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Sequential Block Copolymers of Polyisobutylene and Polyolefins

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Sequential Block Copolymers of Polyisobutylene and Polyolefins
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Submitted in Partial Fulfillment
Seniors Honors Project
By Manwel Labib

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Abstract: A two-step approach was utilized to synthesize random polyolefin multiblock-copolymers. This strategy takes advantage of α,ω-terminated telechelic polyolefins. Isotactic polypropylene (iPP) and polyethylene (PE) are picked because of their strength, and polyisobutylene (PIB) because of its hemocompatibility. We developed a synthetic mechanism to achieve on average 4-5 block copolymers. These copolymers are theorized to make for robust bio-inert plastic, which can be used for surgical mesh implants.

Introduction

Recently, it was found that polypropylene-based plastic used for surgical treatments of stress urinary incontinence (SUI) and pelvic organ prolapse (POP) in women was associated with significant complications.[1] This quickly became a national public health issue with the involvement of regulatory bodies and national parliaments.[1] These mesh complications are thought to be caused from the oxidation of the methane carbon in amorphous regions of polypropylene and subsequent chain-scission resulting in low Mw PP that was brittle.[1] The aim of this project is to design a brand new material to eventually be used as surgical mesh implants. The underlying mechanisms leading to this type of host response are still unclear.[1] However, we theorize that by combining polypropylene with a hemocompatibility polymer, we can reduce the effects of the immune response.

Multiblock copolymers are a significant interest in polymer chemistry research because of the resulting separated morphologies and differences in mechanical and thermal properties, otherwise not present in homopolymers. Living polymerization has been used to synthesize PCPs, which requires the subsequential addition of distinct monomers.[2] This method was often restricted since it only works on certain monomer types. Recently, a new method that uses acyclic diene metathesis (ADMET) was implemented, which offers synthetic route polymerization of α,ω-terminated diene polymers.[2] This technique utilizes a one-pot protocol to prepare random multiblock segments via sequential depolymerization/repolymerization.[2]

The protocol used semicrystalline polyolefin and amorphous polyolefin.[2] These copolymers showed to possess an elastic segment corresponding to the amorphous domains and a robust segment corresponding to the crystalline domain.[2] The amorphous domain gives the polymer elastic properties, and the crystalline part gives the polymer strength.[2] However, obtaining α,ω-terminated diene polymers is challenging. It was recently demonstrated that it is possible to obtain telechelic polyolefin polymers using a new strategy called ethenolysis.

Ethenolysis utilizes olefine metathesis with ethylene to obtain the attractive α,ω-divinyl-terminated polymers from unsaturated precursors.[3] The technique optimizes ethylene pressure, temperature, catalyst, and time to get a rapid clean route toward the telechelic polymers.[3] The target for the ethenonlysis uses monomer ethylene, toluene, a catalyst, and our starting polymer.[3] The toluene increases the solubility of the starting polymer. Subsequent additions of the catalyst allows for efficient processing without degradation of the catalyst.[3] This technique utilizes an unsaturated iPP and PE to obtain telechelics of the polymers. Polymerization of these polymers was first made and characterized using proton nuclear magnetic resonance (^{1}H NMR) and Gel permeation chromatography (GPC).

Polymerization of unsaturated iPP utilizes the addition of 1,3-butadiene (BD), an isospecific
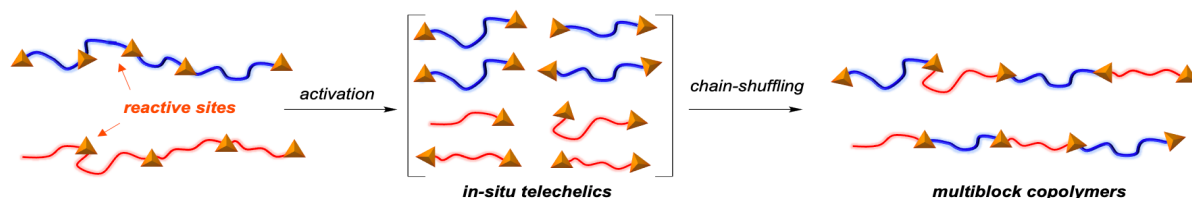

Fig. 1 Schematic illustration of synthetic approaches of activation of polymers using ethenolysis and chain-shuffling to yield the random semicrystalline/amorphous multiblock copolymers via repolymerization.
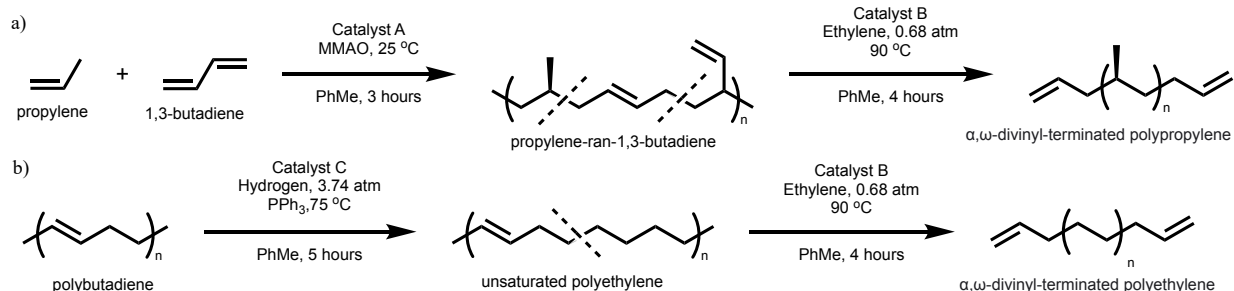
3

Fig. 2a Schematic illustration of the synthesis of unsaturated polypropylene (propylene-ran-1,3-butadiene) and ethenolysis to yield α,ω-terminated diene polypropylene. **Fig. 2b** Schematic illustration of the synthesis of unsaturated polyethylene(ethylene-ran-1,4-butadiene) and ethenolysis to yield α,ω-terminated diene polyethylene.

zirconocene catalyst, dimethysilybis-(1-indenyl)zirconium dichloride, activated by methylaluminoxane (MMAO), with excess propylene.[4] Pressure, time, and additions of each substrate were optimized to obtain a desired amount of unsaturation. The butadiene can be incorporated via a 1,2 BD addition, or a 1,4 BD addition.[4] 1,4-BD has a higher selectivity than the 1,2-BD. It is known that up to 95% of butadiene units in the copolymer reached selectivity toward 1,4-BD.[4] The average amount of 1,4-BD incorporated in the polymer chain was controlled by the butadiene concertation in the feed.[4] The mole fraction of 1,4-BD units increases with a decrease in propylene concentration or an increase in butadiene concertation.[4] This is important because the average number of 1,4-BD in a polymer can help dictate the average length of a propylene unit after ethenolysis.[4]

Polymerization of unsaturated PE employs the hydrogenation of polybutadiene. By controlling the pressure and time of the hydrogenation, the degree of unsaturation was controlled.[5] Partial hydrogenation of PBD was performed using Wilkinson's catalyst (RhCl(PPh₃)₃) under an H₂ atmosphere (3.7 atm) for 5 hours.[5] Monitoring the reactions as a function of reaction time will allow us to convert the vinyl groups into ethyl branches; however, this does not completely reduce the 1,4-

inserted butadiene units.[5] Toluene was used to increase the solubility of the starting polymer, and triphenylphosphine was used in conjunction with the catalyst.

PIB is a hemocompatibility polymer that can be synthesized using living carbocationic polymerization.[6] The process involves the subsequential addition of isobutyl units.[6] This can use mono, di, and tri-functional initiating systems; we will utilize a di-initiating system. Specifically, we will use aliphatic and aromatic tert-esters and ether/TiCl₄ combinations to yield terminally-functional copolymers.[6] Using a quenching reagent such as allyl-trimethylsilane (ATMS), it is possible to control the length of the polymer.[6] This is important because these diene telechelic ends can help us synthesize multiblock copolymers using polyisobutylene.[6]

This project utilized a convenient chain shuffling technique developed in our lab, in conjunction with enthenolysis, to prepare random semicrystalline/amorphous multiblock copolymers, on average of eight blocks per chain, via sequential depolymerization/repolymerization. The process was carried out by isolation of telechelic intermediates by first adding ethylene in one
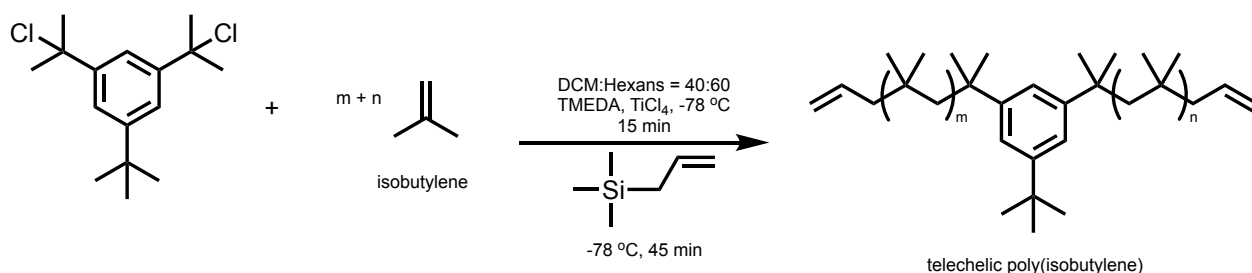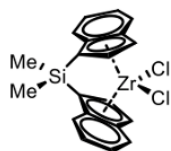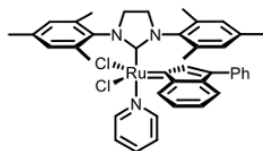

Fig. 3 Schematic illustration of the synthesis of α,ω-terminated diene polyisobutylene. Initiator used is 1-(tert-butyl)-3,5-bis(2-cholorpropan-2-yl)benzene.
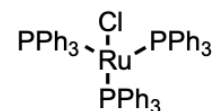
Fig. 4 Schematic illustration of the catalysts utilized in the synthesis of α,ω-terminated diene polyolefins. Catalyst (a) rac-diemethylsilybis(1-indenyl)zironcium dichloride. Catalyst (b) Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](3-phenyl-1H-inden-1-ylidene)(pyridyl)ruthenium(II). Catalyst (c) Tris(phenylphosphine) rhodium (I) chloride (Wilkinson's).

reaction, then removing ethylene in the subsequent reaction. We used iPP and PE as our hard domain and PIB as the amorphous elastic domain. We theorize that this multiblock copolymer could be used as the plastic needed for surgical mesh implants.

Experimental and Methods/Materials

All solvents used are obtained and purified by Vigor Dry Solving System. All reactions discussed were controlled under nitrogen environments at all times. 24 hours prior to the start of any experiment, all fisher porter heads and reusable metal needles were left in a 150 ºC temperature oven to eliminate any moisture.

Polypropylene polymerization was carried out by first measuring 100 mL of toluene. Addition

of the solvent and a magnetic stirring rod were added to a 200-mL Fisher porter vessel (Andrews Glass CO). 1.93 g of MMAO (Sigma-Aldrich) was measured in a 20-mL Scintillation vial. 4.2 mg of catalyst rac-diemethylsilybis(1-indenyl)zironcium dichloride (Strem chemicals) was measured in a separate 20-mL vial (Fig. 4a). Using a Pasteur pipet, the MMAO was transferred into the vial containing the catalyst. The mixture was stirred until all contents were dissolved. A Fisher porter head (Swagelok) was placed to seal the vessel, and all valves were closed. The vessel was left to stir on a magnetic stir plate prior to the addition of any gases at 25 ºC. The stirring rate was adjusted to 300 rpm. 4.0 g of butadiene gas (Matheson) was added at 1.36 atm by opening the side valve on the fisher porter head. 5.0 g of propylene gas (Matheson) was
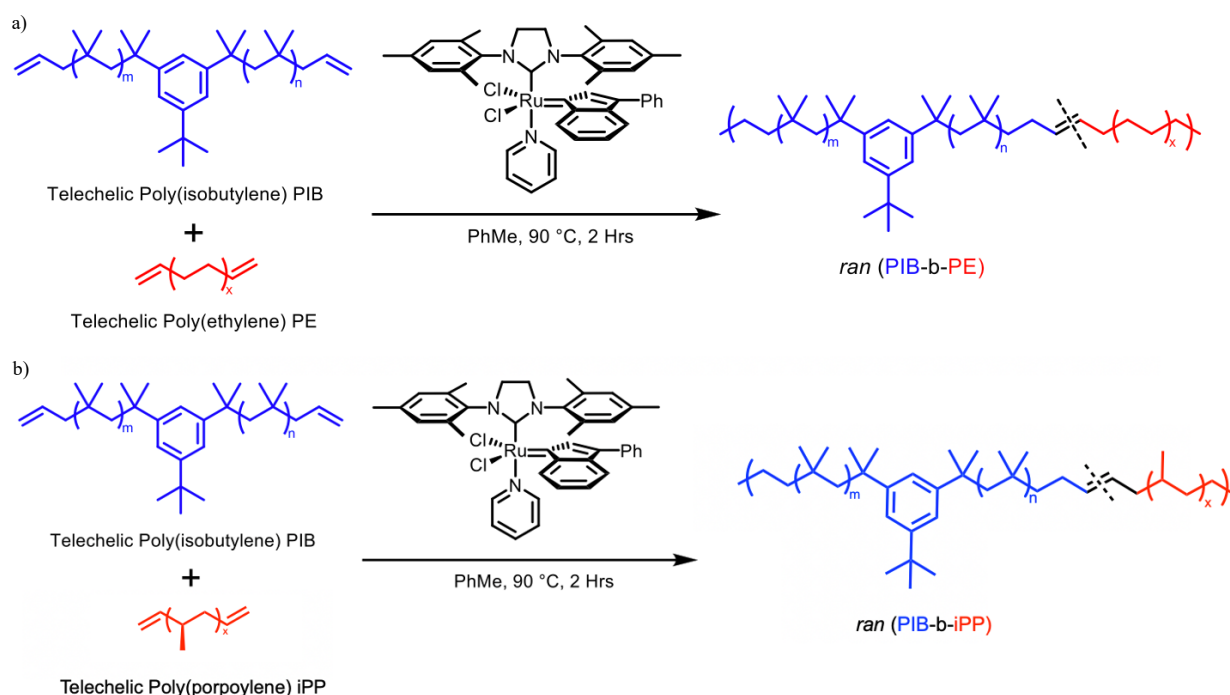

Fig. 5a Schematic illustration of the synthesis of the multiblock copolymer of iPP and PIB. **Fig. 5b** Schematic illustration of the synthesis of the multiblock copolymer of PE and PIB.

added to the same vessel at 2.72 atm. The valves remained closed to allow the system to drop down to 1.36 atm. The second patch of 4.2 mg of catalyst and 1.93 g of MMAO was prepared while the gases dissolve in the solution. Using a 5-mL plastic syringe (fisherbrand) and a reusable metal needle, the mixture was drawn inside the needle with 1.5 mL of headspace left. The tip of the needle was inserted inside the septum to stop any moisture from entering. Simultaneously, the upper valve of the fisher porter head was left open, and the mixture inside the syringe was added quickly.

After the addition, the upper valve was closed, and the valve connected to the propylene tube was left open, allowing propylene to be added throughout the experiment. The needle was rinsed and cleaned with acidic methanol to avoid clogging. The experiment was run for three hours and was quenched by 5% HCl in methanol. The quenching reagent was added slowly to the mixture. The product was filtered and left to dry for 24 hours in a vacuum oven at 65 °C.

Hydrogenation of polybutadiene (PBD) was carried out by first measuring out 100-mL of 20g/1L PBD in toluene (Sigma-Aldrich). This was done using a 200-mL plastic syringe and reusable needle. The PBD and a magnetic stirring rod were added to a 200-mL Fisher porter vessel. 22.5 mg of catalyst Tris(phenylphosphine) rhodium (I) chloride (Wilkinson's) (Fig. 4c) (Sigma-Aldrich) and 21.4 mg of triphenylphosphine were measured in a separate 20-mL Scintillation vial. Additions of these substrates were added, and a Fisher porter head was placed to seal the vessel, where all valves remain closed. A silicon oil (Alfa Aesar) bath was set up on top of a magnetic stir plate, where the temperature was set to 75 °C and the stirring rate was adjusted to 400 rpm. The Fisher porter vessel was placed inside the oil bath. Hydrogen gas (Praxair) was added at 3.74 atm through the side valve of the fisher porter head. The reaction was left to stir for 5 hours. The needle was washed with toluene to avoid clogging. Prior to quenching, the side valve was closed and a nitrogen tube was placed instead of the hydrogen tube. The upper valve was opened slightly to vent the pressure caused by the hydrogen gas. Once

the pressure dropped below 0.15 atm, the side valve was opened to allow nitrogen inside the valve. This process was repeated three more times to ensure that all hydrogen gas has escaped the vessel. Slowly, 5% HCl in methanol was added to quench the reaction. The product was filtered and left to dry for 24 hours in a vacuum oven at 65 °C.

To polymerize PIB, a flame-dried flask and isobutylene condensed flask were obtained.[6] 143.8 mg of the recrystallized initiator (Fig. 3) were added to the reaction flask under dim light conditions. 180 mL of distilled hexane and 120 mL of chloromethane were added to the flask. The reaction flask was cooled with dry ice and acetone to -78 °C. 0.16 mL of proton trap Tetramethylethylenediamine (TMEDA) (Sigma-Aldrich) were added to the flask using a 1-mL plastic syringe and a reusable metal needle. Isobutylene gas (ExxonMobil) was condensed in the IB condensing flask at -78 °C using an acetone-dry ice bath. 6.57 mL of condensed IB were added to the reaction flask using a metal cannula. 8-mL of $TiCl_4$ (Sigma-Aldrich) 1M in DCM were added to the flask with a 10-mL plastic syringe and a reusable metal needle. The needle was washed with methanol to avoid clogging. After 15 minutes of the $TiCl_4$ addition, the quenching reagent Allyl Trimethyl Silane (ATMS) (Beentown Chemical) was added. After 40 minutes, 5% HCl in methanol was added, and the flask contents were allowed to warm up to room temperature. The contents of the flask were transferred to a separatory funnel. The bottom aqueous layer was removed, and distilled water was added to the separatory funnel. This was repeated until the pH of the organic layer became neutral. The polymer was precipitated by adding excess methanol to the organic phase of the funnel. The methanol was decanted, and the product was left to dry for 24 hours in a vacuum oven at 65 °C.

To perform the metathesis of PE and iPP, the polymer was first added to a 200-mL Fisher porter vessel. We added 1.5g of the desired polymer. A Fisher porter head was placed to seal the vessel, and all valves remained closed. A silicon oil bath was set up on top of a magnetic stir plate, where the temperature was set to 90 °C

and the stirring rate adjusted to 500 rpm. The Fisher porter vessel was placed inside the oil bath. The vessel was left to stir on a magnetic stir plate prior to the addition of any gases at 90 °C. Once all contents were dissolved, an ethylene gas (Matheson The gas Professionals) tube was inserted through the side valve of the fisher porter head, but the valve remained closed. 6 mg of catalyst Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](3-phenyl-1H-inden-1 ylidene)(pyridyl)ruthenium(II) (Aldrich) were measured in a 20-mL Scintillation vial (Fig. 4b). Using a Pasteur piper, toluene solvent was added to dissolve the catalyst. Using a 5-mL plastic syringe and a reusable metal needle, the mixture was drawn inside the needle with 1.5 mL of headspace left. The tip of the needle was inserted inside the septum to stop any moisture from entering. Simultaneously, the side valve was opened to allow ethylene to enter, and the upper valve was left open to allow the addition of the catalyst mixture. After the addition, the upper valve was closed. The needle was rinsed and cleaned with methanol to avoid clogging. The catalyst addition was repeated three more times in one-hour increments. Methanol was added slowly to quench the reaction. The product was filtered and left to dry for 24 hours in a vacuum oven at 65 °C.

For the multiblock copolymer synthesis, a 25-mL schlenk flask was cleaned by first adding toluene that was boiled to eliminate any polymer in the flask. The flask was then rinsed with acetone and air-dried. Following this, the flask was flame-dried to eliminate any moisture. Quickly, 300 mg of our crystalline polymer and 700 mg of the amorphous polymer were measured and added to a 25-mL schlenk flask. The schlenk flask was placed inside a 500-mL Erlenmeyer flask to avoid any movement of the polymer throughout the experiment. The flask was then placed in a nitrogen-controlled environment, where a stopper and a valve were used to seal the flask. 5-mL of toluene was added to the mixture. A silicon oil (Alfa Aesar) bath was set up on top of a magnetic stir plate, where the temperature was set to 90 °C and the stirring rate adjusted to 500 rpm. The schlenk flask was placed inside the oil bath. The flask was left to stir on a magnetic stir plate at 90 °C. Once all

polymer has dissolved, 20 mg of catalyst Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](3-phenyl-1H-inden-1-ylidene)(pyridyl)ruthenium(II) were measured in a 20-mL scintillation vial (Fig. 4b) and dissolved in 5-mL of toluene. Using a 5-mL plastic syringe and a reusable metal needle, the mixture was drawn inside the needle with 1.5 mL of headspace left. The tip of the needle was inserted inside the septum to stop any moisture from entering. Three cycles of vacuum followed by the addition of nitrogen through the sidearm of the schlenk flask were performed. The valve was then removed, and a septum was placed quickly in its place. The needle containing the catalyst mixture was inserted through the septum where the catalyst mixture was added. The nitrogen line was switched on, and the needle was left slightly on top of the mixture inside the flask to evaporate any ethylene. After 2 hours, methanol was used to slowly to quench the reaction. The product was filtered and left to dry for 24 hours in a vacuum oven at 65 °C.

Results and Discussion

Confirmation of the chemical structures of our polymers was sought by using proton NMR spectroscopy and GPC. Proton NMR spectra were acquired at 125 °C in tetrachloroethane-d_2, while high-temperature GPC was performed at 140 °C in 1,2,4-trichlorobenzene versus polystyrene standards. The protons NMR (Fig. 7) of the unsaturated isotactic polypropylene showed characteristic peaks of terminated vinyl groups (H2CCH–, 5.00 and 5.70 ppm), along with internal unsaturated peaks (–HCCH–, 5.45 ppm). After the ethenolysis, a decrease in the

Unstarurated iPP: M_n: 32900 M_w: 66200 $Đ$: 2.01
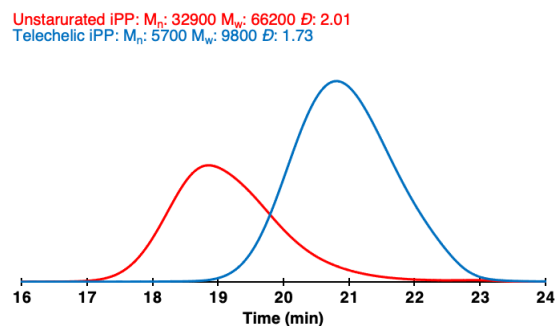Telechelic iPP: M_n: 5700 M_w: 9800 $Đ$: 1.73

Fig. 6 GPC graphs of unsaturated and telechelic iPP in 1,2,4-trichlorobenzene at 140 °C.

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internal unsaturated peak, in conjunction with an increase in terminated vinyl peaks was observed. The GPC analysis (Fig. 6) of the same iPP the starting parent unsaturated iPP (32900 Da at $Đ$ = 2.01) showed a sharp decrease in molecular weight after the ethenolysis (5700 Da at $Đ$ = 1.73).
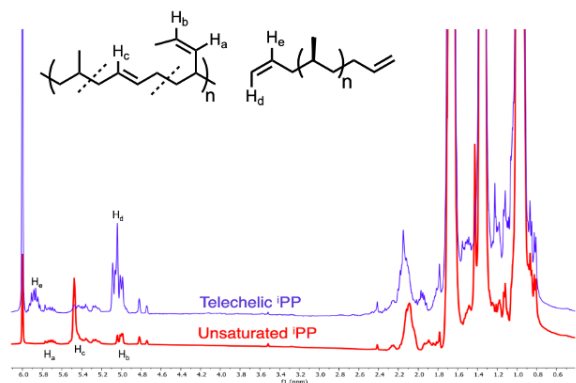

Fig. 7 Proton NMR graphs of unsaturated and telechelic iPP in the ranges of 0.6-6.0 ppm in125 ºC in tetrachloroethane-d2 at 125 ºC.

The protons NMR (Fig. 9) of the unsaturated polyethylene showed characteristic peaks of terminated vinyl groups and internal unsaturated peaks (–HCCH–, 5.5 ppm). After the ethenolysis, an increase in terminated vinyl peaks was observed (H2CCH–, 5.00 and 5.85 ppm). A decrease in the internal unsaturated peak was observed due to incomplete depolymerization. The GPC analysis (Fig. 8) of telechelic PE showed a molecular weight of (2900 Da at $Đ$ = 1.67), which would be a decrease from 192,900 Da.
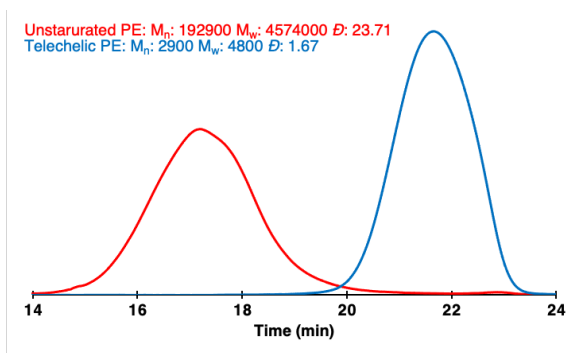

Fig. 8 GPC graphs of unsaturated and telechelic PE in 1,2,4-trichlorobenzene at 140 ºC.

Confirmation of polymerization of PIB was also done using proton NMR spectroscopy and GPC. The protons NMR of the polyisobutylene

(Fig. 10b) showed distinctive aromatic imitator protons (7.2 ppm) and terminated vinyl groups (H2CCH–, 5.00 and 5.80 ppm). The allylic end groups can be quantitated relative to the aromatic initiator residue in the polymer. The sum of the terminal -CH=CH2 protons was compared to the three aromatic protons to yield that
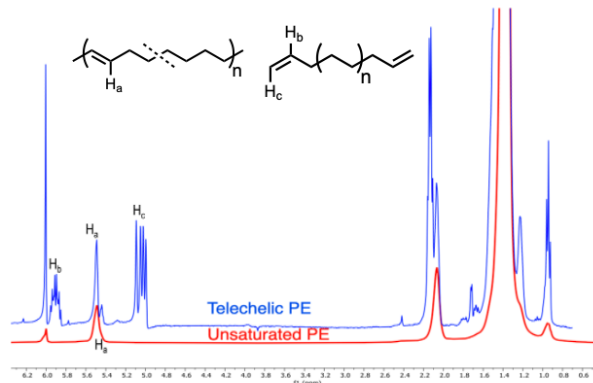

Fig. 9 Proton NMR graphs of unsaturated and telechelic PE in the ranges of 0.6-6.0 ppm in125 ºC in tetrachloroethane-d2 at 125 ºC.

approximately 100% of our polymer yielded in diene terminated PIB. The GPC analysis (Fig. 10a) of the PIB showed a molecular weight of (14600 Da at $Đ$ = 1.16).
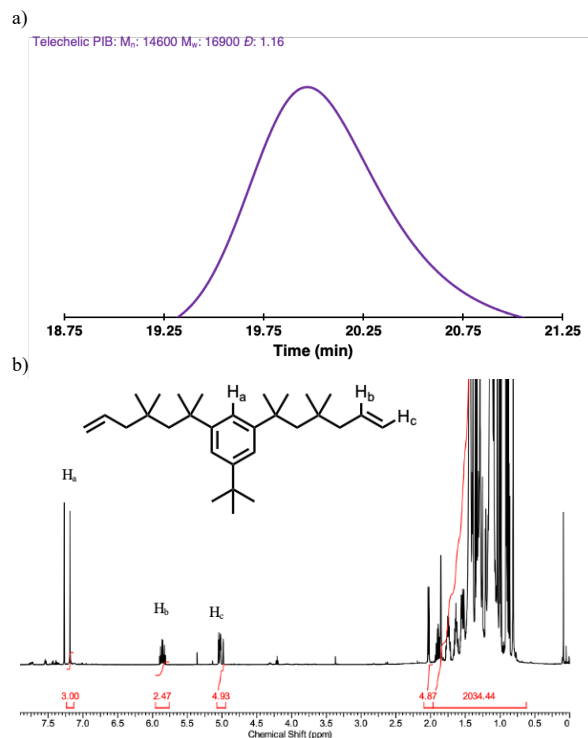
a)

b)

Fig 10a GPC graphs of telechelic PIB in 1,2,4-trichlorobenzene at 140 ºC. **Fig. 10b** Proton NMR graphs of telechelic PIB in the ranges of 0.6-7.5 ppm in125 ºC in tetrachloroethane-d2 at 125 ºC.

Label	M_n	Mw	Đ	T_m	T_c
Unsaturated PE	192,900	4,574,000	23.71	119 °C	98 °C
Telechelic PE	2,900	4,800	1.67	116 °C	104 °C
Unsaturated iPP	32,900	66,200	2.01	130 °C	98 °C
Telechelic iPP	5,700	9,800	1.73	135 °C	104 °C
Ran (PIB-b-PE)	10,000	42,400	4.20	114 °C	101 °C
Ran (PIB-b-iPP)	22,300	60,700	2.72	92 °C	131 °C

Table. 1 DSC and GPC results of unsaturated and telechelic polyolefins and multiblock copolymers ran (PIB-b-PE) and ran (PIB-b-iPP). T_m and T_c values are reported in °C. DSC was determined at 10 °C min^{-1}.

The thermal properties of the parent and telechelic polyolefins were analyzed using differential scanning calorimetry (DSC) (Fig. 11–12). Unsaturated PE displayed a T_m of 119 °C, similar to the literature value.[2] Telechelic PE
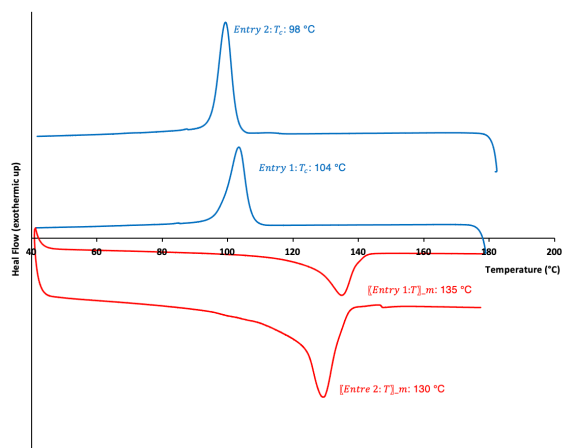

Fig. 11 DSC curve (10 °C min^{-1}) for unsaturated and telechelic iPP. Telechelic iPP is indicated as entry 1 and unsaturated iPP is indicated as entry 2.
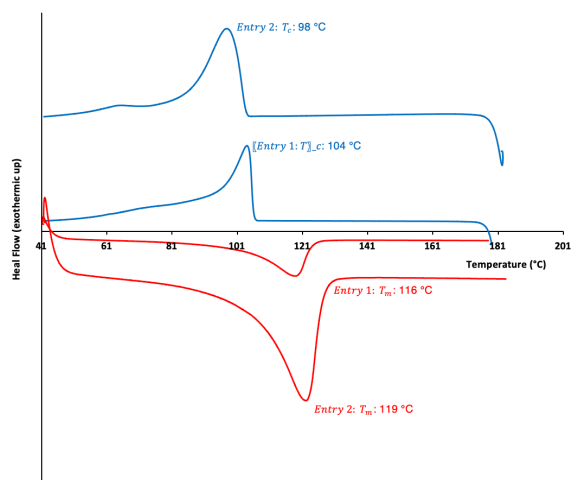

Fig. 12 DSC curve (10 °C min^{-1}) for unsaturated and telechelic PE. Telechelic PE is indicated as entry 1 and unsaturated PE is indicated as entry 2.

showed a similar T_m of 116 °C, slightly lower than the parental chain. Unsaturated iPP also displayed a T_m value similar to the literature of 130 °C. Telechelic iPP displayed a slightly higher T_m of 135 °C (Table. 1)

Multiblock copolymer ran (PIB-b-iPP) was characterized using GPC (Fig. 13). Confirmation of our multiblock copolymer was done by observing the spike increase in the internal unsaturated peak (–HCCH–, 5.50 ppm). The GPC analysis of Ran (PIB-b-iPP) showed a molecular weight of (22300 Da at Đ = 2.72). On average, approximately four blocks of our polymers were incorporated. Further analysis of the alkane region of the NMR is needed to indicate exactly how many units of each polymer were incorporated.
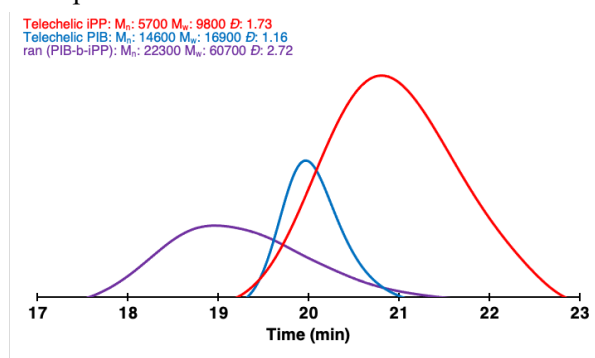

Fig. 13 GPC graphs of telechelic iPP, telechelic PIB, and the multiblock copolymer ran (PIB-b-iPP) in 1,2,4-trichlorobenzene at 140 °C.

Multiblock copolymer ran (PIB-b-PE) was also characterized using GPC and proton NMR (Fig. 14–15). ran (PIB-b-PE) was confirmed by observing the same increase in the spike of the internal unsaturated peak (–HCCH–, 5.50 ppm). The GPC analysis of Ran (PIB-b-iPP) showed a molecular weight of (10000 Da at Đ = 4.20). On average, approximately five blocks of our polymers were incorporated. While these copolymers were shorter than ran (PIB-b-iPP), more blocks were incorporated. Carbon NMR analysis is needed to indicate the exam number of each polymer that is incorporated.

The thermal properties of the copolymers were analyzed using differential scanning calorimetry (Fig. 16). Ran (PIB-b-iPP) displayed a melting peak (T_m) of 131 °C similar to the value of the starting crystalline block, iPP. Ran (PIB-b-PE)
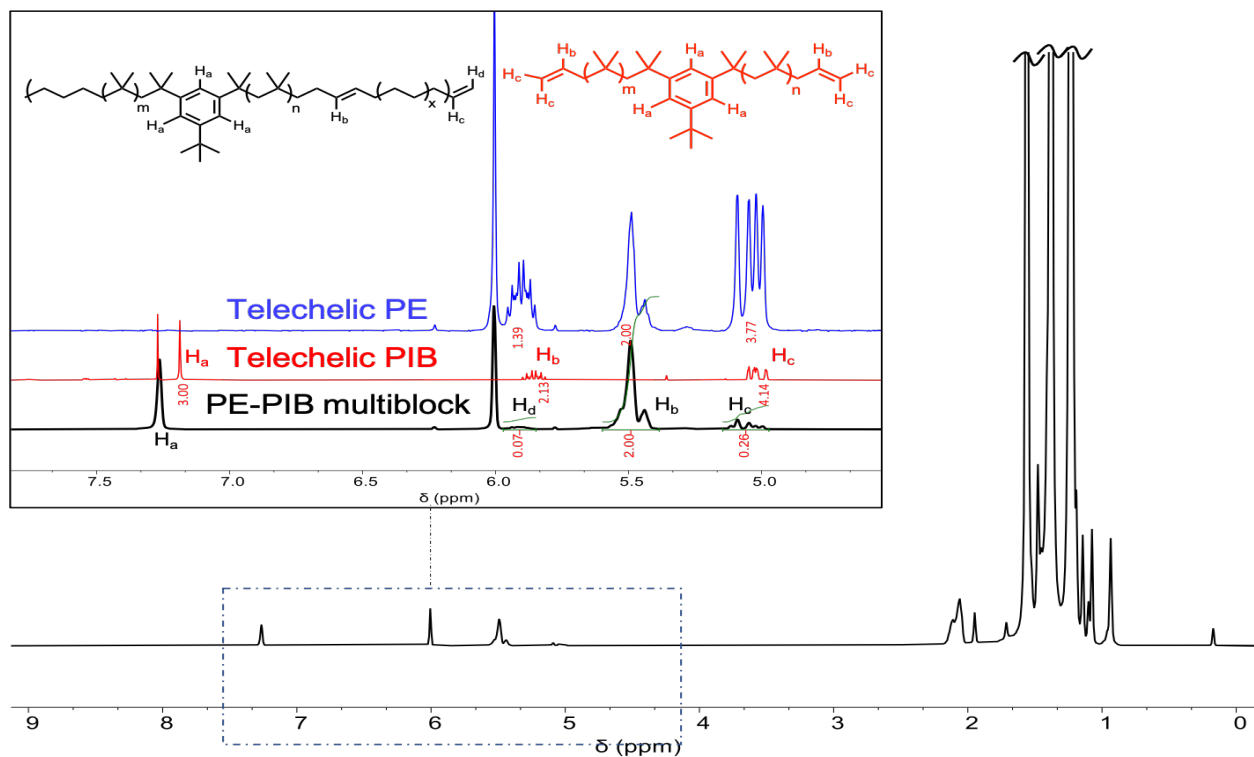
Fig. 14 Proton NMR graphs of telechelic iPP, telechelic PIB, and multiblock copolymer ran (PIB-b-iPP) in the ranges of 0.6-7.5 ppm in tetrachloroethane-d₂ at 125 °C.
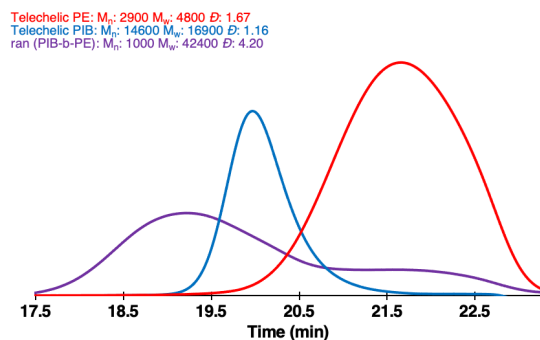

Fig. 15 GPC graphs of telechelic PE, telechelic PIB, and the multiblock copolymer ran (PIB-b-PE) in 1,2,4-trichlorobenzene at 140 °C.

also displayed a T$_m$ value of 131 °C similar to that of the starting crystalline block polyethylene.

To evaluate the mechanical properties of the multiblock-copolymer, tensile testing of the copolymer were performed. Representative nominal stress versus % elongation curves were chosen. Polymer dogbones were prepared and cut out. An Instron was used and the dogbones were clamped on both sides. The dogbone was stretched and elasticity was observed. Ran (PIB-
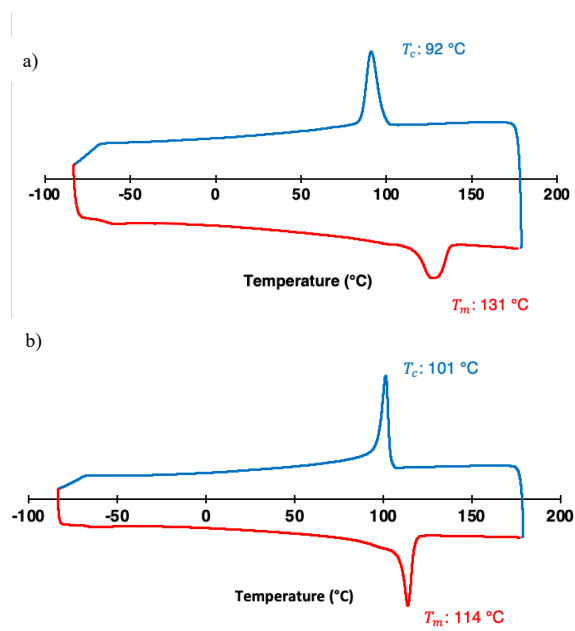

Fig. 16a DSC curve (10 °C min⁻¹) for ran (PIB-b-iPP). A T$_m$ value of 131 °C was displayed. **Fig. 16b** DSC curve (10 °C min⁻¹) for ran (PIB-b-PE). A T$_m$ value of 114 °C was displayed.

b-iPP) displayed a 76% elongation before breaking, a modulus of 23 MPa, and tensile strength of 1.65 MPa (Fig. 17b). Ran (PIB-b-PE)

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copolymer exhibited a 21% elongation prior to breaking, a modulus of 43 MPa, and tensile strength of 2.40 MPa (Fig. 17a).
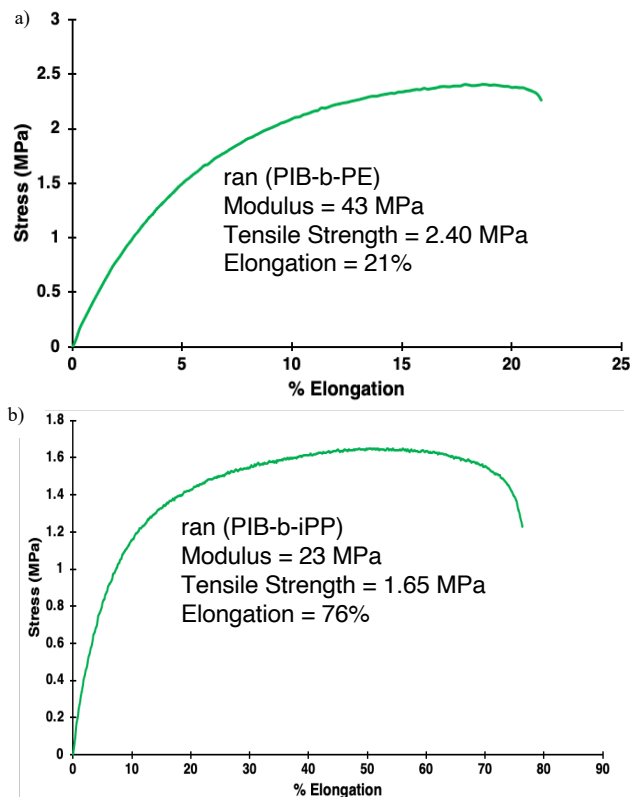

Fig. 17a Representative tensile stress-versus-% Elongation curves for (PIB-b-PE). **Fig. 17b** Representative tensile stress-versus-% Elongation curves for (PIB-b-iPP).

In conclusion, a convenient one-pot synthesis protocol can be used to synthesize crystalline/amorphous multiblock copolymers from telechelic macromonomers. The process involved depolymerization, repolymerization, and shuffling of the polymers. We were are able to achieve 4-5 blocks of repolymerization of the α,ω-divinyl telechelics via the sequential block addition technique. The multiblock copolymers produces displayed a T_m similar to the starting crystalline polymer. The multiblock also displayed improved mechanical properties. Ran (PIB-b-PE) exhibited a higher modulus and tensile strength, while Ran (PIB-b-iPP) was more elastic. We were also able to achieve a higher number of blocks with Ran (PIB-b-PE). Ran (PIB-b-iPP) was on average longer, but this is due to longer telechelic iPP. We predict that by varying the ratios of the starting polymers, we can adjust the mechanical properties in our favor. We also theorize that achieving a higher number of blocks in the repolymerization can improve the overall tensile strength and modulus. This versatile synthetic tool can be applied to a variety of other polymers and expands viable routes to multiblock copolymers.

Works Cited

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