New, Aqueous Radical (Co)Polymerization of Olefins at Low Temperature and Pressure

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Abstract: In this communication, we describe our preliminary results for the development of a new method of ethylene and propene (co)polymerization at low pressure at room temperature, using cyclodextrin-assisted aqueous radical polymerization for the first time. For polypropylene homopolymerization, the cyclodextrin was entirely removed, and the partially soluble polymer was characterized. The purification of polyethylene was not complete, since the threaded cyclodextrins remained on the polymer chain, enhancing its solubility and enable to analyze the sample. With this environmentally benign method, polyolefines could be produced, for the first time. The estimated yield was low, and therefore the conditions should be further tuned for industrial application. This straightforward approach could also be applied to synthesize poly(ethylene-*co*-vinyl acetate) copolymer with an ethylene content of 20 mol% and enhanced yield. Although the procedure in this stage of research has some limitations, the theory behind can later be applied to develop new, energy-efficient, and versatile industrial processes for olefin copolymerizations for a wide range of comonomers.

Keywords: polyethylene; polypropylene; cyclodextrin; poly(ethylene-co-vinyl acetate); free-radical polymerization

1. Introduction

Polyolefines such as polyethylene and polypropylene, with the highest production and consumption volume in the world, are unquestionably the most important polymers in the world. For the industrial synthesis of low-density polyethylene (LDPE), free radical polymerization (FRP) of ethylene at high temperatures and pressures (>>100 °C and >>1000 bar) is used [1,2]. This polymerization results in a branched structure wherein the degree of branching is determined by the pressure and temperature of the reaction. For the synthesis of an approximately linear polyethylene through FRP, a pressure of 5000 bar is required [1,2]. Polymerizations can also be performed both in bulk and in aqueous emulsion [3–11]. Not only linear polymers but also nanocomposites have been prepared by the polymerization of ethylene in emulsion [12–15]. There have been many attempts to carry out radical ethylene polymerization under milder conditions (<100 °C and <1000 bar) [16]. Still, these attempts were not of industrial interest because of the low yields achieved [17–21]. The radical polymerization is only possible for ethylene, but no other olefins, such as propylene, due to the rapid chain transfer caused by allylic hydrogen abstraction; therefore, industrial polypropylene synthesis uses Ziegler–Natta, or metallocene catalyst systems [1,2].

The radical copolymerization of ethylene with more reactive monomers such as styrene and vinyl acetate proceeds under significantly milder conditions than the homopolymerization of ethylene

and therefore controlled polymerization techniques can also be used [22,23]. The copolymerization parameters of ethylene with the comonomers vinyl acetate and styrene usually differ from ideal copolymerization ($r_{ethylene}$ = 0.04−0.82, and $r_{comonomer}$ = 0.99−2.00), but are tunable with pressure and temperature [24,25]. The copolymerization of ethylene and vinyl acetate at low-pressure and low-temperature yields only low molecular weights (~10 kDa) [26–28], although higher molecular weights were achieved with cobalt-mediated radical polymerization (up to 35 kDa), the reaction was extremely slow [29]. Therefore, there is still a need for improved copolymerization processes of ethylene at low temperature and pressure.

The aforementioned aqueous emulsion polymerization of olefines applies a temperature above 80 °C, pressure around and above 200 bars, and high amounts of hardly removable surfactants [12–16]. Cyclodextrins (CDs) are widely used to complex and solubilize different hydrophobic substances, even monomers, and polymers [30–32]. The hydrophobic cavity of CDs binds suitable organics by hydrophobic interactions and/or H-bonds, while the hydrophilic outer shell provides the water solubility. Ritter et al. successfully polymerized various hydrophobic monomers, such as styrene [33–38], (meth)acrylates [33,34,39–44], phenol derivatives [45,46], fumarates [47,48], dienes [49,50], halo-olefins [51–53], and other non-commercial ones [54–61] in water, solubilized by CD, via free radical polymerization methods. During the polymerization, the CD, every time, slips off from the last monomeric unit of the polymer, and the product precipitates, resulting in a pure product, or simple purification.

Here, we aim to test the CD-assisted free radical polymerization in the production of polyolefins and their copolymers on a low-temperature and reduced pressure.

2. Materials and Methods

2.1. Materials

α- and β-cyclodextrins (α-, and β-CD) were donated by Wacker Chemie (Münich, Germany) and was dried overnight under reduced pressure at 60 °C. Ethylene (99.9%, Gerling Holz+Co, Germany), propylene (99.5%, Air Liquide Deutschland GmbH, Germany), 2,2′-azobis [2″-(2‴-imidazoline-2‴-yl)propane] dihydrochloride (VA-044, 95%, Fluorochem, Germany), and urea (99.9%, Grüssing GmbH, Germany) were used as received. Vinyl acetate (≥99%, Sigma Aldrich, Germany) was freshly distilled under reduced pressure before used. Deuterated solvents (TCI Deutschland GmbH., Germany) were used as received.

2.2. Methods

2.2.1. Polyethylene Prepared via Free Radical Polymerization

A total of 242.5 mg (0.75 mmol) 2,2′-azobis[2-(2-imidazoline-2-yl)propane] dihydrochloride (VA-044, radical initiator), was dissolved in 200 mL 30 wt.% aqueous α-cyclodextrin (α-CD, 60 g, 61.70 mmol) suspension. The system was bubbled through with nitrogen gas for 30 min under stirring. Ethylene was added by 4.5 bar pressure, and the system was stirred for another 2 h in order to achieve α-CD/ethylene complex formation. The reactor was heated to 35 °C to start the reaction and was stirred for two days.

After the reaction, the resulting solid was filtered, dissolved in Dimethyl sulfoxide (DMSO), heated up to 60 °C, and was precipitated into aqueous NaCl solution (5 wt.%). Yield = 0.6 g

^{1}H NMR (DMSO-d6, 400 MHz) δ/ppm = 1.30 ppm (methylene) for polyethylene. The broad, undefinable peaks around 3.0–4.0 ppm, 4.5 ppm, and 5.0–6.0 ppm belonging to threaded α-CD ensure the solubility of polyethylene in DMSO. From the integral values, the ethylene/PEG molar ratio is 1/0.05.

2.2.2. Polypropylene Prepared via Free Radical Polymerization

A total of 242.5 mg (0.75 mmol) VA-044 was dissolved in 200 mL aqueous 8 M urea/β-cyclodextrin (β-CD, 40 g, 41.12 mmol) solution. The system was bubbled through with nitrogen gas for 30 min under stirring. Propylene was added by 4.5 bar pressure, and the system was stirred for another 2 h in order to β-CD/propylene complex formation. The reactor was heated to 35 °C to start the reaction and was stirred for two days.

After the reaction, the clear solution was purified by ultrafiltration (10 kDa MWCO). After freeze-drying, the resulting product was reprecipitated from DMSO into 0.1 M aqueous NaCl solution. Yield = 1.0 g

^{1}H NMR (CDCI$_3$, 400 MHz) δ/ppm = 0.80, 1.25, and 1.55 ppm for the methyl methylene methine protons of polypropylene.

2.2.3. Poly(Ethylene-*co*-Vinyl Acetate) Prepared via Free Radical Polymerization

242.5 mg (0.75 mmol) VA-044 was dissolved in 200 mL 30 wt.% aqueous α-CD (60 g, 61.70 mmol) suspension. 18.4 mL (17.2 g, 200 mmol) of vinyl acetate was added to this solution. The system was bubbled through with nitrogen gas for 30 min under stirring. Ethylene was added by 4.5 bar pressure, and the system was stirred for another 2 h in order to α-CD/ethylene complex formation. The reactor was heated to 35 °C in order to start the reaction and was stirred for two days.

After the reaction, the resulting whiteish gluey-solid was centrifuged. Yield = 12 g

^{1}H NMR (DMSO-d6, 400 MHz) δ/ppm = 0.90–1.40 ppm for methylenes with various connections of polyethylene, 1.75–2.00 ppm for methyl and methylene protons for poly(vinyl acetate), 4.87 ppm (methine) of poly(vinyl acetate).

2.2.4. Blind Tests and Reproducibility

The same reactions as above were carried out without the addition of an initiator and cyclodextrin solubilizer. The same conditions and feed compositions were used as in Section 2.2.1 and Section 2.2.2, and the reaction mixture was kept at 35 °C for three days. After the appropriate workup procedure, no products were found in these reactions.

The reproducibility of all the reactions was examined by successively performing three polymerizations with the above-mentioned monomers and reaction conditions.

2.3. Analytical Methods

The ^{1}H NMR measurements were performed on a Bruker AVANCE Ultrashield 400 (400.2 MHz) instrument (Billerica, MA, USA).

IR spectra were obtained with a Bruker Tensor 27 Fourier transform infrared (FT-IR) spectrometer (Bruker Rheinfelden, Germany) in transmission mode using the software OPUS by Bruker.

Gel permeation chromatography of the polymer samples was performed with a standard setup that consisted of SDV 103 and 105 Å columns from Polymer Standards Service (PSS) (Mainz, Germany) and a Shodex RI-101 (Tokyo, Japan) refractive index detector. The mobile phase was chloroform and THF, and the flow rate was 1.0 mL/min at 25 °C using a Viscotek VE1121 GPC pump. The column was calibrated with narrow linear polystyrene standards (PSS, from 1.04 to 1090 kDa). Data evaluation was performed with the WinGPC Unity 7 program (PSS).

3. Results and Discussion

First, the homopolymerization of ethylene and propene in water was tested via cyclodextrin (CD)-assisted radical polymerization.

Ethylene was complexed with α-cyclodextrin in water, and the complex was polymerized using VA-044 radical initiator at 35 °C, as shown in Figure 1. The monomer was added with 4.5 bar over the reaction; therefore, no long polymer chains or high yield was expected using such small pressure at

around room temperature. After the 36 h of reaction, the white solid was centrifuged, dissolved in DMSO, and precipitated into 5 wt.% NaCl solution. The product yielded as white solid around 0.6 g, was lyophilized and analyzed.
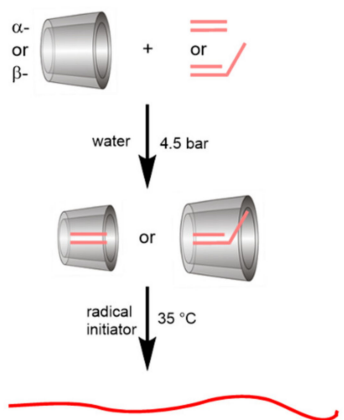

Figure 1. General scheme of the cyclodextrin-assisted aqueous radical polymerization of ethylene and propylene.

Because of the insolubility of polyethylene in most of the commercial solvents, the characterization of the polymer is challenging. The IR spectrum of the polymeric product (Figure S1) shows several different peaks. First, significant absorbances of CDs were seen in the fingerprint region and above 3000 cm^{-1}. Strong peaks at 2800 and around 1500 cm^{-1} belonged to the C-H stretching and bending, respectively. Even though the intensity of these second peaks was higher than that for pure CDs, the overlapping absorbances of the two components, i.e., polymer and CD, at these wavenumbers did not support the characterization of the product. Nevertheless, it can give some hint, and let us assume that, with CD-assisted polymerization, the resulting product still contained some threaded macrocycles. The threaded CDs provide the solubility of the polyethylene, facilitated to investigate via NMR spectroscopy (Figure S2).

The peaks around 3.0–4.0 ppm, and between 4.5 and 5.5 ppm belong to threaded α-CD, which ensures the solubility of polyethylene in DMSO, while the chemical shift at 1.20 ppm belongs to the polyethylene. From the integral values of the methylenes of polymer and the anomeric proton of the cyclodextrin, the ethylene/CD molar ratio is 1/0.85. These findings show that *pseudo*-polyrotaxanes of polyethylene and α-CD have been formed, which was also supported by the fact that the CD peaks are broadened, because of their restricted mobility, as a consequence of threading.

Because of the strong hydrogen bonds between the native CDs, it can be assumed that the polymerization of the complexed monomer runs in a channel formed by the organization of the CDs [62]. Therefore, a small amount (five orders of magnitude lower than CD in moles) of poly(ethylene glycol) (PEG, Mn~35kDa) was added to the system. PEG forms *pseudo*-polyrotaxane with α-CD in water [63], and due to the length of this additive, the development of more elongated channels, consequently longer polymers, is expected. Based on the NMR spectrum (see supporting information, Figure S3), it can be concluded that the PEG could not be removed from the system, but the ethylene/CD molar ratio significantly decreased to 1/0.35.

Gel permeation chromatographic (GPC) investigation was not possible of this complex superstructure, because of the dynamics of threading–dethreading of CD from the polymer, in the mobile phase, resulted in precipitation in the column. For the same reason, molar mass determination with other simple methods, such as viscometry or osmometry, was not possible.

The radical polymerization of propylene is highly unfavorable because of the allylic hydrogen abstraction [1,2]. Based on the results of the CD-assisted aqueous radical polymerization of ethylene, propylene was also tested in this reaction (see general scheme in Figure 1). Propylene was added with

4.5 bar to aqueous cyclodextrin solution. In this case, β− instead of α−CD was used because propylene could not fit into the cavity of the α variant, with a low cross-section. β−CD has only limited solubility in water but has enhanced solubility in a urea/water system; therefore, 8M aqueous urea was used as the reaction medium [22]. After 36 h of reaction, within similar conditions as the aforementioned ethylene, the clear solution was purified by ultrafiltration (10 kDa MWCO), and the resulting product was reprecipitated from DMSO into 0.1 M aqueous NaCl solution. The 1.0 g white solid polymer product was analyzed via FT-IR and NMR spectroscopy.

From the IR spectrum of the produced polypropylene (Figure S4), the strong peaks of C-H stretching and bending at 2800 and around and below 1500 cm^{-1} can be identified, respectively. These are much stronger absorbances than those for O-H stretching (above 3000 cm^{-1}) for the CD solubilizer, meaning that only a tiny amount of threaded macrocycles are present.

Even polypropylene has low solubility in most of the common solvents; short oligopropylenes can be dissolved in chloroform. Hence, a fraction of the sample with a small degree of polymerization was dissolved for NMR and GPC analyses. Only three signals can be seen in the NMR spectrum (Figure 2) at 0.74, 1.19, 1.48 ppm, belong to the methyl, methylene and methine groups of oligo/polymeric propylene, formed in this aqueous polymerization, respectively. No, or very weak, peaks in CD are present, indicating almost complete purification after the reaction.
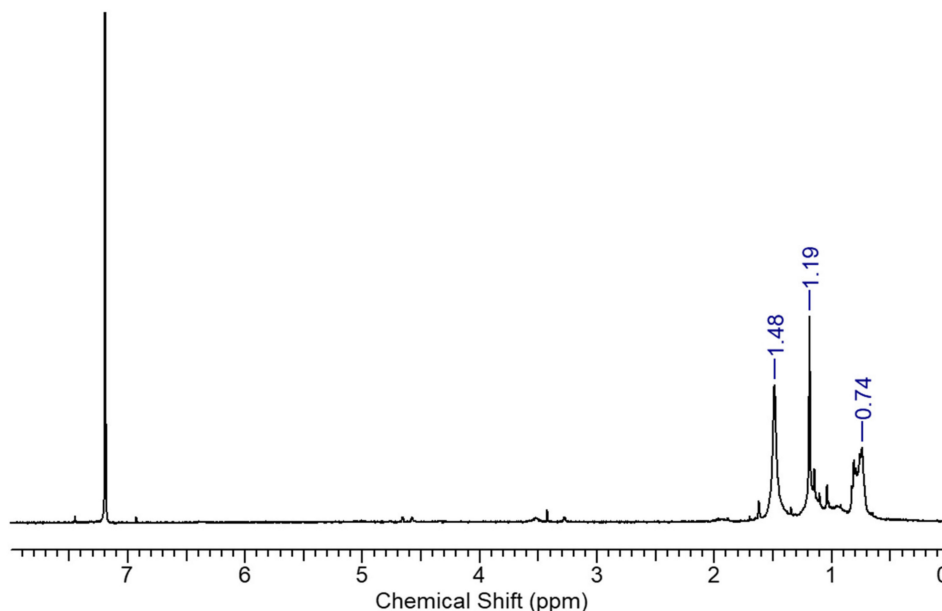

Figure 2. 400 MHz ^{1}H NMR spectrum of the polypropylene, produced via cyclodextrin (CD)-assisted aqueous free radical polymerization, in CDCl3.

The results of GPC chromatography (Figure S5) show multimodal molar mass distribution with molar masses up to 70 kDa. Some reservations have to be expressed about these results, due to the insolubility of the polypropylene, especially in the higher molar mass region, in the mobile phase.

The free-radical polymerization of propylene was possible, most probably because of some shielding effect of the cyclodextrin. Not only the monomer but also the polymeric chain-ends were complexed in the CD and no hydrogen abstraction; consequently, no chain transfer could have occurred.

Because of the problematic purification of polyethylene together with the low yield, copolymerization of ethylene was also investigated. The copolymer of ethylene and vinyl acetate is an important product; its application ranged from material science to biomedicine. α-CD assisted aqueous radical copolymerization of ethylene and vinyl acetate was carried out at 35 °C, utilizing the previously used VA-044 thermal radical initiator. After 36 h reaction, the produced polymer was centrifuged and dried under vacuum, resulting in 12 g whiteish solid-gluey product.

　　　The IR spectrum (Figure 3) of the product, in comparison with the CD-assisted aqueous homopolymerization of ethylene, shows a strong absorbance at 1700 cm^{-1} for C=O stretching, as an indication of the presence of vinyl acetate. The intensity of the broad O-H stretching peak of CD is also decreased, in comparison to the homopolymerization trial, suggesting better purification than after the first polymerization.
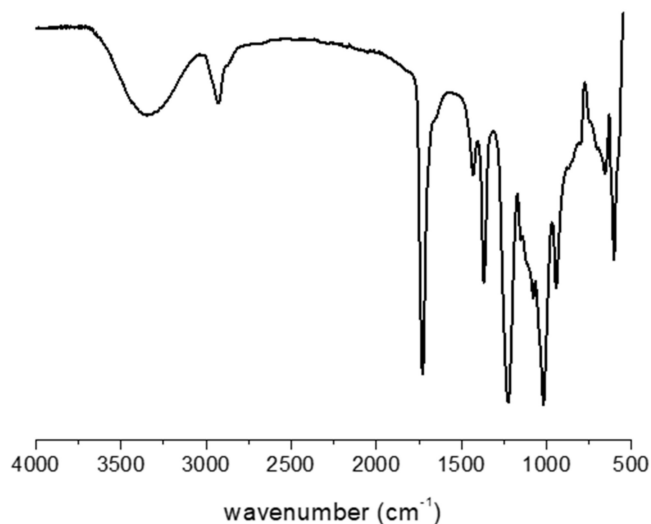

Figure 3. FT-IR spectrum of the poly(ethylene-*co*-vinyl acetate), produced via CD-assisted aqueous free radical polymerization.

　　　The copolymer was partially soluble in apolar solvents, such as THF and chloroform. Even the formed clear solution, during sample preparation, particles were filtered out, with around 20wt.% of the total product. Therefore, the results of the composition and molar mass determination, again, pertained to the soluble fraction.

　　　From the NMR spectrum of the copolymer (Figure 4), the composition of the product could be calculated. The integral values of CH$_3$-O- of the vinyl acetate at 4.85 ppm and the polymeric backbone between 0.5 and 2.0 ppm show that 20 mol% ethylene and 80 mol% of vinyl acetate built into the copolymer. This result suggests 57% monomer conversion for vinyl acetate. A lower pressure of ethylene was used in this reaction to test its effect on the composition. Two bars of ethylene led to very low olefin content, within the error range of integration of the NMR spectrum. Higher pressure could not be applied by our equipment.
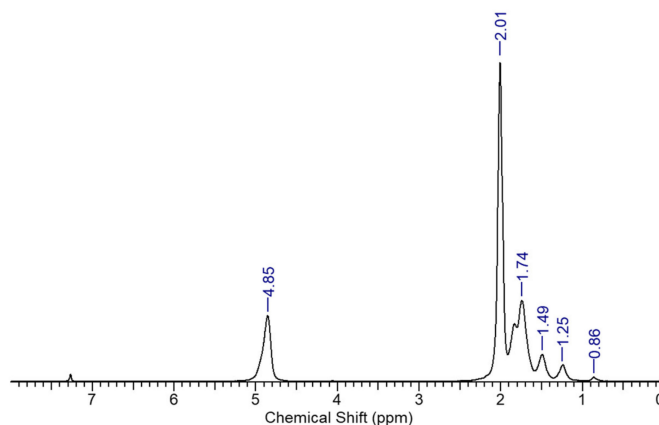

Figure 4. 400 MHz ^{1}H NMR spectrum of the poly(ethylene-*co*-vinyl acetate), produced via CD-assisted aqueous free radical polymerization, in CDCl$_3$.

Molar mass was determined via GPC in tetrahydrofuran (THF). The molar mass of the soluble fraction of 85 kDa was determined for the copolymer sample with a dispersity of 3.2 (Figure 5).
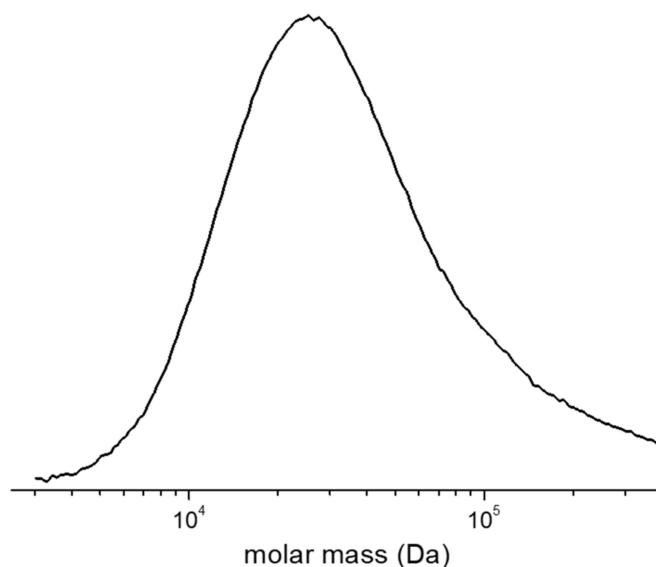

Figure 5. Molar mass distribution of poly(ethylene-*co*-vinyl acetate), produced via CD-assisted aqueous free radical polymerization, in THF.

Here, it should be noted that, for all the (co)polymerizations, test reactions were carried out without CD, initiator, or monomer. Neither homo- nor copolymerization resulted in a product when the initiator was not present. No product was detected in homopolymerizations either when CD or monomer was not added to the system. This result supports our assumption that only CD solubilized hydrophobic monomers have participated in these polymerizations.

3.1. Recovery of the CD

After all the reaction, the CD was recovered from the reaction mixture by ultrafiltration (0.5 kDa MWCO membrane), followed by freeze-drying. The regained macrocycles (up to 80%) could be recycled and used in the further reaction, making the application of the solubilizer in such a high amount environmentally and financially not disadvantageous.

3.2. Reproducibility of the Reactions

In this early stage of the development of such a new method, the investigation of the reproducibility of the reaction is crucial. We repeated all the reactions several times, but at least three polymerizations with all monomers/comonomers were carried out. From the results of these reactions, we have learned that the reactions are satisfactorily reproducible, using the same workup procedure. For ethylene homopolymerization, the CD could be removed only until the above-mentioned limit, while propylene homopolymerization resulted in a pure product, always in the molar mass range ~1–70 kDa. The copolymerization of ethylene and vinyl acetate resulted in a similar product every time, with a maximum deviation from the described results ±5%.

4. Conclusions

Ethylene and propylene were polymerized radically in water, close to room temperature, at low pressure, using cyclodextrin as a solubilizer, leading to polyolefines with a low yield. The purification of polyethylene was not ideal, but polypropylene could be easily separated from the CD. The copolymerization of ethylene and vinyl acetate resulted in a copolymer with 20 mol% of ethylene content. This method opens new routes for environmentally friendly, energy-efficient,

and inexpensive polyolefin synthesis and could lead to endless possibilities to generate a wide range of copolymers for these olefins. In the future, the effect of the pressure of the gaseous monomer on the product's molar mass and composition has to be investigated. It is highly expected that, at higher pressure, which consequently uses higher concentrations, the molar mass will be increased, and the purification will be more successful. Poly(ethylene-*co*-vinyl acetate) copolymer with a higher portion of ethylene can also be produced by utilizing higher ethylene pressure.

Supplementary Materials: The following are available online at http://www.mdpi.com/2227-9717/8/6/688/s1, Figure S1: IR spectrum of the formed polyethylene pseudorotaxane via cyclodextrin assisted aqueous radical polymerization of ethylene, Figure S2. 400 MHz 1H NMR spectrum of the polyethylene, produced via CD assist-ed aqueous free radical polymerization, in d6-DMSO, Figure S3: 400 MHz 1H NMR spectrum of the polyethylene, produced via CD assisted aqueous free radical polymerization with the addition of poly(ethylene glycol), in d6-DMSO, Figure S4: IR spectrum of the formed polypropylene via cyclodextrin assisted aqueous radical propylene polymerization, Figure S5. Molar mass distribution of the polypropylene, produced via CD assisted aqueous free radical polymerization, in chloroform.

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