

Effects of Propylene Oxide End Capping on Amination of Polyalkylene Glycols

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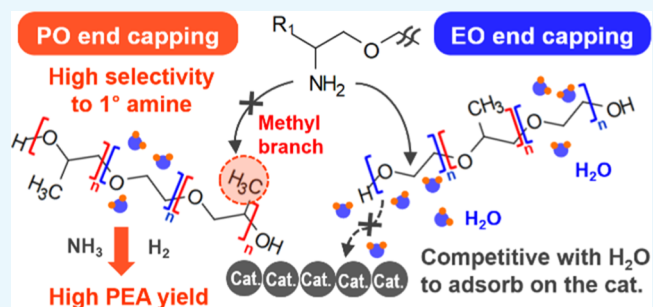


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Supporting Information

ABSTRACT: Polyalkylene glycols with two different end-capping groups of ethylene oxide (EO) and propylene oxide (PO) were used for amination to produce polyetheramine (PEA) on cobalt-based catalysts. Although it is known that the amination of secondary alcohol is more difficult than that of primary alcohol, PO end-capped block copolymers showed remarkably enhanced activity toward PEA and selectivity toward the primary amine compared to EO end-capped block copolymers.



INTRODUCTION

Polyetheramine (PEA) is a crucial intermediate used for epoxy resin and polyurea. It also can be used to provide a hydrophilic property to maleated polypropylene by adding ethylene oxide (EO) as a repeating unit to PEA's backbone. Amine is prepared from alcohol under NH₃ and H₂ in one-pot synthesis by amination.^{1,2} For PEA, polyalkylene glycol (PAG) is first dehydrogenated to ketone (aldehyde), and then ketone (aldehyde) is aminated to imine, releasing water. Finally, imine is hydrogenated to amine. The amination normally involves some kinds of side products such as imine and secondary and tertiary amines.^{3–5} However, it is very difficult to separate PEA from the product mixture because PEA has quite low vapor pressure (for PEA having molecular weight 2000, 1.24×10^{-3} bar at 235 °C). It is thus important to obtain high levels of activity and selectivity in the PEA reaction step.

In the amination process, various kinds of starting materials such as alcohol, ketone, and aldehyde can be used.^{6–10} In particular, the reaction of ketone with ammonia is known to be more challenging compared to aldehyde because of its lower reactivity.^{10–12} Developing a catalyst for the synthesis of a broad scope of amines from the wide range of ketones and aldehydes has been very limited.¹⁰ For alcohols as starting materials, only a few works studying the difference in reactivity and selectivity between primary and secondary alcohols have been reported.^{13,14} However, it was difficult to compare the structural effect of primary and secondary alcohols on the activity and selectivity of amination because the selected alcohols were not structurally analogous.

For PEA, the existence of unreacted alcohol and side products such as secondary and tertiary amines in the final product causes the decline of the reaction rate in subsequent reactions. It is thus important to confirm which factors affect

the activity toward PEA and selectivity toward the primary amine to obtain high purity of the desired PEA.

This work reports the effect of the terminal end group on amination of PAG under a Y₂O₃-inserted Co–Pd/molecular sieve 13X (MS 13X) catalyst (for catalyst properties, refer to Table S1 and Figure S1). This catalyst showed a remarkable performance for amination of polypropylene glycol in our previous study.² To the best of our knowledge, this is the first report to prove that a terminal end group comprising EO and propylene oxide (PO) units can influence selectivity toward the primary amine.

Also, this work first demonstrates that the secondary alcohol (PO end-capped PAG) can considerably improve the activity toward PEA compared to the primary alcohol (PAG containing EO units in end-sides), a result that is counterintuitive in light of previous works.^{4,10,12}

RESULTS AND DISCUSSION

Improved Primary Amine Selectivity by PO End-Capping. Various kinds of PAGs were prepared to confirm factors to determine activity and selectivity in amination toward PEA (Scheme 1). Commercial polyethylene glycol-200 (PEG-200) and polypropylene glycol-200 (PPG-200) are composed of EO and PO repeating units, respectively. The other PAGs are synthesized block copolymers consisting of EO or PO repeating units in their backbone, specifically named as

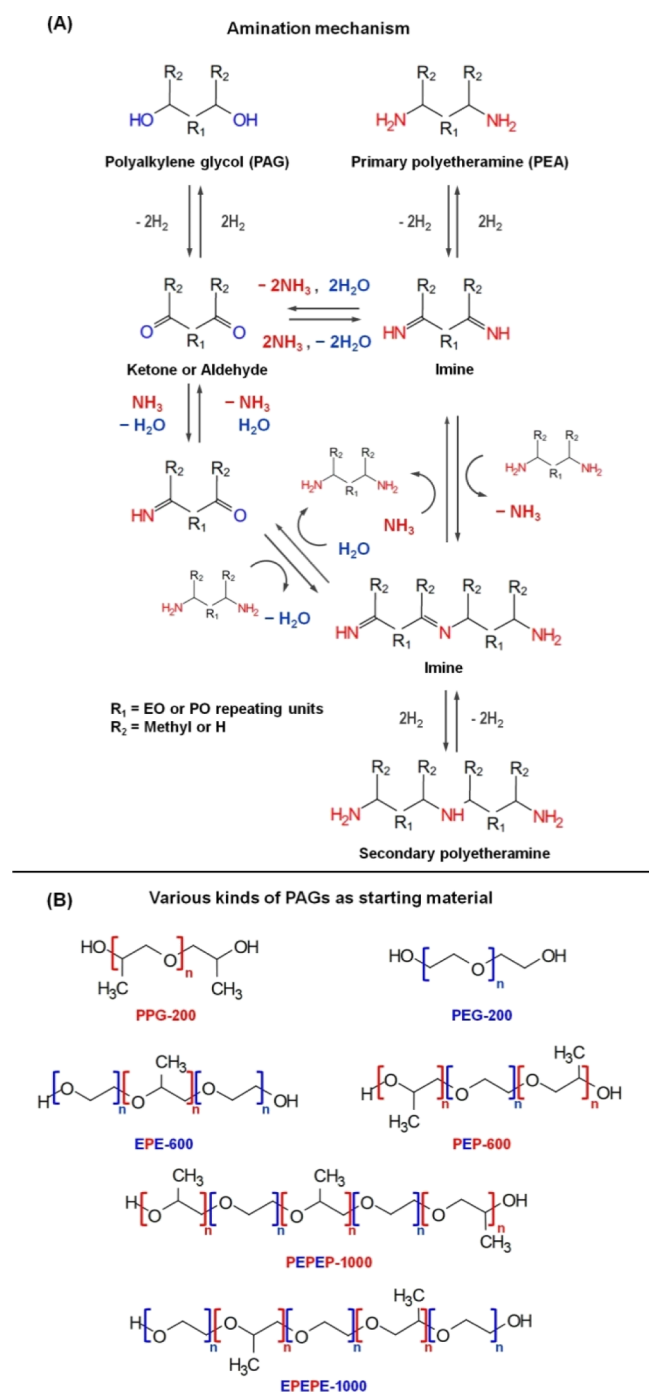
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Scheme 1. Reaction Mechanism for Amination of Polyalkylene Glycols (A) and Starting Materials' Structure (B)



EPE-600, PEP-600, PEPEP-1000, and EPEPE-1000, where E and P denote EO and PO, respectively. Table 1 shows the ratio of EO to the PO amount, the molecular weight, and residual K ion contents in synthesized PAGs (for more data, refer to Figure S2).

In addition, the synthesized PAGs only have alcohol groups without any amine groups in both end sides (refer to Figures S3 and S4). EPE-600 and EPEPE-1000 are classified as primary alcohols because EO was finally added to both end sides in PPG-200 and PEP-600, respectively, while PEP-600 and PEPEP-1000 are secondary alcohols due to PO end-capping of PEG-200 and EPE-600. In order to check if the terminal end group affects activity and selectivity, amination was carried out for PEG-200, PPG-200, and the other synthesized PAGs (Scheme 1).

It was noted that the starting materials having PO units in both terminal end sides, such as PPG-200, PEP-600, and PEPEP-1000, showed remarkably enhanced selectivity toward the primary amine compared to the PAGs containing EO units in both end sides, such as PEG-200, EPE-600, and EPEPE-1000, respectively, as shown in Figure 1. Considering the

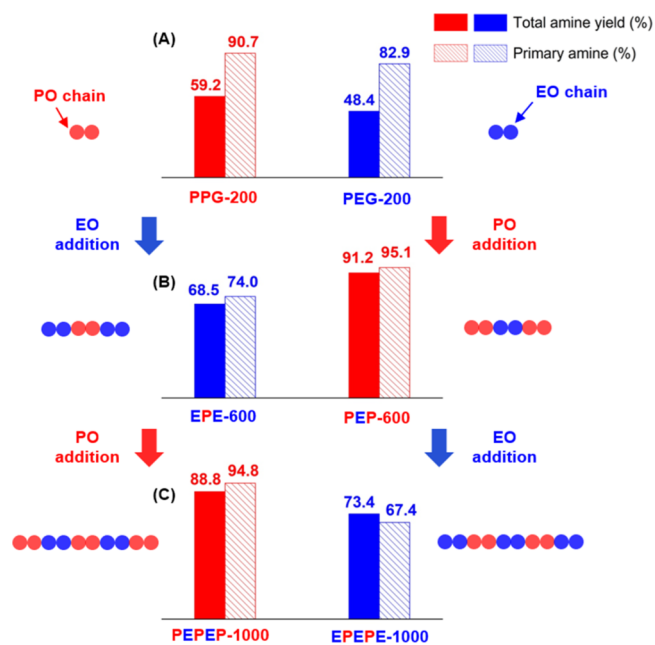


Figure 1. Reaction results (titration results) depending on the terminal end-group in PPG-200 and PEG-200 (A), in EPE-600 and PEP-600 (B), in PEPEP-1000 and EPEPE-1000 (C). Reaction conditions: PAG 30 g, $\text{NH}_3/\text{OH} = 5$, temperature 220°C , time 2 h, H_2 0.268 mol, catalyst 1.5 g.

selectivity results between EPE-600 and PEP-600, the kinds of repeating units that exist in their backbone was not a critical

Table 1. Synthesized Polyalkylene Glycols' Properties

PAGs	ratio of EO to PO		OH value (mg KOH/g)	molecular weight (g/mol) ^b	residual K ion contents (ppm) ^c
	¹ H NMR	theoretical calculation ^a			
EPE-600	3.08	2.96	184.5	608.1	1.3
PEP-600	0.62	0.64	194.9	575.7	1.1
PEPEP-1000	0.91	0.96	113.6	987.7	2.5
EPEPE-1000	1.90	1.93	119.0	942.9	1.2

^aCalculated from molecular weight of EO, PO, and PAGs. ^bCalculated from the OH value. ^cDetermined by ICP-OES analysis for PAGs.

factor influencing the selectivity to the primary amine. This decisive difference in selectivity was ascribed to the existence of the methyl branch in carbon adjacent to the terminal OH group in PPG-200, PEP-600, and PEPEP-1000.

It is known that the secondary amine forms through the reaction of ketone (aldehyde) or imine as an intermediate with the primary amine.¹⁵ The methyl group in a ketone or imine can inhibit the access of the primary amine to the partially positive carbon atom in the ketone or imine, which suppresses the formation of the secondary or tertiary amine. For example, PPG-200 consisting of PO chains showed relatively high selectivity (90.7%) to the primary amine. However, when EPE-600 in which EO was attached to PPG-200 was used, its primary amine selectivity dropped to 74.0% because EPE-600 has no methyl branches in the end sides. It was quite noticeable that the primary amine selectivity in PEPEP-1000 that is end capped by PO from EPE-600 dramatically increased to 94.8% (Figure 1). Such a change in selectivity was also found in PEG-200, PEP-600, and EPEPE-1000, depending on which component is end-capped to the starting materials. The selectivity results in each starting material were also confirmed from ¹³C NMR spectroscopy results in Table 2 (refer to Figures S5 and S6) and IR (peak in about 1640 cm⁻¹) in Figure 2.

Table 2. ¹³C NMR Results for PEA Products Aminated from Polyalkylene Glycols

PAGs	total amine yield ^a (%)	primary amine ^b (%)	PAGs	total amine yield ^a (%)	primary amine ^b (%)
PPG-200	62.0	93.0	PEG-200	51.0	83.7
EPE-600	74.8	78.8	PEP-600	93.9	98.6
PEPEP-1000	89.3	99.9	EPEPE-1000	85.9	75.7

^aCalculated from total amine divided by the sum of total amine and alcohol. ^bCalculated from primary amine divided by total amine.

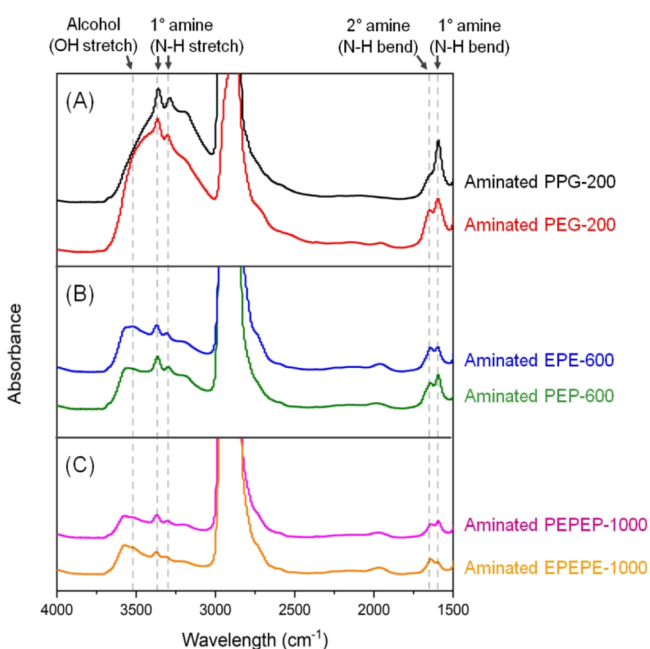


Figure 2. IR results for PEA products aminated from PPG-200 and PEG-200 (A), from EPE-600 and PEP-600 (B), from PEPEP-1000 and EPEPE-1000 (C).

Enhanced Activity toward PEA by PO End-Capping.

In addition to the improved selectivity by PO end-capping, it was shown that the existence of PO in both end sides of starting materials dramatically increased the total amine yield compared to that of EO end-capped PAGs (Figure 1 and Table 2). For instance, the secondary alcohols having PO units in both end sides such as PPG-200, PEP-600, and PEPEP-1000 showed around 11 to 23% higher total amine yield than that of the primary alcohols such as PEG-200, EPE-600, and EPEPE-1000, respectively. The improved total amine yield was also confirmed by the results of IR spectroscopy. The peak intensity in about 1595, 3300, and 3360 cm⁻¹, which indicates amine¹⁶ was higher for PPG-200, PEP-600, and PEPEP-1000 than PEG-200, EPE-600, and EPEPE-1000, respectively in Figure 2. Also, more unreacted alcohol was found from the peak around 3500 cm⁻¹ for PEG-200, EPE-600, and EPEPE-1000.

The enhanced activity toward PEA and selectivity toward the primary amine were also found in the Co/ γ -Al₂O₃ catalyst, which has widely been used for the amination of alcohol.¹⁷ The Co/ γ -Al₂O₃ catalyst was prepared through the same procedures with Y₂O₃-inserted Co–Pd/MS 13X. When it was used for the amination of PEP-600 (PO units in both end-sides) and EPE-600 (EO units in both end sides), the total amine yield (45.4%) for PEP-600 was higher than that (23.4%) of EPE-600. Also, the primary amine selectivity (97.9%) in PEP-600 was higher than that (91.7%) of EPE-600.

Many prior studies reported that the reaction of secondary alcohol⁴ or ketone^{10–12} with ammonia is more difficult than the reaction of primary alcohols or aldehyde because secondary alcohol or ketone has lower reactivity. In contrast to previous studies, the activity results in this present study showed that the PO-end-capped PAGs showed more enhanced activity toward PEA than EO-end-capped PAGs, which is presumably ascribed to the hydrophobic property of PO. It is known that PO has a more hydrophobic property than EO¹⁸ and its hydrophobicity is intensified with the increasing PO portion of PAGs. As mentioned above, water is generated in the amination step during the PEA reaction. It can be considered that the EO-end-capped PAGs attract more water in their terminal end groups than the PO-end-capped PAGs. Thus, water gathered in EO units in end sides will be competitive with starting materials to adsorb on the surface of the catalyst. However, the PO-end-capped PAGs are probably less competitive with water because of its hydrophobic property.

The influence of H₂O generated during the reaction on the catalytic activity can be further supported by the amination results of PPG-200 and PEG-200. They had a lower total amine yield than that of the other longer PAGs because both PPG-200 and PEG-200 released more amount of H₂O due to three or five times lower molecular weight than the other PAGs, whereas the catalyst weight introduced was fixed in all reactions.

The cloud point was measured to confirm whether the PO end-capping affected the hydrophobic property, as shown in Figure 3. This indicates that the lower cloud point is, the greater the hydrophobicity will be; 1.0 wt % of PAGs in 10 wt % NaCl aqueous solutions were prepared,¹⁹ and measurements were carried out from room temperature to 90 °C.

For PEG-200, the cloud point was not found at 90 °C, which means PEG-200 has strong hydrogen bonding with water. However, PEP-600 showed a low cloud point (63 °C) by PO end-capping to PEG-200; its cloud point in EPEPE-1000 (EO end-capped PEP-600) increased again to 71 °C because of the

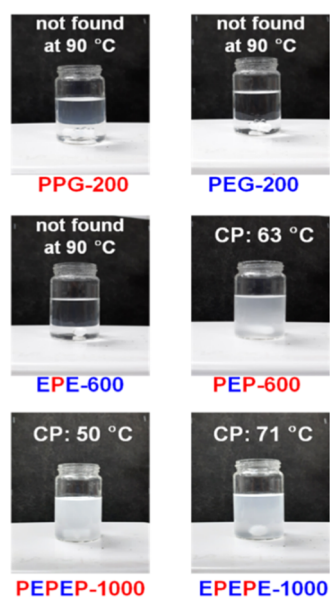


Figure 3. Cloud point measurements for polyalkylene glycols (PAGs) (1.0 wt % of PAGs in 10 wt % NaCl aqueous solutions were measured from room temperature to 90 °C).

hydrophilic property of EO. Also, the cloud point in PEPEP-1000 decreased to 50 °C owing to the increased hydrophobicity by the PO end-capping in EPE-600, whereas the cloud point in EPE-600 was not found at 90 °C because EO end-capping led to increased hydrophilicity. For the cloud points of aminated PAGs after reaction, they were almost similar with the cloud points of the PAGs before amination (Table S2). However, the cloud points of aminated EPE-600 and EPEPE-1000 were lower than EPE-600 and EPEPE-1000 before amination because aminated EPE-600 and EPEPE-1000 products had long-chain backbones including PO, ascribed to the low primary amine selectivity. The cloud points of PPG-200, PEP-600, and PEPEP-1000 before and after amination were almost the same because of high primary amine selectivity.

Cloud point measurements support that EO and PO end capping provide hydrophilicity and hydrophobicity, respectively, to terminal end sides. From the amination results (Figure 1) and cloud point measurements (Figure 3), it was found that although the PO end-capped PAGs are secondary alcohols, the PO end-capping can improve activity toward PEA by preventing the access of water to the end sides in starting materials that should adsorb on the surface of the catalyst for amination.

CONCLUSIONS

The PO end-capping played a crucial role in increasing not only primary amine selectivity but also activity toward PEA. The existence of the methyl branch in carbon adjacent to the terminal OH groups led to high selectivity by its steric hindrance. Also, the hydrophobic property in end sides by PO addition brought enhanced activity by suppressing the approach of water. The terminal hydrophobic group influencing activity and selectivity would help obtain high yield and purity of PEA, thereby overcoming the difficulty in its separation from the product mixture.

EXPERIMENTAL SECTION

Preparation of the Catalyst. The Co–Y₂O₃–Pd/MS 13X catalyst was prepared by following the same procedure in our prior work.²

Characterization of the Catalyst. Inductively coupled plasma mass spectroscopy (ICP–MS) was used to obtain the elemental composition by an Agilent ICP–MS 7700S. The surface area of the catalysts was determined by N₂ adsorption–desorption at a liquid nitrogen temperature of 77.30 K by BEL Japan Belsorp Max. High-resolution powder X-ray diffraction (RIGAKU SmartLab) was utilized to check the crystalline phases of the catalysts.

Preparation of Polyalkylene Glycols. Various kinds of PAGs were synthesized by varying the ratio of EO (LOTTE Chemical) and PO (Sigma-Aldrich) in a stainless steel batch reactor (1500 mL) at between 130 and 160 °C in the presence of a KOH catalyst. All PAGs underwent a dehydration process at 110 °C under vacuum conditions for 0.5 h to remove water generated in the reaction of PAGs (OH group) with KOH before introduction of EO or PO. The PEP-600 copolymer was prepared through adduction of PO (the mole ratio of PO to PEG-200 is 6.9) to PEG-200 (LOTTE Chemical), which has a PO end-capped structure in both end sides of PEG-200. When EO (the mole ratio of EO to PEP-600 is 9.1) was adducted again to PEP-600, EPEPE-1000 was prepared by EO end-capping on both terminal end sides of PEP-600. For the EPE-600 copolymer, PPG-200 (KPX Chemical) was end-capped by EO (the mole ratio of EO to PPG-200 is 9.1). Also, PEPEP-1000 was prepared by PO end-capping (the mole ratio of PO to EPE-600 is 6.9) from the EPE-600 copolymer. Then, either unreacted EO or PO was removed from all PAGs at 110 °C under vacuum for 0.5 h. After synthesis of each PAG, alkali metal ions (K⁺ ions) in all PAGs were removed through ion exchange of K⁺ with H⁺ ions by aluminum silicate (KW700SL, Kyowa Chemical) at 120 °C for 2 h, followed by separation of PAGs from aluminum silicate. Then, neutralized PAGs were obtained. Also, PEG-200 and PPG-200, whose alkali metal ion was removed, were also used.

Amination Test. Catalyst Activation. The amination was carried out in a stainless autoclave (0.2 L). A total of 30 g of PEG-200 (LOTTE Chemical), PPG-200 (KPX Chemical), and the synthesized PAGs (EPE-600, PEP-600, PEPEP-1000, and EPEPE-1000) and 1.5 g of the Co–Y₂O₃–Pd/MS 13X catalyst powder were placed in the autoclave. In order to remove air, N₂ purge was implemented five times, and then, H₂ was charged into the autoclave until the pressure approached 50 bar. The catalyst activation was carried out at 220 °C and around 80 bar for 2 h. After the activation step, the temperature decreased to 170 °C, and the autoclave was vented down to 10 bar at this temperature. (For PPG-200 and PEG-200, the vent at 170 °C was not carried out because of their low molecular weight.) The autoclave was cooled at room temperature and 5 bar of H₂. Then, H₂ was removed at 1 bar.

Amination. At room temperature, NH₃ was charged into the autoclave. The NH₃ amount introduced was fixed to a mole ratio of NH₃ to PAG equal to 10 (NH₃/OH = 5). Also, 0.268 mol of H₂ was introduced into the autoclave. Amination was carried out at 220 °C for 2.0 h. Reaction pressure was around 230 bar for PPG-200 and PEG-200, around 140 bar for EPE-600 and PEP-600, and around 110 bar for PEPEP-1000 and EPEPE-1000. After reaction, the temperature decreased to 170 °C, and residual gases were discharged to around 90 bar at

that temperature. (For PPG-200 and PEG-200, the vent at 170 °C was not carried out because of their low molecular weight.) The autoclave was cooled until it reached room temperature and around 30 bar of NH₃ and H₂. Then, NH₃ and H₂ were discharged down to 1 bar, and N₂ purge was applied to remove remaining NH₃.

Post-Treatment and Titration Analysis. Post-treatment and titration analysis were performed by following the same procedure mentioned in our prior work.²

Instrumental Analysis. Fourier transform infrared spectroscopy was used to confirm the amine formation on a Thermo Scientific Nicolet iS50 with ZnSe windows through the transmission method. Each IR spectrum represents an average of 64 scans for only PEA products whose background spectrum was excluded.

Carbon nuclear magnetic resonance spectroscopy (¹³C NMR) was also employed to check the amine formation in the product using an Agilent DD2-500. In order to verify EO and PO in the backbone structure of PAGs, proton nuclear magnetic resonance spectroscopy (¹H NMR) was performed on an Agilent DD2-500. Chemical shifts were reported in parts per million (δ) with reference to residual solvent resonances for ¹H NMR and ¹³C NMR (CDCl₃: ¹H, δ 7.23 ppm; CD₂Cl₂: ¹³C, δ 53.5 ppm). Sixteen scans with 16 k data points each were acquired for each ¹H NMR spectrum. The relaxation delay was 1 s. Each ¹³C NMR spectrum comprised 5000 scans with 32k data points. The relaxation delay was 10 s.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c03295>.

Catalyst characterization (ICP-mass, BET, XRD), characterization of synthesized starting materials (NMR, IR), characterization of synthesized products (NMR), and cloud point measurements of aminated PAGs (PDF)

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Notes

The authors declare no competing financial interest.

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