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RESEARCH ARTICLE

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Chain extension epoxide polymerization to well-defined block polymers using a N-Al Lewis pair catalyst

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Abstract

Block polyethers comprised of poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEG or PEO) segments form the basis of ABA-type PEO-*b*-PPO-*b*-PEO poloxamer materials. The inverse architecture with an internal hydrophilic PEO segment flanked by hydrophobic blocks can be difficult to prepare with control of architecture by use of traditional anionic polymerization. These oxyanionic polymerizations are plagued by chain-transfer-to-monomer side reactions that occur with substituted epoxides such as propylene oxide (PO). Herein, we report a new method for the preparation of block polymers through a controlled polymerization involving a N-Al Lewis adduct catalyst and an aluminum alkoxide macroinitiator. The Lewis pair catalyst was able to chain-extend commercial PEO macroinitiators to prepare di-, tri-, and pentablock polyethers with low dispersity and reasonable monomer tolerance. Chain extension was confirmed using size exclusion chromatography and diffusion ordered nuclear magnetic resonance spectroscopy. The resulting block polymers were additionally analyzed with small-angle X-ray scattering to correlate the morphology to molecular architecture.

KEYWORDS

block polymers, Lewis pair catalysis, polyethers, polymerization catalysis, reverse poloxamers

1 | INTRODUCTION

Polyethers are widely used in drug and vaccine delivery and as polymer electrolytes and non-ionic surfactants.[1–10] Poloxamer materials are a particular subset of non-ionic, ABA block polyethers containing a central hydrophobic PPO block flanked by two outer hydrophilic poly(ethylene oxide) (PEO) blocks (i.e., PEO-*b*-PPO-*b*-PEO). Other poloxamer-like materials with diverse architectures have been developed with the same design strategy of a hydrophobic midblock with PEO outer blocks on either side.[11–13] In recent years, the prevalence of these polymer architectures has increased with the rising need for materials with more complex polymer architectures for drug delivery, surfactant, electrolyte, and structural applications.[8–10]

Reverse poloxamers (RPs) are BAB triblock materials with hydrophilic midblocks surrounded on both sides by hydrophobic outer blocks. RPs have been successfully demonstrated as potential drug delivery vehicles in both in vivo and in vitro studies.[7,14] Unfortunately, many studies utilizing BAB triblock polymers focus on polymers

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with relatively short end blocks compared to their poloxamer counterparts.[10,15–21] Jung et al. showed that simply tuning the hydrophobicity of BAB triblocks by altering the hydrophobic block composition could significantly alter hydrogel relaxation dynamics; however, none of their hydrophilic end blocks exceeded 3.0 kg/mol in total.[16] Even traditional PPO-*b*-PEO-*b*-PPO RP materials such as the commercially available 25R4 and 31R1 RPs are lower molecular weight (ca. 3.0 kg/mol) compared to their poloxamer counterparts, such as the commercially available P407, a PEO-*b*-PPO-*b*-PEO copolymer (ca. 12.6 kg/mol).[14] These RPs have molecular weights that are too low to form micelles in aqueous solutions, limiting their use in many applications. Combining traditional pluronic materials with commercially available RPs was shown to dramatically alter the microstructures and moduli of resultant hydrogels.[22] A copolyether based on a poly(allyl glycidyl ether)-*b*-PEO-*b*-poly(allyl glycidyl ether) has been utilized by several research groups in recent years as a starting material for complex coacervate hydrogels. These materials, however, have been difficult to prepare with poly(allyl glycidyl ether) blocks of significant molecular weight (>10 kg/mol) and low dispersity (i.e., ≤1.10).[12,13,15] Other reported polyether BAB structures tend to be limited to materials with mixed polymer backbone types and no contiguous polyether backbone, which often necessitates additional coupling reactions of polymer chains to the polyether midblock.[23–25]

While the simplest epoxide monomer, EO, undergoes a controlled anionic polymerization to produce polymers with well-defined molecular weight and end group fidelity, polymerizations of more complex mono- and di-substituted epoxides often suffer from chain-transfer-to-monomer, which hinders the preparation of RPs.[26–28] *N*-heterocyclic olefin-based catalysts have been used in recent years to prepare controlled high-molecular weight RP materials with either propylene oxide (PO) or butylene oxide (BO) as the chain-extended block. Unfortunately, the molecular weight of the hydrophobic blocks reported were still less than 10 kg/mol.[29,30] These synthetic challenges have limited the development of RP systems by both limiting the molecular weight of the chain-extended block and by introducing homopolymer impurities initiated after chain-transfer-to-monomer that must be removed before the desired polymer can be studied.

Lewis pair catalysts have risen in prominence in recent years following the first report of frustrated Lewis pairs (FLPs) by Stephan and coworkers as a method of splitting molecular hydrogen.[31–33] Newly-developed Lewis pair catalytic systems such as those incorporating metal free borane catalysts in cooperation with organic superbases for epoxide polymerization have shown promise as methods for the preparation of polyethers with M_n >10,000 g/mol, monomer versatility, and reasonably rapid reaction kinetics.[34–41] BAB structures have been prepared by Volger and Naumann using combinations of phosphazene superbases with triethylborane to promote the facile chain extension of PEO macroinitiators with PO.[42] Chiral diborane catalysts have additionally been utilized alongside organobase to yield high-molecular weight (M_n >100,000 g/mol) PPO with isotactic diads up to 88%.[43] Inspired by the Vandenberg catalyst, other groups have developed catalyst-initiator systems that promote the synthesis of polyethers with similar control.[44–46] Exploration of the mechanisms of these systems led to the decoupling of catalysis and initiation through the use of an aluminum alkoxide initiator and a simple Lewis pair catalyst between a tertiary amine and a trialkylaluminum.[46,47] This N-Al catalyst was able to effectively catalyze the polymerization of allyl glycidyl ether (AGE) initiated with a small molecule aluminum alkoxide with good end group fidelity and control over molecular weight and polydispersity.[46]

Herein, we adapt the aluminum alkoxide/N-Al Lewis pair approach to chain-extension polymerization starting with polymeric macroinitiators to prepare functional RP materials with di-, tri-, and pentablock polymer architectures at higher molecular weights than were previously accessible. The morphologies of the chain-extended materials were then studied using small-angle X-ray scattering (SAXS) to corelate morphology to architecture control.

2 | MATERIALS AND METHODS

2.1 | Materials

Triethylamine (Acros Organics, 99%), hexanes (Millipore-Sigma, ACS reagent, >99.5%), trimethylaluminum (2.0 M in hexanes, Millipore-Sigma), triethylaluminum (1.0 M in hexanes, Millipore-Sigma), hydrochloric acid (Millipore-Sigma, 37%), $CDCl_3$ (Cambridge Isotope Laboratories) were obtained and used as provided. AGE (Aldrich, >99%), PO (Millipore-Sigma, >99%), epichlorohydrin (TCI, >99%), *n*-butyl glycidyl ether (VWR, ≥98.0%) were dried over calcium hydride, distilled, and stored under a nitrogen glovebox atmosphere prior to use. Poly(ethylene glycol) methyl ether average M_n ca. 2.0 kg/mol (MeO-PEO-2000) (Millipore-Sigma), poly(ethylene glycol) average M_n ca. 3.0 kg/mol (PEO-3000) (Millipore-Sigma) and poly (ethylene glycol) average M_n ca. 8.0 kg/mol flakes (PEO-8000) (Millipore-Sigma) were purified prior to use by recrystallization in ethanol to remove impurities. The PEO flakes were then dissolved in dry toluene and heated under vacuum in an azeotropic distillation to remove any residual water. PEO macroinitiators were then further dried in vacuo overnight and stored

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under a nitrogen glovebox atmosphere prior to use. All other solvents were collected from a J.C. Meyer dry solvent system and brought into the glovebox. All air and moisture sensitive reactions were conducted under a dry nitrogen glovebox atmosphere.

2.2 | Equipment

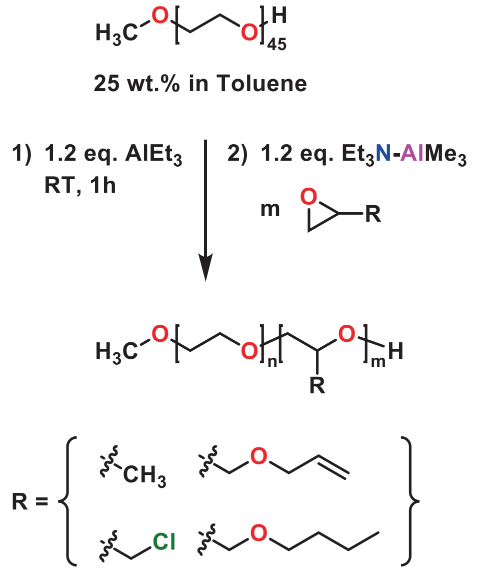
^{1}H NMR spectroscopy was performed on a 400 MHz Agilent MR spectrometer at room temperature and referenced to the residual solvent signal of $CDCl_3$. Size exclusion chromatography (SEC) was carried out on an Agilent system with a 1260 Infinity isocratic pump, degasser, and thermostatted column chamber held at 30 °C containing an Agilent PLgel 10 μm MIXED-D column with an operating range of 200–400,000 g/mol relative to polystyrene standards. HPLC-grade chloroform was used as the mobile phase. Polymer samples were dissolved in HPLC-grade chloroform to concentrations of approximately 2.0 mg/mL prior to analysis. This system was equipped with an Agilent 1260 refractometer and Infinity Bio-inert Multi-Detector suite featuring dual-angle static and dynamic light scattering detection.

2.3 | Small angle X-ray scattering

All data were collected on a SAXSLabs Ganesha 300 K with an X-ray wavelength of 1.5418 Å. Kapton tape and a stainless-steel washer were used to contain the polymer samples. The stainless-steel washer was placed on the Kapton tape, and a polymer sample was then added to fill the washer with another piece of Kapton tape placed on top to cover the sample. Data were collected on each sample for 30 minutes at room temperature unless otherwise specified.

2.4 | Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-tof-MS)

All analysis was conducted on a Bruker autoflex maX MALDI-tof instrument. 2,5-dihydroxybenzoic acid (DHB) matrix was dissolved in tetrahydrofuran (THF) to a concentration of 2.0 mg/mL. Sodium trifluoroacetate in THF 2.0 mg/mL and polymer 5.0 mg/mL solutions were also prepared. Solutions were prepared for spotting onto a stainless steel MALDI plate by combining 10 μL each of matrix, salt, and polymer solutions. Of this solution 2.0 μL were then spotted on the MALDI plate and allowed to dry before analysis.



SCHEME 1 Unidirectional chain extension from a MeO-PEO-OH macroinitiator.

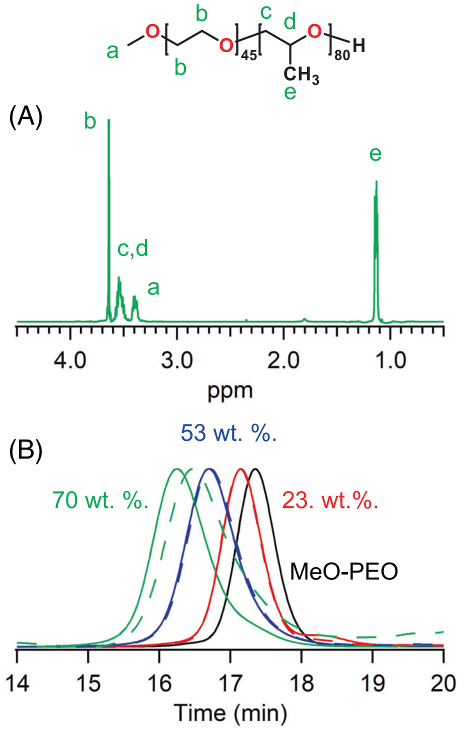


FIGURE 1 (A) ^{1}H NMR spectroscopy in $CDCl_3$ of PEO-*b*-PPO ($PEO_{45}PPO_{80}$). (B) Size exclusion chromatography traces of unidirectional chain extension of a MeO-PEO-OH macroinitiator with either 10 (ca. 23 wt%) (red), 40 (ca. 53 wt%) (blue), or 80 equivalents (ca. 70 wt%) (green) of PO. Solid and dashed lines of the same color show the two trials of each polymerization. Molecular weight characterization data can be found in Table 1.

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2.5 | Synthesis of the N-Al catalyst

A reaction vessel was charged with a stir bar and placed in a −78 °C cool-well in a dry nitrogen glovebox. 6.35 mL of anhydrous hexanes and 6.35 mL of 2.0 M of trimethylaluminum in hexanes were added slowly to the cooled vial and allowed to equilibrate over 10 min while stirring. Triethylamine (1.77 mL, 12.7 mmol) was then added dropwise to the cooled vial containing the alkylaluminum solution. The solution was then allowed to warm slowly to room temperature while stirring overnight. The catalyst was purified by directly cooling the solution to −40 °C to crystallize the Lewis adduct. The resultant crystals were washed three times with anhydrous hexanes and dried in vacuo. Isolation of the crystalline adduct ensures 1:1 stoichiometry of the amine and alkylaluminum.

2.6 | General synthesis of α-methoxy-poly(ethylene oxide)-*b*-poly(ether)

A reaction vial was charged with a stir bar and 500 mg of MeO-PEO-2000. The PEO was dissolved in 2.0 mL

TABLE 1 Unidirectional chain extension of polyethers from a MeO-PEO-2000 macroinitiator.

Sample name	[M]/[I]	Time (h)[a]	Conv (%)[b]	[PEO]:[M] (mol %$^{(th)}$)[c]	[PEO]:[M] (mol %$^{(obs)}$)[d]	M_n ^{theo} (kg/mol)	M_n (kg/mol)[e]	M_n (kg/mol)[f]	Đ[g]
BnO-PAGE$_{90}$[h]	90	24	97	0:100	0:100	10.3	11.1	5.8	1.29
PEO$_{45}$PPO$_{10}$	10	24	98	82:18	81:19	2.6	2.6	4.9	1.07
PEO$_{45}$PPO$_{10}$	10	24	96	82:18	84:16		2.5	4.9	1.08
PEO$_{45}$PPO$_{40}$	40	24	94	53:47	53:47	4.3	4.3	6.7	1.14
PEO$_{45}$PPO$_{40}$	40	24	96	53:47	52:48		4.4	6.7	1.14
PEO$_{45}$PPO$_{80}$	80	24	92	36:64	36:64	6.6	6.6	9.5	1.16
PEO$_{45}$PPO$_{80}$	80	24	96	36:64	25:75		9.9	7.4	1.20
PEO$_{45}$PAGE$_{10}$	10	48	78	82:18	90:10	3.1	2.6	5.1	1.10
PEO$_{45}$PAGE$_{10}$	10	48	99	82:18	81:19		3.2	5.1	1.13
PEO$_{45}$PAGE$_{40}$	40	48	94	53:47	60:40	6.6	5.4	7.0	1.16
PEO$_{45}$PAGE$_{40}$	40	48	98	53:47	51:49		7.0	8.2	1.04
PEO$_{45}$PAGE$_{80}$	80	48	98	36:64	54:46	11.1	6.4	9.8	1.20
PEO$_{45}$PAGE$_{80}$	80	48	96	36:64	37:63		10.9	9.6	1.22
PEO$_{45}$PnBGE$_{10}$	10	48	84	82:18	58:42	3.3	6.2	5.3	1.09
PEO$_{45}$PnBGE$_{10}$[g]	10	48	88	82:18	78:22		3.7	5.5	1.12
PEO$_{45}$PnBGE$_{40}$	40	48	91	53:47	53:47	7.2	7.2	7.2	1.14
PEO$_{45}$PnBGE$_{40}$	40	48	94	53:47	49:51		8.0	7.6	1.15
PEO$_{45}$PnBGE$_{80}$	80	48	87	36:64	48:52	12.4	8.3	10.2	1.13
PEO$_{45}$PnBGE$_{80}$	80	48	94	36:64	35:65		13.1	10.4	1.17
PEO$_{45}$PECH$_{10}$	10	24	91	82:18	82:18	2.9	2.9	5.5	1.27
PEO$_{45}$PECH$_{10}$	10	24	93	82:18	52:48		5.9	5.5	1.32
PEO$_{45}$PECH$_{40}$	40	24	99	53:47	50:50	5.7	6.2	9.0	1.54
PEO$_{45}$PECH$_{40}$	40	24	98	53:47	37:63		9.0	14.4	1.33
PEO$_{45}$PECH$_{80}$	80	24	99	36:64	30:70	9.4	11.8	12.0	1.73
PEO$_{45}$PECH$_{80}$	80	24	99	36:64	25:75		14.3	10.6	3.24

Note: PEO chain-extension was conducted in duplicate unless otherwise noted.

[a] Time at which reaction was terminated.

[b] Conversion based on ^{1}H NMR spectroscopy end group analysis.

[c] Theoretical mole percentage of [PEO] compared to monomer [M].

[d] Observed mole percentage of [PEO] compared to monomer [M] as determined by NMR spectroscopy.

[e] M_n calculated from ^{1}H NMR spectroscopy end group analysis.

[f] M_n from SEC relative to polystyrene standards.

[g] (M_w/M_n) relative to polystyrene standards.

[h] Initiation from benzyl alcohol results are from a single polymerization.

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toluene, after which 0.30 mL 1.0 M triethylaluminium in hexanes (1.2 eq.) was added. The mixture was allowed to stir at room temperature overnight. After 24 h, 520 mg of N-Al adduct catalyst was added, followed by 10, 40, or 80 molar equivalents of either PO, AGE, epichlorohydrin (ECH), *n*-butyl glycidyl ether (nBGE), or propargyl glycidyl ether (PPGE) relative to hydroxyl end groups on the MeO-PEO starting block. The reaction was heated to 60 °C in the case of AGE and nBGE, or room temperature in the case of PO, ECH, or PGE. The conversion of monomer was monitored over time via ^{1}H NMR spectroscopy of reaction aliquots. Once it was apparent that the conversion of monomer had converged, the vials were removed from the glovebox. The copolymer was dissolved in dichloromethane, washed twice with 0.1 M HCl in MeOH followed by DI water. The copolymer was then isolated from dichloromethane by rotary evaporation and then dried in vacuo. Chain extension was characterized via ^{1}H NMR spectroscopy and SEC in chloroform and analyzed against polystyrene standards.

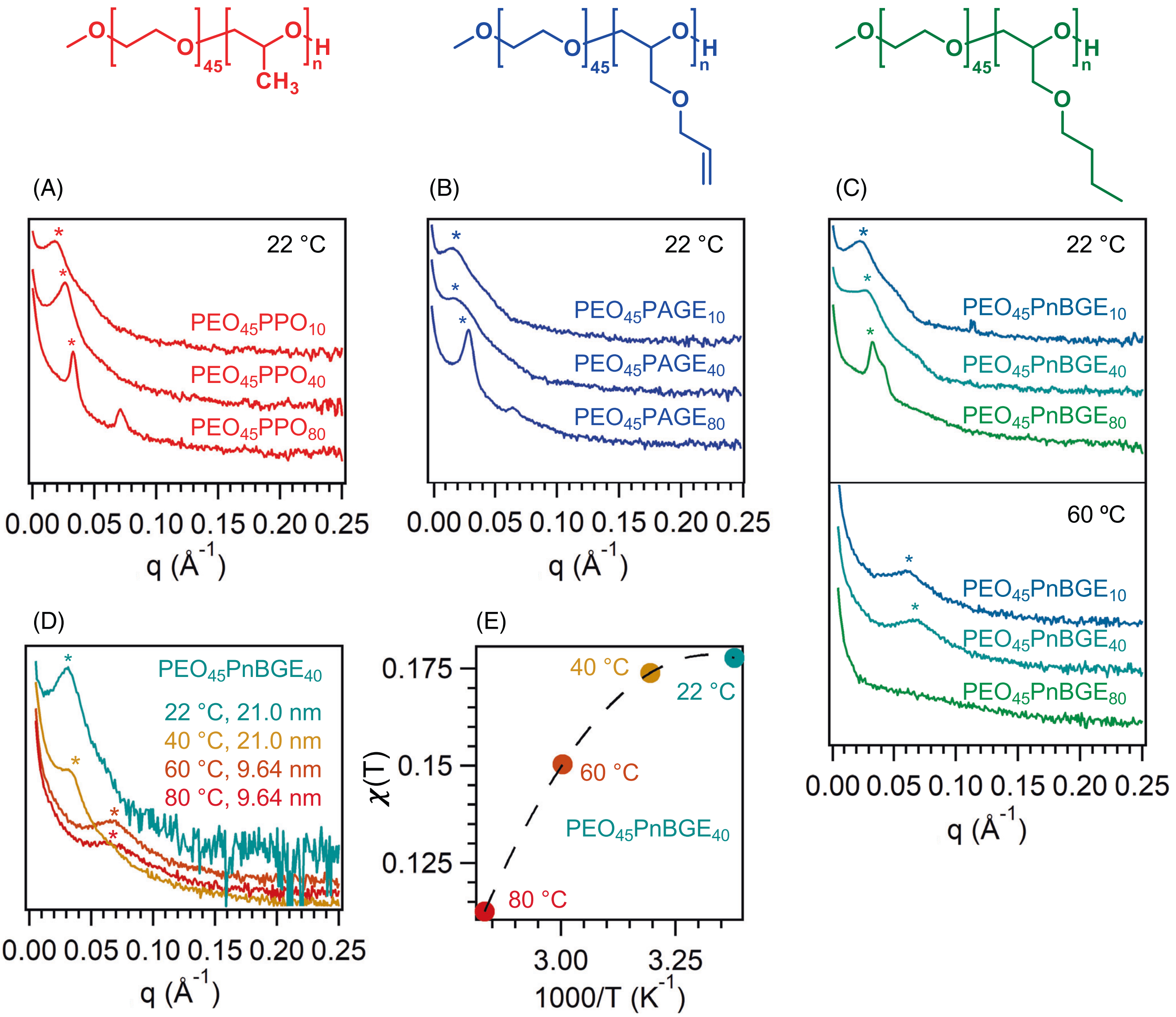

FIGURE 2 SAXS of unidirectional chain extension of a MeO-PEO-OH macroinitiator with PO (red), AGE (blue), or nBGE (green). Log intensity is offset for clarity. Each sample used for SAXS was the first sample listed in the table for each duplicate polymer trial. Traces are stacked in decreasing order of hydrophobic block length within each subset. (A) PEO-*b*-PPO of 70, 54, and 23 wt% PPO collected at room temperature. (B) PEO-*b*-PAGE of 82, 70, and 36 wt% PAGE collected at room temperature. (C) Top: PEO-*b*-PnBGE of 84, 72, and 39 wt% PnBGE. Data collected at room temperature. Bottom: PEO-*b*-PnBGE collected at 60 °C. (D) PEO-*b*-PnBGE (72 wt% PnBGE) spectra as a function of temperature. Scattering patterns were collected at 23, 40, 60, and 80 °C. (E) Effective interaction parameter (χ_{eff}) as a function of temperature corresponding to fits to the scattering data in (D). AGE, allyl glycidyl ether; SAXS, small-angle X-ray scattering.

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2.7 | General synthesis of BAB poly(ether)-b-poly(ethylene oxide)-b-poly(ether)

A reaction vial was charged with a stir bar and 500 mg of PEO-3000. The PEO was dissolved in 4.0 mL toluene and 0.167 mL of 1.0 M triethylaluminium in hexanes (1.0 eq.) was added for most polymerizations unless otherwise stated. In experiments where triethylaluminum was varied, 0.250 mL (1.5 eq.) or 0.333 mL (2.0 eq.) of 1.0 M triethylaluminium in hexanes was used to form the initiating complex. The mixture was allowed to stir at room temperature overnight. In each case, after several hours, the solutions solidified into a colorless gel. After 24 h, 54.15 mg (5.0 eq.) of N-Al adduct catalyst was added. The reaction mixture was allowed to equilibrate for half an hour. For chain extension, appropriate monomer equivalents relative to hydroxyl end groups on the PEO macroinitiator were added to the solution. The reaction was then heated to 60 °C in the case of AGE and nBGE, and room temperature in the case of PO and ECH. The conversion of the monomer was monitored over time via ^{1}H NMR spectroscopy of reaction aliquots. Once it was apparent that the conversion of monomer had converged, the vials were removed from the glovebox. The copolymer was dissolved in dichloromethane and washed twice with 0.1 M HCl in MeOH followed by DI water. The clean copolymer was then dried in vacuo. Chain extension was characterized via SEC in chloroform and analyzed against polystyrene standards. For polymerizations using a PEO-8000 macroinitiator, 1.0 g of PEO-8000 was dissolved in 4.0 mL of dry toluene. 0.275 mL of triethylaluminium (1.0 M in hexanes, 2.2 eq.) were added and allowed to stir at room temperature overnight to form the initiating complex. 26.0 mg (5.0 eq.) of N-Al adduct were added to the initiating complex and allowed to equilibrate for half an hour before the addition of monomer. Purification and characterization were performed in the same manner as the diblock polymers.

2.8 | General synthesis of CBABC pentablock polyethers

A reaction vial was charged with a stir bar and 500 mg PEO-3000. The PEO was dissolved in 2.0 mL toluene and 0.167 mL of 1.0 M triethylaluminium in hexanes was added to form the initiating complex. The mixture was allowed to stir at room temperature overnight. In each case, after several hours, the colorless solutions gelled. After 24 h, 54.15 mg (5.0 eq.) of the N-Al adduct catalyst was added. The reaction was allowed to equilibrate for

TABLE 2 Domain spacing for unidirectional chain extension of polyethers from a MeO-PEO-2000 macroinitiator.

Sample	Monomer[a]	SAXS temperature (°C)	Wt% extended block[b]	Domain spacing (nm)[c]
$PEO_{45}PPO_{10}$	PO	22	23	16.9
$PEO_{45}PPO_{40}$	PO	22	54	20.5
$PEO_{45}PPO_{80}$	PO	22	70	27.6
$PEO_{45}PAGE_{10}$	AGE	22	36	18.3
$PEO_{45}PAGE_{40}$	AGE	22	70	28.5
$PEO_{45}PAGE_{80}$	AGE	22	82	28.5
$PEO_{45}PnBGE_{10}$	nBGE	22	39	17.2
$PEO_{45}PnBGE_{40}$	nBGE	22	72	21.0
$PEO_{45}PnBGE_{80}$	nBGE	22	84	23.9
$PEO_{45}PnBGE_{10}$	nBGE	60	39	-
$PEO_{45}PnBGE_{40}$	nBGE	60	72	9.6
$PEO_{45}PnBGE_{80}$	nBGE	60	84	10.5
$PEO_{45}PnBGE_{40}$	nBGE	40	72	20.1
$PEO_{45}PnBGE_{40}$	nBGE	80	72	9.6

Abbreviations: AGE, allyl glycidyl ether; SAXS, small-angle X-ray scattering.

[a] PEO macroinitiator was chain extended with 10, 40, or 80 repeat units of PO, AGE, or nBGE. Data corresponds to the molecular weight characterization data found in Table 2.

[b] Wt% of extended block determined by comparison of the total molecular weight of the polymer to the molecular weight of the PEO macroinitiator.

[c] Domain spacing (d) calculated using $d = 2\pi/q^*$.

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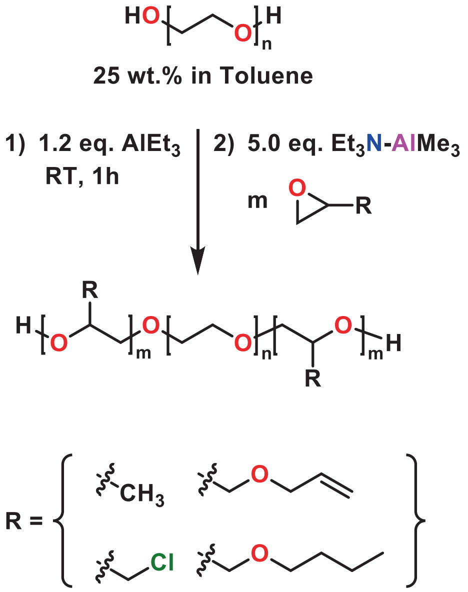
half an hour prior to monomer addition. For chain extension, appropriate monomer equivalents of PO or AGE relative to hydroxyl end groups of the PEO were added to the solution. The reaction was then allowed to progress at 60 °C in the case of AGE and room temperature in the case of PO. The conversion of the monomer was monitored over time via ^{1}H NMR spectroscopy of reaction aliquots. Once it was apparent that the conversion of monomer was no longer increasing, aliquots of 0.500 mL of the reaction volume were removed from the glovebox for characterization. Polymerizations were allowed to equilibrate at their new reaction temperatures for half an hour prior to the introduction of the next monomer in the sequence. PO chain extensions were performed at room temperature, while AGE chain extensions were conducted at 60 °C. After addition of the second monomer, the conversion was monitored over time via ^{1}H NMR spectroscopy of reaction aliquots. Once it was apparent that the conversion of monomer was no longer increasing, the vials were removed from the glovebox.



SCHEME 2 Bidirectional chain extension from a difunctional HO-PEO-OH macroinitiator.

TABLE 3 Bidirectional chain extension of polyethers from a HO-PEO-OH macroinitiator.

Sample name	[M]/[I]	Time (h)[a]	Conv (%)[b]	[PEO]:[M] (mol %$^{(th)}$)[c]	[PEO]:[M] (mol %$^{(obs)}$)[d]	M_n ^{theo} (kg/mol)	M_n (kg/mol)[e]	M_n (kg/mol)[f]	$Đ$[g]
PAGE$_{45}$BDOPAGE$_{45}$[h]	90	24	95	0:100	0:100	10.3	7.2	4.8	1.38
PPO$_{26}$PEO$_{68}$PPO$_{26}$	52	72	90	57:43	43:57	6.0	8.3	8.6	1.14
PPO$_{26}$PEO$_{68}$PPO$_{26}$	52	72	91	57:43	45:55		7.9	9.9	1.09
PPO$_{61}$PEO$_{68}$PPO$_{61}$	122	144	97	36:64	31:69	10.1	11.7	15.4	1.08
PPO$_{61}$PEO$_{68}$PPO$_{61}$	122	144	96	36:84	27:73		13.8	15.8	1.08
PPO$_{150}$PEO$_{68}$PPO$_{150}$	350	120	92	18:82	18:82	23.3	20.4	23.1	1.15
PPO$_{150}$PEO$_{68}$PPO$_{150}$	350	120	96	18:82	18:82		21.5	27.2	1.13
PAGE$_{31}$PEO$_{68}$PAGE$_{31}$	63	192	88	52:48	62:38	10.2	7.7	10.5	1.23
PAGE$_{31}$PEO$_{68}$PAGE$_{31}$	63	192	88	52:48	60:40		8.1	10.9	1.10
PAGE$_{100}$PEO$_{68}$PAGE$_{100}$	200	168	86	25:75	51:49	25.8	10.5	10.0	1.32
PAGE$_{100}$PEO$_{68}$PAGE$_{100}$	200	168	91	25:75	51:49		10.6	11.7	1.53
PnBGE$_{27}$PEO$_{68}$PnBGE$_{27}$	54	192	91	56:44	63:37	10.0	8.1	9.0	1.24
PnBGE$_{27}$PEO$_{68}$PnBGE$_{27}$	54	192	91	56:44	56:44		9.9	6.4	1.35
PECH$_{50}$PEO$_{68}$PECH$_{50}$	100	24	>99	40:60	58:42	12.3	7.6	12.0	1.81
PECH$_{50}$PEO$_{68}$PECH$_{50}$	100	24	>99	40:60	48:52		9.7	13.8	2.16
PPO$_{40}$PEO$_{180}$PPO$_{40}$[i]	80	168	86	69:31	77:23	12.6	11.2	21.0	1.06
PPO$_{40}$PEO$_{180}$PPO$_{40}$[i]	80	168	90	69:31	70:30		12.4	21.7	1.09

Note: PEO chain-extension was accomplished in duplicate unless otherwise noted.

[a] Time at which continued conversion of monomer was no longer observed by ^{1}H NMR spectroscopy.

[b] Conversion based on ^{1}H NMR spectroscopy at termination.

[c] Theoretical mole percentage of [PEO] compared to monomer [M].

[d] Observed mole percentage of [PEO] compared to monomer [M] as determined by NMR spectroscopy.

[e] M_n calculated based on ^{1}H NMR spectroscopy.

[f] M_n from SEC relative to polystyrene standards.

[g] M_w/M_n relative to polystyrene standards.

[h] Initiation from a 1,4-butanediol small molecule results are from a single polymerization.

[i] Initiation from a M_n ca. 8000 g/mol PEO macroinitiator.

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The copolymer was dissolved in dichloromethane, washed twice with 0.1 M HCl in methanol followed by DI water. The clean copolymer was then dried in vacuo. Chain extension was characterized via SEC in chloroform and analyzed against polystyrene standards.

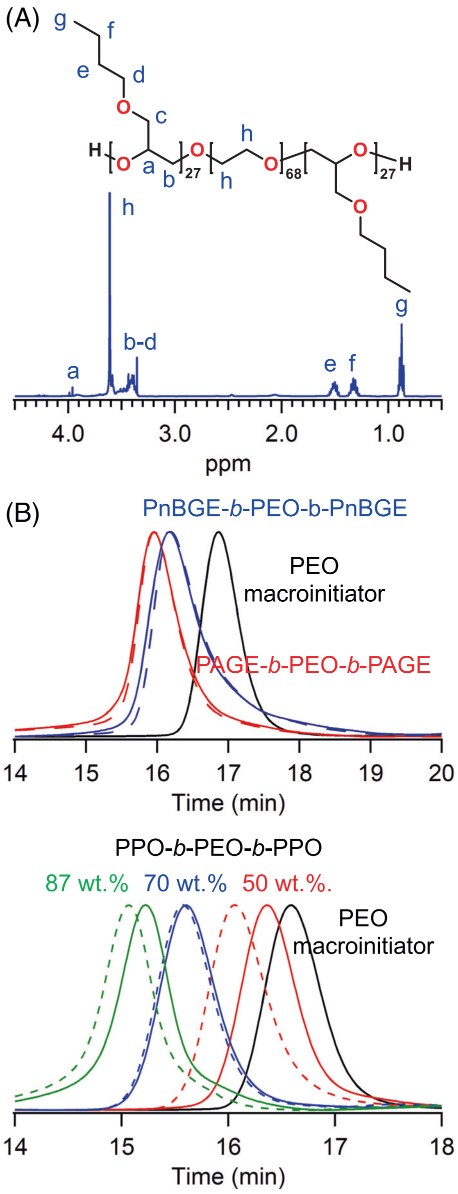
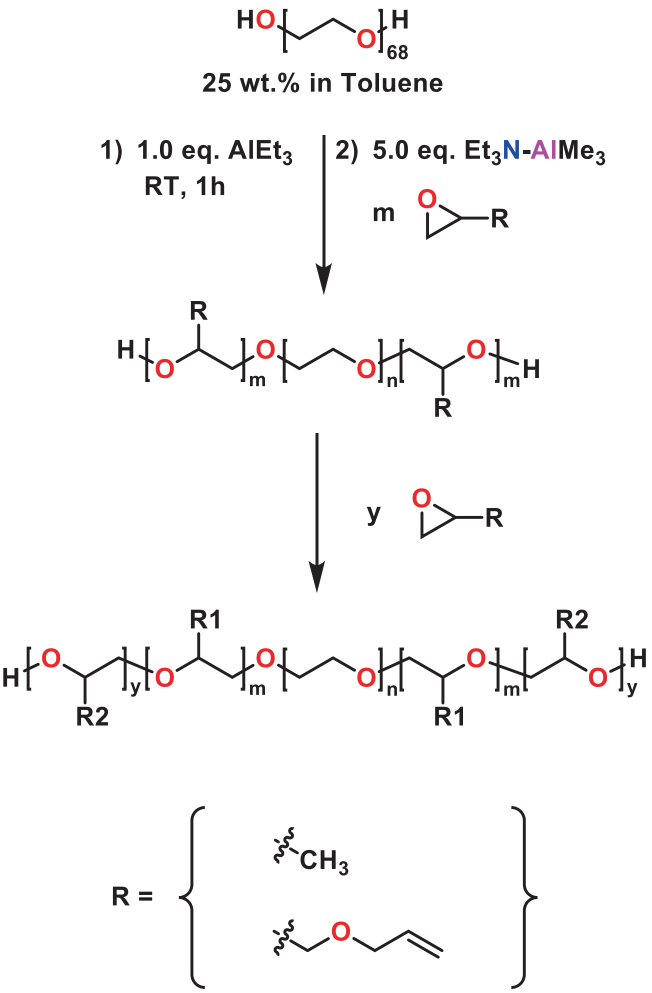


FIGURE 3 (A) ^{1}H NMR spectrum (CDCl$_3$) of a ca. 10,000 g/mol PnBGE-*b*-PEO-*b*-PnBGE (ca. 70 wt% PnBGE) corresponding to the solid blue line in (B). (B) SEC traces of two-directional chain extension of a HO-PEO-OH macroinitiator with PAGE (red) (ca. 71 wt% PAGE) $M_n = 10{,}000$ g/mol $Đ = 1.23$ (solid line) $M_n = 10{,}900$ g/mol $Đ = 1.10$ (dashed line) or PnBGE (blue) $M_n = 9000$ g/mol, $Đ = 1.24$ (solid line), $M_n = 6400$ g/mol, $Đ = 1.35$ (dashed line) as the extended block. Solid and dashed lines of the same color show results from two identical trials. (B) PPO-*b*-PEO-*b*-PPO with either 52 (ca. 50 wt%) (red), 122 (ca. 70 wt%) (blue), or 350 (87 wt%) (green) equivalents of monomer. Molecular weight characterization data can be found in Table 3.

3 | RESULTS AND DISCUSSION

Preparation of well-defined unidirectional chain extended AB block polyethers was accomplished starting with a 2.0 kg/mol monomethyl-PEO aluminum alkoxide macroinitiator using 1.2 equivalents of a previously reported N-Al adduct catalyst for a variety of epoxide monomers.[46] Triethylaluminum was chosen as the alkylaluminum most suitable for chain activation without causing parasitic initiation by the alkyl aluminum that in turn generates homopolymer impurities, as previous work on similar MOB catalysts showed a trend in alkyl aluminum reactivity where iBu > Me > Et in regards to rates of monomer consumption.[45] A slight excess of alkyl aluminum was used to fully activate the macroinitiator for monomer enchainment (Scheme 1). 1.2 equivalents of catalyst were found to promote controlled enchainment of monomer at convenient reaction times of less than 2 days.



SCHEME 3 Pentablock chain extension from a difunctional HO-PEO-OH macroinitiator.

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TABLE 4 Pentablock chain extension of polyethers from a HO-PEO-OH macroinitiator.

Sample name	[M]/[I]	Time (h)[a]	Conv (%)[b]	M_n ^{theo} (kg/mol)	[PEO]:[M_1]:[M_2] (mol %$^{(th)}$)[c]	[PEO]:[M_1]:[M_2] (mol %$^{(obs)}$)[d]	NMR M_n (kg/mol)[e]	GPC M_n (kg/mol)[f]	$Đ$[g]
$PPO_{61}PEO_{68}PPO_{61}$	122	96	86	10.0	36:64:0	41:59:0	5.8	17.1	1.11
$PAGE_{44}PPO_{61}PEO_{68}PPO_{61}PAGE_{44}$	88	168	89	20.1	24:44:32	34:24:41	15.2	18.1	1.37
$PAGE_{44}PEO_{68}PAGE_{44}$	88	96	97	20.1	44:56:0	46:54:0	12.0	11.9	1.26
$PPO_{61}PAGE_{44}PEO_{68}PAGE_{44}PPO_{61}$	122	168	83	20.1	24:32:44	29:34:36	16.9	18.8	1.22

[a] Time at which continued conversion of monomer was no longer observed by ^1H NMR spectroscopy.

[b] Conversion based on ^1H NMR spectroscopy at termination.

[c] Theoretical mole percentage of [PEO] compared to monomer [M], where [M_1] is the first added monomer and [M_2] is the second added monomer.

[d] Observed mole percentage of [PEO] compared to monomer [M], where [M_1] is the first added monomer and [M_2] is the second added monomer. as determined by NMR spectroscopy.

[e] M_n calculated based on ^1H NMR spectroscopy.

[f] M_n from SEC relative to polystyrene standards.

[g] (M_n/M_w) relative to polystyrene standards.

For PO, AGE, and nBGE, control over targeted molecular weight was achieved. Figure 1 demonstrates the unidirectional chain extension of MeO-PEO-OH with PO to prepare a series of block copolymers. Table 1 shows the resulting populations of chain-extended material with low dispersity for the monomers tested in this study. Polymerizations were performed in duplicate unless otherwise noted. Diffusion Ordered Spectroscopy ^1H NMR spectroscopy (DOSY) of a PO-extended MeO-PEO macroinitiator verified that the increase in molecular weight by SEC was indeed due to covalent extension (Figure S45). Although a clear chain extension with ECH was apparent, the dispersity was typically higher for ECH than for the other monomers. Additionally, macroinitiator conversion was incomplete, indicating poor initiation efficiency. For ECH, the rate of polymerization was significantly higher than for other monomers, leading to a large initial adiabatic temperature increase due to ring strain release that likely prevented adequate control over the chain-extension.

The block polymer materials were characterized in the melt state by small angle X-ray scattering (SAXS) to investigate polymer-polymer interactions as described by an effective interaction parameter, χ_{eff}, and domain spacing, D.[48–51] Figure 2 shows the effect of block length on the morphology of the polyether material, with block polymer morphology controlled by the relative block sizes. The scattering patterns were consistent with weakly ordered or disordered morphologies.

The χ_{eff} and D as a function of temperature was calculated for a representative 72 wt% PnBGE, PEO-*b*-PnBGE copolymer Figure 2D,E. As the temperature increased, the domain spacing decreased from 20.1 nm at room temperature to 9.6 nm from 60 to 80°C (Figure 2D). As the temperature increased there was also a proportional decrease in the interaction parameter χ_{eff}, indicating that there was better miscibility between the PEO and PnBGE blocks at higher temperatures (Figure 2E). Domain spacing for unidirectional chain-extended polyethers can be found in Table 2.

Preparation of well-defined BAB triblock materials was accomplished through the enchainment of monomer onto a difunctional PEO alkoxide macroinitiator (Scheme 2). Although the macroinitiator solution gelled upon addition of the alkylaluminum solution, adding monomer caused each polymerization to quickly redissolve into a viscous solution that could be magnetically stirred. The amount of alkylaluminum used for the preparation of the aluminum alkoxide initiator was determined to be important, with greater than one equivalent of aluminum relative to the hydroxyl PEO chain ends resulting in parasitic initiation and homopolymer contaminants.

As with the unidirectional chain extension, bidirectional chain extension (Table 3) was readily accomplished with the use of PO, AGE, or nBGE, with moderate success in the case of ECH. When 1.0 or 1.5 equivalents of triethylaluminum relative to moles of macroinitiator were used, dispersity remained low (Figure S62). Polymerizations were performed in duplicate unless otherwise noted. To ensure the full activation of macroinitiator, a loading of 1.0 equivalents of triethylaluminum was utilized for preparation of all triblock materials unless otherwise stated. 5.0 equivalents of catalyst relative to the macroinitiator were necessary for slower reactions. Even with the increased catalyst concentration, some polymerizations required over a week to reach full conversion of monomer, likely due to the increased solvent concentrations.

The resulting PPO, PAGE, and PnBGE polyethers had narrow dispersity with good molecular weight control up to 10 kg/mol for the full triblock polymer. Chain extension also showed consistent reproducibility for glycidyl ether monomers (Figure 3). For ECH, the same issues

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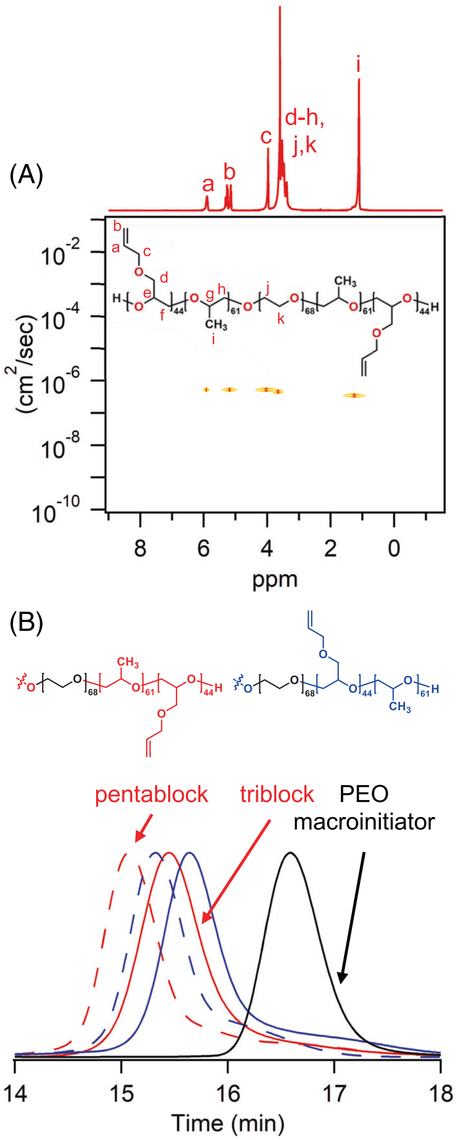

FIGURE 4 (A) DOSY NMR spectrum showing the diffusion of PAGE-*b*-PPO-*b*-PEO-*b*-PPO-*b*-PAGE as a pentablock $M_n = 18{,}100$ g/mol, $Đ = 1.37$. (B) SEC traces of bi-directional chain extension of a HO-PEO-OH macroinitiator after one chain extension step (solid lines) or two chain extension steps (dashed lines). The red traces correspond to PPO-*b*-PEO-*b*-PPO (red solid) and PAGE-*b*-PPO-*b*-PEO-*b*-PPO-*b*-PAGE (red dashed). The blue traces correspond to PAGE-*b*-PEO-*b*-PAGE (blue solid) and PPO-*b*-PAGE-*b*-PEO-*b*-PAGE-PPO (blue dashed).

with adiabatic temperature increases were observed, leading to a mixture of both chain-extended and non-extended PEO macroinitiator and a relatively high dispersity. Polymerizations using a higher M_n PEO-8000 macroinitiator (Table 3, Figure S61) were also conducted. Higher molecular weight chain extensions were attempted for PEO extended with both PPO or PAGE segments, with a target extended block of ~20,000 g/mol. For PPO, the resulting BAB copolymers had molecular weights in good agreement with the target, with conversions of >90% and $Đ \leq 1.15$. For PAGE, however, the resulting BAB polymers remained in the molecular weight range closer to 10,000 g/mol, but retained a relatively high conversion of ≥86% with a $Đ \leq 1.53$. For both of these reactions, the polymerizations were relatively slow, taking 5 and 7 days respectively to reach final conversion.

Direct sequential addition of a second monomer after the complete conversion of the first chain-extended monomer led to the one-pot preparation of pentablock polymers with low dispersity, demonstrating that the chain ends of triblock materials remain living after several days (Scheme 3, Table 4). Previous work on the N-Al catalyst system reported by Imbrogno et al. suggested that the adduct was able to support the living polymerization of AGE.[46] The living nature of the polymerization was confirmed by the continued chain extension with additional monomer to produce a pentablock polymer from the living triblock polymer. The chain ends were sufficiently active as to promote the quantitative enchainment of monomer, shown by the lack of remaining triblock in the size exclusion chromatograph or the DOSY ^{1}H NMR spectroscopy of the final pentablock (Figure 4). The architecture of the triblock intermediate and pentablock polymers were analyzed by SAXS. Results from SAXS shown in Figure S53 suggest that there was a change in the morphology of the block polymer with the introduction of an additional polyether block, which would be expected as the polymer architecture and composition changes.

4 | CONCLUSION

The N-Al adduct catalyst, first introduced by Imbrogno et al., has shown promise as a general catalyst for the preparation of a wide range of block polymers with tolerance of functional groups, molecular weight control, and polymer architectural control. Di-, tri-, and pentablock polyethers were obtained using this simple Lewis pair catalyst via a living polymerization mechanism. Chain extension of a bidirectional PEO macroinitiator was able to prepare PPO-*b*-PEO-*b*-PPO with PPO blocks of ~20 kg/mol, far exceeding those typical for anionic methods.[12,13,15] Future optimization will need to be done, however, to prepare materials with PPO segments in the same molecular weight regime as BAB materials prepared using other catalytic techniques, such as those reported by Vogler.[42] Materials prepared using this chain-extension method demonstrated variable morphology based on the identity of the hydrophobic block and composition. With a need for well-defined RP materials for emerging applications, this Lewis pair catalyst method provides additional pathways for the preparation

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of materials that were previously inaccessible by anionic ring-opening polymerization and offer an alternative to the use of other methods, such as novel borane catalysts. Polymer architectures made more widely available with this Lewis pair methodology will provide several avenues for future research. Fundamental catalysis research is needed to gain a better understanding of how these Lewis pair catalysts behave so that the methodology can be further improved for increased control, monomer tolerance, and faster reaction kinetics while maintaining end-group fidelity. The variety of novel materials that are now accessible with this N-Al platform will increase access to numerous functional RP materials not previously available for study.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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