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The Effect of Reaction Conditions on the Synthesis of Thermoplastic Elastomers Containing Polyalloocimene, Polyisobutylene and Tapered Blocks

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Abstract This work investigates the effect of reaction conditions on the copolymerization of isobutylene (IB) with alloocimene (Allo) in methyl chloride (MeCl) using AlCl_3 and ethylaluminum dichloride (EtAlCl_2) as coinitiators and adventitious moisture as the initiator. Both AlCl_3 and EtAlCl_2 produced high molecular weight ($M_n > 1.0 \times 10^5$ g/mol) thermoplastic elastomers (TPEs) with good mechanical properties in short reaction time (< 10 min). These unique TPEs have unsaturations in the end blocks, leading to easy functionalization and/or crosslinking.

Keywords Polyisobutylene; Alloocimene; Triblock copolymer; Carbocationic polymerization

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INTRODUCTION

The copolymerization of isobutylene (IB) with isoprene (IP) in methyl chloride (MeCl) using AlCl_3 as a coinitiator with an initiator (water or HCl) is an important industrial process to produce butyl rubber. We discovered that copolymerizing IB with alloocimene (Allo) using the same conditions produces linear copolymers having diblock, triblock, and multiblock structures. We found that Allo polymerized much faster than IB, forming a diblock at the beginning of the reaction as shown in Fig. 1. The copolymerization exhibited living/controlled characteristics up to about 40% conversion. When a second Allo charge was added to the reaction at this point, still in the living/controlled stage, triblocks and tetrablocks formed.^[1,2]

Under laboratory conditions H_2O addition is not necessary, as traces of moisture already present in the system are enough for initiation. AlCl_3 was added in the form of a saturated stock solution in MeCl (0.9 g/100mL). After initiation, a red color appeared that turned into yellow and white and milk-like over time while maintaining low viscosity.^[2] This was described as an emulsion, with the PAllo-PIB diblocks acting as stabilizing agents (Fig. 1b) since PAllo is partially soluble in MeCl, while PIB is insoluble. The phenomenon that a diblock can act as a stabilizer has been reported by

Okubo *et al.* They synthesized poly(methyl methacrylate) (PMMA) by radical polymerization using a poly(dimethyl siloxane) (PDMS)-based azoinitiator (called “inistab”), and the formed PDMS-PMMA diblocks stabilized the emulsion.^[3] The same PDMS-based macroinitiator was also used for stabilizing the emulsion in living free radical polymerization of styrene in supercritical CO_2 , producing PDMS-*b*-PS block copolymer.^[4] In our case, the poly(Allo-IB) diblock serves as the stabilizing agent. Triblocks and tetrablocks of IB and Allo formed after the addition of a second Allo increment into the polymerization mixture. Since the adventitious moisture content in the lab cannot be controlled, the amount of AlCl_3 solution necessary was established in a so-called “sacrificial” reaction when small increments of AlCl_3 solution were added to the monomer mixture until the temperature started to rise.^[5] Then a second reaction was performed that produced triblocks or tetrablocks with high molecular weights ($M_n > 2.0 \times 10^5$ g/mol) that displayed thermoplastic elastomeric (TPE) properties as well as excellent filler interaction with carbon black and silica. We coined the name “Allomatrix” for the new family of TPEs.

This work investigates the effect of reaction conditions on the molecular weight and tensile properties of the copolymers synthesized with the use of AlCl_3 and ethylaluminum dichloride coinitiators.

EXPERIMENTAL

Materials

Isobutylene (IB, 99.9%) was received by courtesy from

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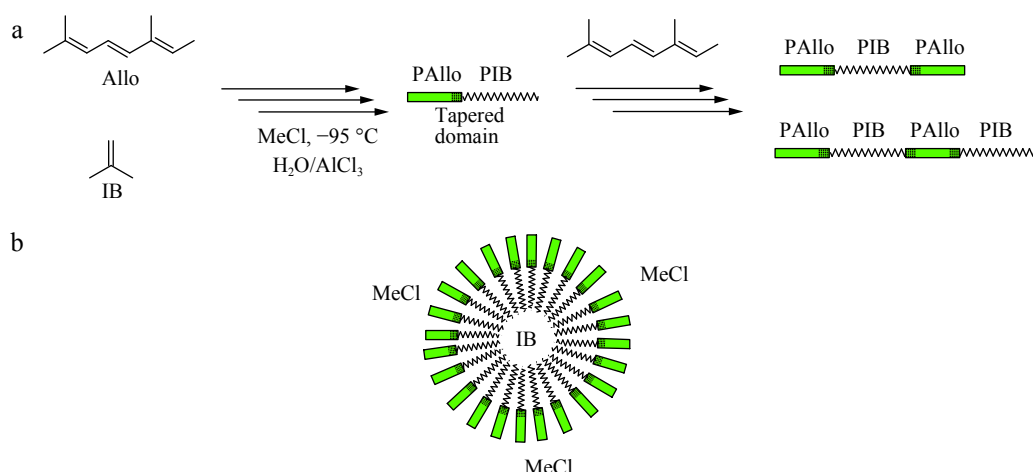


Fig. 1 Di-, tri-, and tetrablock copolymer synthesized from isobutylene (IB) and alloocimene (Allo) (a), and micelle stabilization by diblocks (b)

ExxonMobil, and was condensed before use. Methyl chloride (MeCl, 99.5%, Praxair) was passed through an Al_2O_3 column before condensing. Alloocimene (Allo, technical grade 80%, Aldrich) was filtered through an Al_2O_3 column and 0.45 μm PTFE filter, treated with *n*-butyllithium (0.5 mL/20 mL Allo), and cryodistilled before use. Aluminum chloride (AlCl_3 , 99.99%, Aldrich), ethylaluminum dichloride (EtAlCl_2 , 25 wt% in toluene, Aldrich), *n*-butyllithium (1.6 mol/L in hexane, Aldrich), sodium hydroxide (NaOH, 98.9%, Fisher), and methanol (MeOH, 99.9%, Fisher) were used as received.

Syntheses

The carbocationic polymerization of isobutylene was carried out under a dry nitrogen atmosphere in an MBraun 200B dry box ($\text{H}_2\text{O} < 6$ ppm, $\text{O}_2 < 10$ ppm). The cooling was provided by liquid nitrogen passing through a heat exchanger coil immersed in a continuously stirred hexane cooling bath.

*Synthesis of poly(alloocimene-*b*-isobutylene) triblock copolymers with AlCl_3 coinitiator*

At -30 $^\circ\text{C}$, 200 mL of MeCl was collected and added to a 500 mL Erlenmeyer flask. The sealed AlCl_3 ampoule was broken, and 2 g of AlCl_3 was added to MeCl. The solution was kept at -30 $^\circ\text{C}$ for 30 min and shaken every 5 min. At -80 $^\circ\text{C}$, 900 mL of MeCl was collected and added to a 3-neck 3000 mL round bottom flask (reactor), followed by 17 mL of Allo (0.09 mol/L) and 190 mL of IB (2.2 mol/L). The reactor was then cooled to -95 $^\circ\text{C}$ and AlCl_3 stock solution was added at concentrations specified in the Results and Discussion section. The reactions were performed in pairs: the first reaction of the series was a “sacrificial” reaction, during which the amount of AlCl_3 necessary to initiate the reaction was determined. For sacrificial reactions, AlCl_3 was gradually added in 5–10 mL increments until the temperature started rising. The sacrificial reaction was followed by a “one-shot” reaction, in which the AlCl_3 amount measured during the sacrificial reaction was added at once. After the desired reaction time was reached, an additional 17 mL of Allo (0.09 mol/L) was added to the reactor. The reactions were terminated 2 min after the 2nd Allo addition with 70 mL of 0.1 mol/L NaOH solution in MeOH.

*Synthesis of poly(alloocimene-*b*-isobutylene) triblock copolymers with EtAlCl_2 coinitiator*

At -80 $^\circ\text{C}$, 190 mL of MeCl was collected and added to a 3-neck 300 mL round bottom flask (reactor), followed by 3.6 mL of Allo (0.09 mol/L), and 40 mL of IB (2.2 mol/L). At -95 $^\circ\text{C}$, EtAlCl_2 solution in toluene (25 wt%) was added to the reactor; the concentrations are specified in the Results and Discussion section. Some reactions were performed in pairs: the first reaction of the series was the “sacrificial” reaction, during which the amount of EtAlCl_2 necessary to initiate the reaction was determined. For sacrificial reactions, EtAlCl_2 was gradually added in 0.9–1 mL increments until the temperature started rising. The sacrificial reaction was followed by a “one-shot” reaction, in which the EtAlCl_2 amount measured during the sacrificial reaction was added at once. After the desired reaction time was reached, an additional 3.6 mL of Allo (0.09 mol/L) was added to the reactor. The reactions were terminated 2 min after the 2nd Allo addition with 30 mL of 0.1 mol/L NaOH solution in MeOH.

Characterization Techniques

Thermogravimetric analysis (TGA)

TGA of the AIBA samples was performed with a TA Q50 thermogravimetric analyzer. The sample size was 10 mg, and the heating rate was 10 $^\circ\text{C}/\text{min}$ from 25 $^\circ\text{C}$ to 500 $^\circ\text{C}$. The TGA results were used to determine the Allo content of the samples.

Size exclusion chromatography (SEC)

SEC measurements were performed using a system consisting of an Agilent 1260 infinity isocratic pump, a Wyatt Eclipse DUALTEC separation system, an Agilent 1260 infinity variable wavelength detector (UV), a Wyatt OPTILAB T-rEX interferometric refractometer, a Wyatt DAWN HELOS-II multi-angle static light scattering detector (MALS) with a built-in dynamic light scattering (DLS) module, a Wyatt ViscoStar-II viscometer, an Agilent 1260 infinity standard autosampler, and 6 StyragelVR columns (HR6, HR5, HR4, HR3, HR1, and H0.5). The columns were thermostated at 35 $^\circ\text{C}$ and tetrahydrofuran (THF), continuously distilled from CaH_2 , was used as the mobile phase at a flow rate

of 1 mL/min. The results were analyzed using the ASTRA 6 software (Wyatt Technology). Absolute molecular weights were obtained using $dn/dc = 0.108$ mL/g established for PIB^[6] and $dn/dc = 0.122$ mL/g for PAllo.^[7]

SEC was also used to estimate the Allo content of aliquot samples (wt%). The ratio of the integrated areas under UV and dRI traces was compared to the UV/dRI ratio of pure PAllo. To verify the accuracy of this method, the estimated values were compared to Allo content (wt%) measured by TGA (see Table 1). The agreement is satisfactory and can conveniently be used for rapid screening. Allo content calculated with dRI and UV data is marked in particular in the Results and Discussion section.

Table 1 Comparison of Allo content from SEC and TGA

Allo content from TGA (wt%)	Allo content from SEC (wt%)	Difference (%)
34.9	39.5	13.2
43.2	46.2	6.9
28.5	35.5	24.6
20.5	23.4	14.1
11	11.4	3.6
30.5	35.4	16.1
25.2	18.5	26.6
	Average	15.0

Compression molding

The PIB-PAllo block copolymers were molded at 100 °C under steadily increasing pressure from 0 MPa to 2 MPa for 8 min, followed by 4 MPa pressure for 12 min.

Tensile testing

Microdumbbells were cut from compression molded sheets. The cut specimens were 1 mm in thickness, 45 mm in length, and 3 mm in width at the neck. Tensile tests were conducted on an Instron 5567 instrument equipped with a 1 kN load cell at (23 ± 2) °C. The crosshead speed was set as 500 mm/min, according to ASTM D 412-06a. The strain was measured by the grip displacement. Five specimens were tested for each sample.

RESULTS AND DISCUSSION

$AlCl_3$ Coinitiator

In our earlier work, we carried out sacrificial reactions to establish the amount of $AlCl_3$ solution to initiate the reactions before producing triblocks with one-shot initiations.^[5] In this work, triblock copolymers were prepared from both sacrificial and one-shot reactions. Fig. 2 shows the temperature profiles. In the sacrificial reaction the temperature started to rise after the addition of the fourth $AlCl_3$ increment. The second Allo portion was added at 6.5 min after the temperature jump, and the reaction was allowed to proceed for two more minutes before termination to avoid tetrablock formation—these optimized times were established earlier.^[5] In the one-shot reaction the temperature started to rise immediately. The second Allo portion was added at 5 min and the reaction was allowed to proceed two more minutes before termination.

The SEC traces are shown in Fig. 3. It can be seen that in the sacrificial reaction the UV trace is skewed towards the low molecular weight fraction (right), indicating no or little

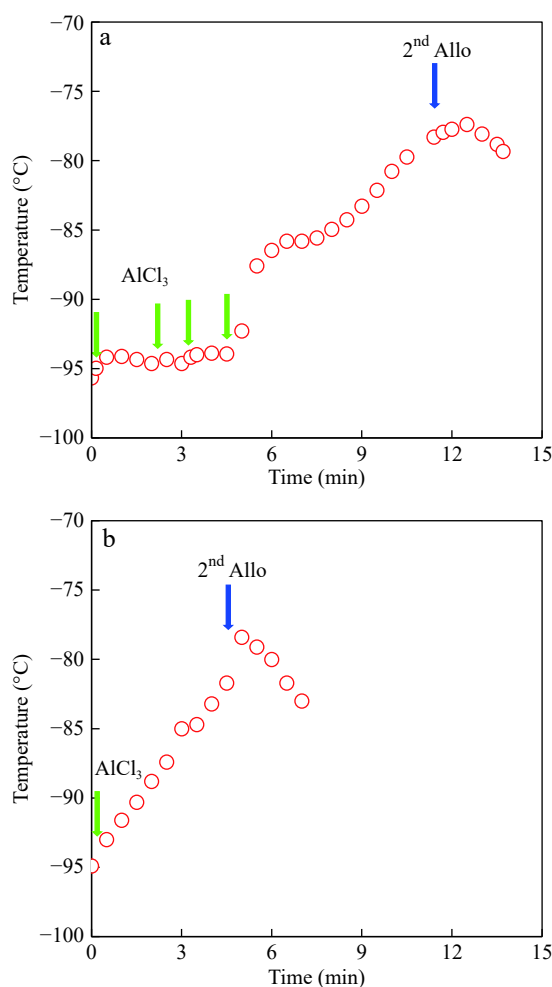


Fig. 2 Temperature profiles of IB-Allo copolymerizations: “sacrificial” reaction (a), and one-shot reaction (b)

Allo in the high molecular weight fraction. The material was very weak, and tensile test was not performed on it. By contrast, in the one-shot reaction the high molecular weight fraction has a strong UV signal. However, in the low molecular weight side a shoulder can be seen with very strong UV activity, indicating homo-Allo formation. In spite of this, the final material had very good tensile properties, having 16.9 MPa tensile strength on average (Table 2).

Next, reactions based on temperature profiles were carried out (A1, A2, and A3). The reactions were started by more than the critical $AlCl_3$ concentration established in a series of sacrificial reactions, and the second Allo was added when the temperature reached ~ -80 °C; an example is shown in Fig. 4(a). Fig. 4(b) shows the SEC traces, where the RI and UV signals indicate even distribution of Allo content across the molecular weight distribution. Data for three experiments carried out based on the temperature profile are summarized in Table 3.

The mechanical properties are very similar in spite of the high molecular weight of the A3 sample which also has the broadest distribution.

In summary, AIBA block polymers with good mechanical properties can be synthesized in a wide range of reaction conditions, indicating a very robust process.

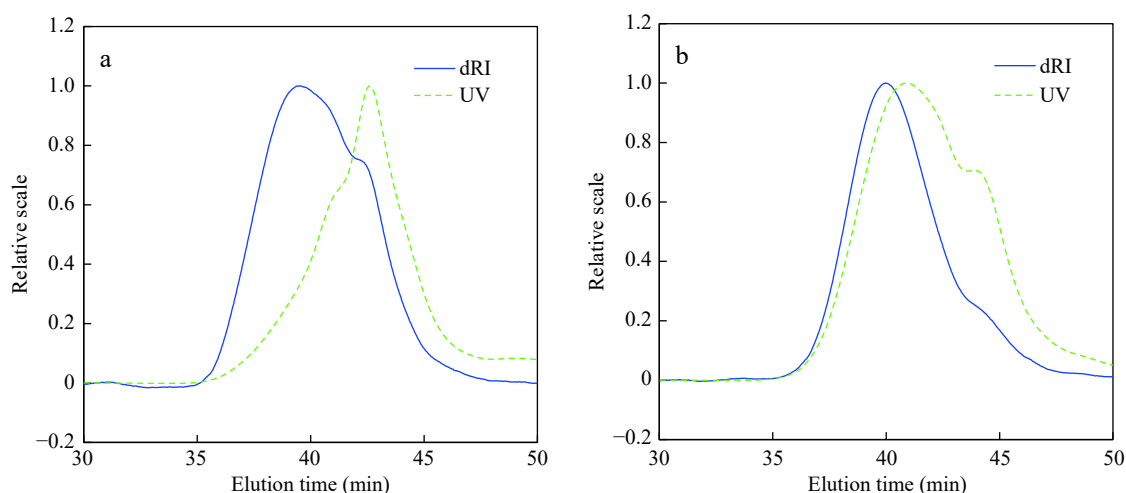


Fig. 3 Comparison of the SEC chromatograms of the copolymers obtained in the “sacrificial” reaction (a) and the one-shot reaction (b) ([IB] = 2.15 mol/L, [Allo] = 0.09 mol/L ($\times 2$), [AlCl₃] = 3.9×10^{-3} mol/L (a) or 3.4×10^{-3} mol/L (b), V = 1200 mL)

Table 2 Conversion and molar mass data, and mechanical properties of the copolymers obtained in the sacrificial and one-shot reactions ^a

Batch	AlCl ₃ concentration $\times 10^3$ (mol/L)	Conv. (%)	Allo content (wt%)	M_n (kg/mol)	$\bar{D}$	[P] $\times 10^3$ (mol/L)	UTS (MPa)	Ultimate strain (%)
A-Sacrificial	3.9	78.7	21.3	174	1.99	0.61	— ^b	—
A-One-shot	3.4	53.5	31.2	144	1.96	0.50	16.9 ± 1.5	630.4 ± 46.2

^a [IB] = 2.15 mol/L, [Allo] = 0.09 mol/L ($\times 2$), V = 1200 mL; ^b Weak material, not tested

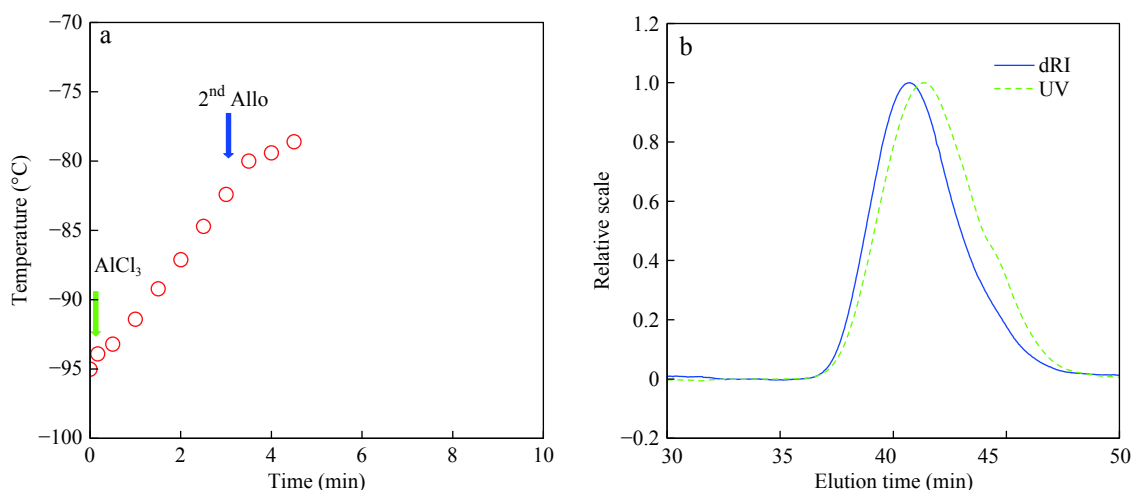


Fig. 4 Temperature profile (a) and SEC chromatograms (b) of A1 ([IB] = 2.15 mol/L, [Allo] = 0.09 mol/L ($\times 2$), [AlCl₃] = 4.1×10^{-3} mol/L, V = 1200 mL)

Table 3 Conversion and molar mass data, and mechanical properties of AIBA triblock copolymers synthesized with AlCl₃ coinitiator ^a

Batch	AlCl ₃ concentration $\times 10^3$ (mol/L)	Conv. (%)	Allo content (wt%)	M_n (kg/mol)	$\bar{D}$	[P] $\times 10^3$ (mol/L)	UTS (MPa)	Ultimate strain (%)
A1	4.1	54.8	28.2	110	1.68	0.67	10.4 ± 0.2	817 ± 48.7
A2	3.9	45.0	28.6	132	1.55	0.46	11.8 ± 1.6	700.5 ± 71.8
A3	3.7	51.2	32.0	233	2.12	0.29	11.6 ± 0.5	653 ± 21

^a [IB] = 2.15 mol/L, [Allo] = 0.09 mol/L ($\times 2$), V = 1200 mL

EtAlCl₂ Coinitiator

A series of experiments were conducted using EtAlCl₂ as the coinitiator. The usage of EtAlCl₂ is cheaper at the laboratory scale and easier to handle because it dissolves in toluene or hexane and can be bought in solution instead of as an anhydrous powder. Similarly to the reactions with AlCl₃ coinitiator, the first reaction was a “sacrificial reaction” in order

to establish the critical EtAlCl₂ concentration. Fig. 5 compares the temperature profiles of the sacrificial reaction and one-shot reaction performed with 7.0 mol/L EtAlCl₂, somewhat higher than the 5.7 mol/L measured in the sacrificial reaction.

Fig. 6 compares the SEC chromatograms of the sacrificial and one-shot reactions. In the case of the sacrificial reaction

the RI trace shows a low molecular weight shoulder, with a corresponding strong UV signal. This indicates Allo homo-polymer formation, with less blocking. By contrast, in the one-shot reaction the RI and UV traces almost coincide. Table 4 summarizes the data.

Conversion was higher in the sacrificial reaction, but the Allo content and M_n were lower, while D and polymer concentration $[P]$ were higher than those in the one-shot reaction. The poorer blocking in the sacrificial reaction is corresponding with the much lower tensile strength. Fig. 7 shows the tensile plots. The one-shot reaction showed yielding due to the high Allo content.

These data indicated that the reaction rate was lower than that with $AlCl_3$, so we carried out kinetic investigations next.

Fig. 8 compares the temperature profiles of polymerizations carried out with three different $EtAlCl_2$ concentrations. E1 maintained an almost flat temperature profile, staying around $-94^\circ C$, so it was reacted for 10 min before adding the 2nd Allo charge. In the case of E2, the temperature started increasing 2 min after the $EtAlCl_2$ addition. The second Allo charge was added at 8 min reaction time. In the case of E3, the temperature also started rising after 2 min. The increase was faster than in the case of E2, reaching $-80^\circ C$ after 6.5 min when the second Allo increment was added.

Two (three in case of (c)) aliquots were taken throughout each reaction and Table 5 summarizes the results. Due to the small sample sizes, conversion measurements seem to be inaccurate so only final conversions are given. In reaction E1,

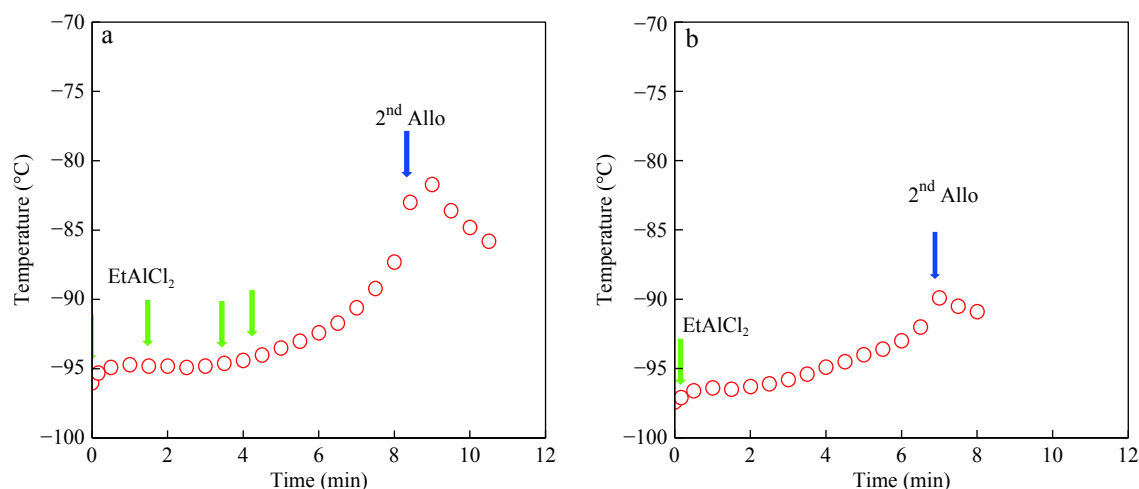


Fig. 5 Temperature profiles of the sacrificial reaction and one-shot reaction performed with $EtAlCl_2$ ($[IB] = 2.15 \text{ mol/L}$, $[Allo] = 0.09 \text{ mol/L} (\times 2)$, $[EtAlCl_2] = 5.7 \times 10^{-3} \text{ mol/L}$ (a) or $7.0 \times 10^{-3} \text{ mol/L}$ (b), $V = 235 \text{ mL}$)

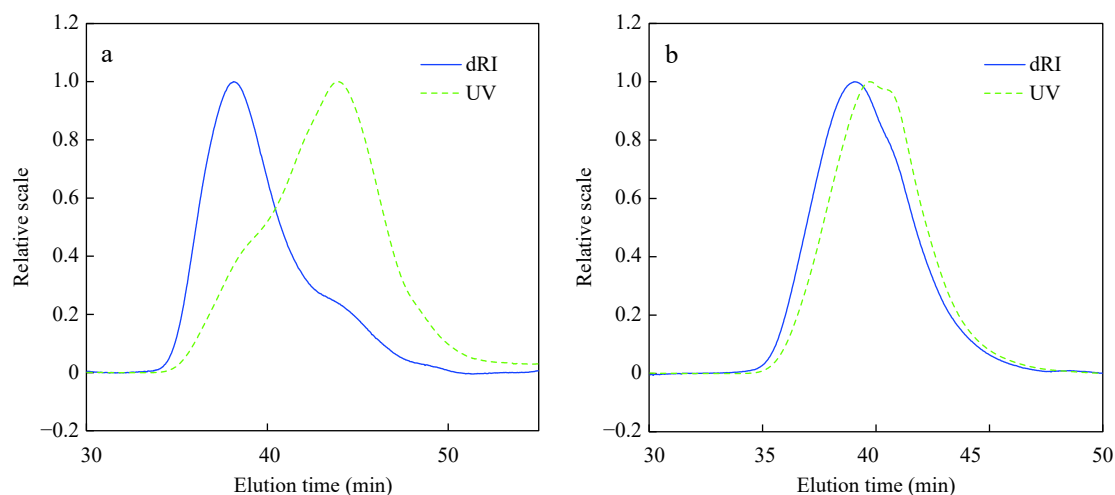


Fig. 6 SEC chromatograms of the copolymers obtained in the sacrificial and one-shot reactions performed with $EtAlCl_2$ ($[IB] = 2.15 \text{ mol/L}$, $[Allo] = 0.09 \text{ mol/L}$, $[EtAlCl_2] = 5.7 \times 10^{-3} \text{ mol/L}$ (a) or $7.0 \times 10^{-3} \text{ mol/L}$ (b), $V = 235 \text{ mL}$)

Table 4 AIBA triblock synthesis *via* incremental (sacrificial experiment) and one-shot addition of $EtAlCl_2$ ^a

Batch	$AlCl_3$ concentration $\times 10^3 \text{ (mol/L)}$	Conv. (%)	Allo content (wt%)	M_n (kg/mol)	D	$[P] \times 10^3 \text{ (mol/L)}$	UTS (MPa)	Ultimate strain (%)
E-Sacrificial	5.7	39	21 ^b	172	2.87	0.28	3.62 ± 0.75	840 ± 110
E-One-shot	7.0	32	43.2	218	1.77	0.20	13.36 ± 0.28	575 ± 22

^a $[IB] = 2.15 \text{ mol/L}$, $[Allo] = 0.09 \text{ mol/L} (\times 2)$, $[EtAlCl_2] = 5.7 \times 10^{-3} \text{ mol/L}$ and $7.0 \times 10^{-3} \text{ mol/L}$, $V = 235 \text{ mL}$; ^b From SEC

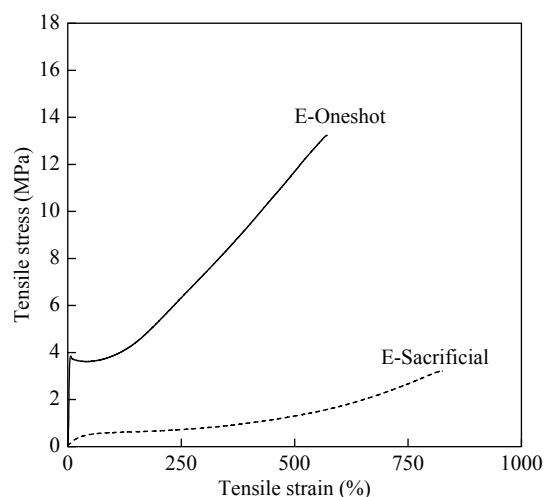


Fig. 7 Representative stress-strain plots of the copolymers obtained in the sacrificial and one-shot reaction performed with EtAlCl₂

low monomer conversion was achieved. M_n increased with reaction time and $\bar{D}$ was constant at 1.56–1.58, which indicates the absence of chain transfer. The Allo content was high in the first sample and lower in the second sample, thus Allo polymerizes faster than IB with this coinitiator as well. However, the overall reaction was relatively slow with low IB conversion and the final Allo content after the addition of the second Allo increment was high at 48%.

In reaction E2, M_n increased in the first two samples but dropped in the last sample, on account of the increasing $\bar{D}$, indicating chain transfer. The polymer concentration $[P]$ was more than twice as high as that in E1. E3 showed a behavior similar to E2, but with more chain transfer with $\bar{D} = 2.13$. E2 and E3 triblocks had 29 wt% and 22 wt% Allo content, respectively. While the Allo content in the first samples in all three experiments was high at 63 wt%, 31 wt%, and 59 wt%, these values are lower than those found with AlCl₃ (> 90 wt%), so the blocks are tapered. Fig. 9 compares the RI and UV traces of the final triblock from reactions E1, E2, and E3.

In E1, the UV traces overlap well with the dRI traces, indicating Allo content throughout the distribution. In E2 and E3, the UV trace is skewed towards lower molecular weights, which suggests that the final products also contained a fraction of diblocks and Allo homopolymer. No major differences can be found between E2 and E3; however, the mechanical properties were drastically different. Fig. 10 compares representative tensile plots of the triblocks. It can be seen that E2 displayed excellent TPE properties, with strain hardening due to crystallization that is typical for PIB-containing TPEs. E3 was much weaker but also displayed a rubbery plateau and some strain hardening. E3 had lower M_n (1.89×10^5 versus 2.99×10^5 g/mol), somewhat broader distribution ($\bar{D} = 2.13$ versus 1.98) and less Allo content (22 wt% versus 29 wt%) than E2, but we cannot really explain the very large difference in mechanical properties

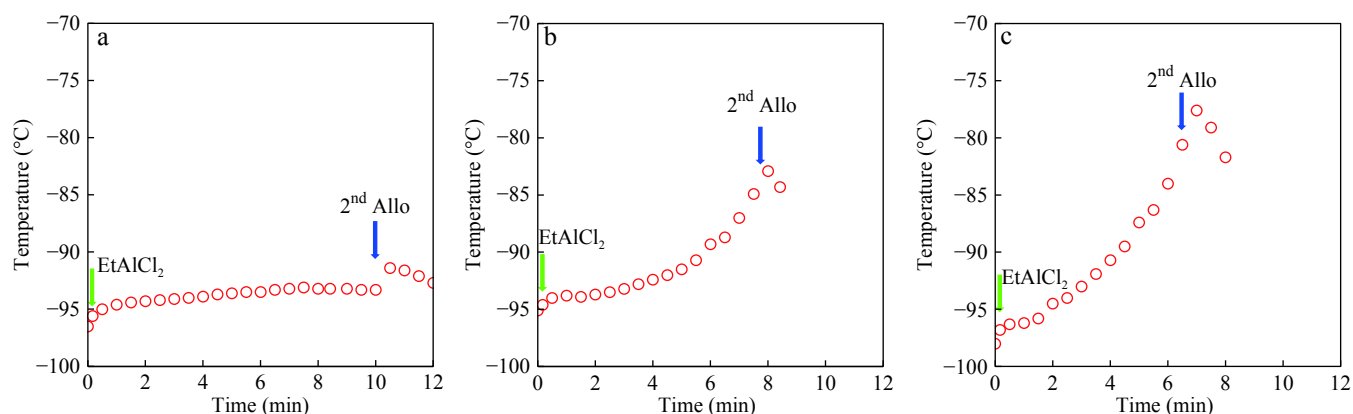


Fig. 8 Temperature profiles of AIBA triblock copolymers synthesized with EtAlCl₂ coinitiator ($[IB] = 2.15$ mol/L, $[Allo] = 0.09$ mol/L ($\times 2$), $[EtAlCl_2] = 3.6 \times 10^{-3}$ mol/L (a), 5.3×10^{-3} mol/L (b), or 7.0×10^{-3} mol/L (c), $V = 235$ mL)

Table 5 Results of the kinetic studies ^a

Batch	EtAlCl ₂ concentration $\times 10^3$ (mol/L)	Reaction time (min)	Conv. (%)	Allo content (wt%)	M_n (kg/mol)	$\bar{D}$	$[P] \times 10^3$ (mol/L)
E1S1	3.6	6.4	—	63 ^b	191	1.56	—
E1S2		9.5	—	38 ^b	233	1.58	—
E1-Triblock		10.3 + 2	19.9	48 ^b	270	1.58	0.105
E2S1	5.3	6.4	—	31	226	1.69	—
E2S2		9.6	—	18 ^b	350	1.75	—
E2-Triblock		10.1 + 2	49.9	29	299	1.98	0.234
E3S1	7.0	2.2	—	59 ^b	103	1.52	—
E3S2		4.8	—	21	186	1.67	—
E3S3		6.3	—	11	240	1.78	—
E3-Triblock		8.5 + 2	54.0	22 ^b	189	2.13	0.377

^a $[IB] = 2.15$ mol/L, $[Allo] = 0.09$ mol/L ($\times 2$), $V = 235$ mL; ^b From SEC

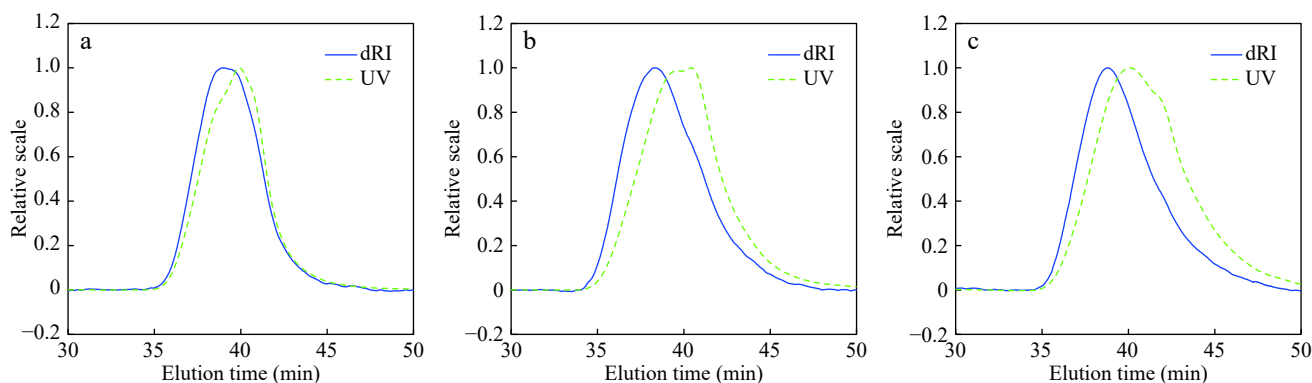


Fig. 9 dRI and UV chromatograms of E1-Triblock (a), E2-Triblock (b), and E3-Triblock (c) ([IB] = 2.15 mol/L, [Allo] = 0.09 mol/L ($\times 2$), [EtAlCl₂] = 3.6×10^{-3} mol/L, V = 235 mL)

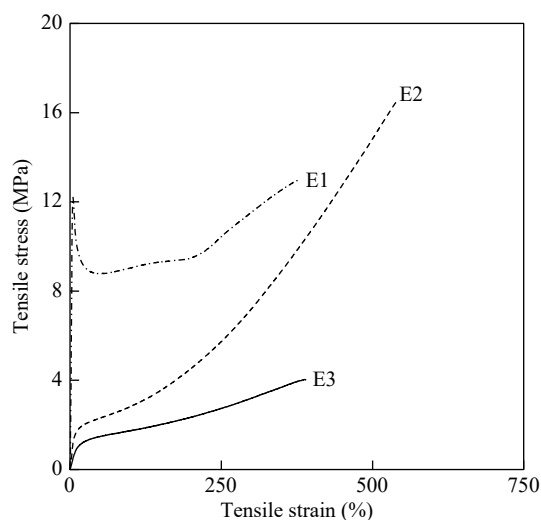


Fig. 10 Representative stress-strain plots of E1-, E2-, and E3-triblocks

between the two polymers. Further investigations are underway to get a better understanding of the polymerization system. E1 behaved like a plastic, with an average yield strength of 12.5 MPa and a Young's modulus of 0.72 GPa, on account of its high Allo content. Past the yield point at 1.75% strain the material showed a plateau up till ~230% strain, after which it also displayed strain-hardening.

CONCLUSIONS

Copolymers of alloocimene and isobutylene with $M_n > 1.0 \times 10^5$ g/mol were synthesized with the AlCl₃/H₂O and EtAlCl₂/H₂O systems. Both systems produced block copolymers that showed excellent TPE properties at around 30 wt% Allo content. The reactions were slower with EtAlCl₂, yielding more tapered blocks than that found with AlCl₃. At [EtAlCl₂] = 3.6×10^{-3} mol/L the reaction was close to isothermal and with limited chain transfer, albeit the overall conversion was also low at 10-min reaction time. More detailed investigations will be carried out with EtAlCl₂, but based on the data presented, this seems to be a better coinitiator under laboratory conditions.

CONFLICT OF INTEREST

PolyFiberMatrix LLC has an exclusive license from the University of Akron for biomedical application of the Allomatrix technology.^[1]

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