilent in-line degasser, auto sampler, and, refractive index detector. An appropriate amount of sample (~ 1 mg/mL) was dissolved in THF and passed through a 0.45 µm PTFE syringe filter (Whatman, Clifton, NJ) prior to injection into the column. Extents of reaction and degrees of polymerization were calculated from the number average molar masses obtained from GPC using the Carothers equation. All synthetic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Glassware was oven-baked and cooled under nitrogen atmosphere. The products were dried under vacuum at least overnight to constant weights before weighing and calculating yields.

2.2 Materials

All solvents were of spectroscopic grade unless otherwise noted. Anhydrous solvents were purchased from Aldrich as Sure-Seal Bottles and used as received. 1,9-decadiene was purified via basic alumina plug prior to polymerization. Diethyl malonate was distilled from CaH₂ prior to use. Grubbs 1st (G1) generation catalyst were kindly provided by Materia, Inc. The deuterated chloroform solvent was used from a freshly opened bottle and stored under nitrogen in a desiccator. All other chemicals were of reagent grade and used as received.

2.3 General procedure for bulk ADMET polymerization

Under constant nitrogen flow, 0.5 g of monomer was added to flame-dried Schlenk flask equipped with a magnetic stir bar and 1.0 mol% of Grubbs 1st generation catalyst was then added. The reaction was then placed under high vacuum (ca 100 mtorr) at 50 °C while stirring. After 48 h the reaction was quenched with a solution of 2 mL

Scheme 1 General mechanism of ADMET polymerization with solvent

of ethyl vinyl ether in 10 mL of toluene. The polymer was then precipitated into 250 mL of cold ethanol, the polymer was isolated via filtration, and GPC was used to determine molecular weights, degree of polymerization, and extent of reaction.

2.4 General procedure for ADMET polymerization in solvent

Under constant nitrogen flow, 0.5 g of monomer was added to flame-dried Schlenk flask equipped with a magnetic stir bar and 2.5 mL of the appropriate solvent was added. This solution underwent three rounds of freeze–pump–thaw before 1.0 mol % of Grubbs 1st generation catalyst was then added to the reaction flask. The reaction was then placed under high vacuum (ca 100 mtorr) at 50 °C while stirring. After 48 h the reaction was quenched with a solution of 2 mL of ethyl vinyl ether in 10 mL of toluene. The polymer was then precipitated into 250 mL of cold ethanol, the polymer was isolated via filtration and GPC was used to determine molecular weights, degree of polymerization, and extent of reaction.

2.5 Polymerization of 6spBnEs

500 mg of 6spBnEs, 1 mol% G1, 2.5 mL of solvent (if used). ^1H NMR (90 MHz, CDCl_3 -d) δ : 7.20 (m, 5H), 5.26 (m, 2H), 5.03 (s, 2H), 1.81 (m, 4H), 1.45 (s, 4H), 1.18 (m, 16H) (Scheme 2).

2.6 Polymerization of 21spOH

500 mg of 21spOH, 1 mol% G1, 2.5 mL of solvent (if used). ^1H NMR (400 MHz, CDCl_3 -d) δ 5.35 (m, $J=3.8$ Hz, 2H), 3.54 (m, $J=3.2$ Hz, 1H), 1.93 (m, $J=6.3$ Hz, 4H), 1.48–0.91 (m, 32H). ^{13}C NMR (100 MHz, CDCl_3 -d) δ 130.31, 71.98, 37.47, 32.58, 29.64, 29.51, 29.16, 27.18, 25.64 (Scheme 3).

Scheme 2 Polymerization of Benzyl-2-(oct-7-en-1-yl)dec-9-enolate (6spBnEs)

Scheme 3 Polymerization of Tricosa-1,22-dien-12-ol (21spOH)

Scheme 4 Polymerization of Tricosa-1,22-dien-12-one (21spKet)

2.7 Polymerization of 21spKet

500 mg of 21spKet, 1 mol% G1, 2.5 mL of solvent. Only low molecular weight material was observed (Scheme 4).

2.8 Large Scale Polymerization of 1,9-decadiene and benzyl 2-(oct-7-en-1-yl) dec-9-enoate

Under constant nitrogen flow, 5.0 g of monomer was added to flame-dried three-neck round bottom flask equipped with a magnetic stir bar and 25 mL of the appropriate solvent was added. This solution underwent three rounds of freeze–pump–thaw before 1.0 mol % of Grubbs 1st generation catalyst was then added to the reaction flask. The reaction was then placed under high vacuum (ca 100 mtorr) at 50 °C while stirring. After 48 h the reaction was quenched with a solution of 2 mL of ethyl vinyl ether in 10 mL of toluene. The polymer was then precipitated into 1000 mL of cold ethanol, the polymer was isolated via filtration and GPC was used to determine molecular weights, degree of polymerization, and extent of reaction.

2.9 Monomer synthesis

Scheme 5 outlines monomer synthesis. Detailed monomer synthesis can be found in the Supplementary Material.

3 Results and discussion

Three solvents with differing polarities and ability to solubilize ADMET monomers were studied for their application in ADMET polymerizations (Fig. 1). Their properties are given in Table 1. These three solvents have been used as plasticizers for a variety of polymers and are all liquid at room temperature [31–34]. Propylene carbonate, (PC)

Synthesis of Benzyl-2-(oct-7-en-1-yl) dec-9-enoate (6spBnEs). **Synthesis of Tricosa-1,22-dien-12-ol (21spOH).** **Synthesis of Tricosa-1,22-dien-12-one (21spKet).** **Scheme 5** Monomer Synthesis

is a small molecule which is often used in the vinyl polymer industry and consumer products such as adhesives, paints and cosmetics and is soluble in water [35, 36]. Its high dielectric constant also makes it useful as a solvent in lithium ion batteries [31, 37, 38]. Diethyl phthalate (DEP) dissolves organics and many polymers and is a binding agent in cosmetics and fragrances [39]. Dioctyl phthalate (DOP) is a high production volume solvent, being made on the scale of three billion kilograms a year around the world at low costs. It is the main plasticizer being used in the production of PVC materials and is immiscible with water [31, 40].

Both liquid and solid monomers were used in these experiments to demonstrate utility of these solvents. In

bulk polymerizations viscosity increases dramatically during the course of the polymerization and using plasticizing agents as solvents would keep the polymer solution viscosity reasonable allowing ethylene to be more easily removed from the mixture using vacuum.

Four monomers were used in the experiment to test the versatility of the solvents. 1,9-decadiene is a simple liquid monomer which was used as a model compound and was distilled prior to use. Benzyl 2-(oct-7-en-1-yl) dec-9-enoate (6spBnEs) was synthesized based on a method previously published by Baughman et al. [7] Two solid monomers were also synthesized, tricosa-1,22-dien-12-one (21spKet) and tricosa-1,22-dien-12-ol (21spOH) from adapted literature procedures [9] and they are shown in Fig. 1.

Fig. 1 Structures of experimental monomers and solvents

Table 1 A list of solvent properties

Properties	PC	DEP	DOP
<i>Experimental solvent properties</i>			
Molar mass (g mol^{-1})	102.1	222.24	390.56
Dipole (D)	4.9	2.4	2.8
Boiling point ($^{\circ}\text{C}$)	242	295	385

1,9-decadiene was used as a model monomer as it is commercially available and relatively inexpensive. All experiments had a 5:1 solvent to monomer ratio and were degassed before polymerization. All solvents were distilled from calcium hydride to ensure absence of impurities before introducing Grubb's 1st generation catalyst (G1). 1 wt% of catalyst was added to the monomer solvent mixture after degassing. Strong vacuum, ~ 100 mTorr, was employed when the solution approached 50°C to activate the catalyst and remove ethylene. Following polymerization, precipitation into cold ethanol was done to isolate the polymer. Gel permeation chromatography was used to obtain molecular weights, degree of polymerization (DP), and dispersity. The results for the first 120 min of polymerization are outlined in Fig. 2 and results for the full polymerization can be found in Fig. SI 1.

PC was found to be too polar of a solvent for 1,9-decadiene, and this monomer was not miscible in the solvent. Upon stirring and heating, the biphasic polymerization

Fig. 2 Polymerization results as a function of time for the first 120 min of the reactions for the solvents: PC (●), DEP (▲), and DOP (■). Molar mass (top) and extent of reaction (bottom)

was initiated with ethylene bubbling out of solution. After about 3 h, solid polymer was formed in the flask and no further ethylene evolution could be observed. An average molecular weight of 10.0 kDa ($\text{DP} \approx 87$) is reported in Table 2 after 24 h. The second solvent, DEP, was miscible with this monomer and after 3 h solid polymer remained dispersed as a suspension. The polymerization was run for 24 h and afforded a M_n 13.0 kDa ($\text{DP} \approx 118$). The final solvent, DOP, and the 1,9-decadiene monomer proved to also be miscible. No solid was formed even after 4 days. The reaction continued until the catalyst decomposed or until new catalyst is introduced to the flask and solubility did not appear to limit the polymerization. At 24 h, a high molecular weight of M_n of 22.3 kDa ($\text{DP} \approx 202$) was achieved, much faster than 3–5 days usually required for bulk ADMET polymerization [27]. After 6 days, a 70.0 kDa number-average molecular weight ($\text{DP} \approx 636$) was obtained from the continued addition of catalyst every 2 days (Fig. SI 1), an over 450% increase from bulk polymerization.

To study in detail how the polymerization proceeded, 1,9-decadiene was used once again as a model system. Aliquots were taken every 10 min for the 1st hour of reaction

Table 2 Molar masses after 24 h of polymerization

Solvent	Monomer	M _n (kDa)	Đ	DP
None	1,9-decadiene	15.1	2.06	137
	6spBnEs	16.6	1.41	49
PC	1,9-decadiene	10.0	3.1	87
	21spOH	2.1	1.66	7
	6spBnEs	30.8	1.52	90
DEP	1,9-decadiene	13.0	1.92	118
	21spKet	1.1	1.52	4
	21spOH	2.6	2.49	8
	6spBnEs	4.4	1.42	13
DOP	1,9-decadiene	22.3	1.8	202
	21spKet	0.9	1.53	3
	21spOH	6.8	1.87	22
	6spBnEs	19.9	2.2	58

because this time frame had the largest increase in conversion. For the first 30 min of the reaction, conversion increased from 0 to 85% in PC, 93% in DEP, and 90% in DOP (Fig. 2). High conversion is achieved at short time scales for every solvent system used and by 24 h we observed 99% or higher conversion in all experiments. As is typical in step growth polymerizations, high conversion is achieved quickly, but the molecular weight is slow to increase as it requires very high conversions. In the case of ADMET, the low concentration of terminal olefins as the polymerization progresses reduces the rate of productive cross metathesis reactions. Additionally, increasing reactions between the less reactive internal double bonds and catalyst become the predominant metathesis pathway. These unproductive metathesis reactions temporarily occupy the catalyst but do not increase the molecular weight of the polymer. After 3 h the reaction slowed in all solvents and conversion only increased 5 to 7% over the remaining 21 h. In DEP and DOP, the change in conversion from 3 to 24 h is prolonged due to the polymer still being suspended in solution while the conversion of model polymerizations carried out in PC and neat plateaued earlier in the reaction due to solidification of polymer (Fig. SI 1).

From initial experiments using 1,9-decadiene as a model monomer, it was determined that DOP would be the best solvent for this monomer since the polymer was the most soluble and reached the highest molecular weight. Further experiments were done on the monomers which are illustrated in Fig. 1 with results of 24 h long polymerizations summarized in Table 2.

The 21spKet monomer is a high melting point solid, therefore bulk polymerization was unfeasible. Due to the strong favorable interactions of the monomer as a solid, solubility in the three solvents was poor. The ketone did

not dissolve at all into PC. Heating the DEP and DOP did dissolve the monomer and was successful for polymerization, although low average molecular weights were obtained due to insolubility of the polymer. Only trimers and tetramers were formed.

The 21spOH also had limited solubility but was able to dissolve in all three solvents with the addition of heat. Low molecular weights were obtained from the polymerization done in PC and DEP (DP ≈ 7 and 8, respectively), but moderate molecular weights were achieved using DOP with DP ≈ 22. At 24 h p(21spOH), behaved similarly in PC and DEP giving a M_n of 2.1 kDa and 2.6 kDa while DOP afforded a M_n of 6.8 kDa.

A neat polymerization of the benzyl 2-(oct-7-en-1-yl) dec-9-enoate (6spBnEs) afforded a M_n of 16.6 kDa (DP ≈ 49). When placed in the solvents, DOP and DEP were expected to have the best results based on the 1,9-decadiene experiments. Interestingly the opposite was true, with PC being the best polymerization solvent for this monomer resulting a polymer with a M_n of 30.8 kDa (DP = 90). This could be due to the increased polarity of pendant group on the monomer interacting with most polar solvent during polymerization. DOP still fared better than both DEP and the neat polymerization. Both phthalates proved to be more difficult to separate from the 6spBnEs polymer even after precipitation. This could be due to the stronger chain interaction effects within the DOP molecule as well as pi-pi interactions in the structures. The poly(benzyl 2-(oct-7-en-1-yl)dec-9-enoate) did precipitate as a solid in PC polymerization but dissolved easily in toluene.

These polymerizations were performed on a typical ADMET scale, with monomer quantities of 500 mg. Part of the appeal of using inexpensive, commercially available solvents was the ability to increase the scale of the reactions to provide polymer for comprehensive testing of properties. To investigate the viability of scaling up these reactions, we performed polymer syntheses at the 5.0 g scale, a ten-fold increase in scale. Since initial experiments with 1,9-decadiene in DOP proved to be the best system for obtaining large linear polymers of this type, a scale up reaction was performed using 5 g of this monomer and 25 g of DOP. After 48 h, a M_n of 54.0 kDa was achieved which closely matches the result of 53.4 kDa obtained from small scale polymerization run for 48 h. A large batch polymerization was also performed with the 6spBnEs, which was done in PC, and afforded a M_n of 30.8 kDa after 24 h which was identical to the results obtained in the small scale reaction as shown in Table 2. Both large scale reactions showed kinetics that were similar to what was observed in the smaller scale reactions, despite having been scaled up by an order of magnitude. This strongly implies that these reactions could be scaled-up considerably more if desired.

4 Conclusions

Here, we have described the use of cheap, high boiling, and commercially available solvents for the successful polymerization of both solid and liquid monomers. Four monomers were tested with three different solvents, PC, DEP, and DOP. A commercially available liquid monomer, 1,9-decadiene, yielded the highest molecular weight in DOP, reaching a maximum number average molecular weight of 70.0 kDa. Conversion of this monomer was greater than 99% in all three solvent systems tested. A benzyl ester functionalized monomer was synthesized and polymerized in the same solvent systems. Its polymerization proceeded more quickly in both DOP and PC, with PC offering a dramatic improvement. These two monomers were then polymerized in their preferred solvents in a 5.0 g scale reaction that definitively proved that these solvent systems allow for scaled-up reactions to proceed with similar kinetics. Ketone and alcohol functionalized diene monomers, which are solid at room temperature, were also able to undergo solution ADMET in these solvents, and polymers and oligomers were obtained. All of these solvents can be purchased cheaply from any chemical retailer and used with minimal purification in ADMET polymerizations.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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