

Polyurethanes and Polyallophanates *via* Sequence-Selective Copolymerization of Epoxides and Isocyanates

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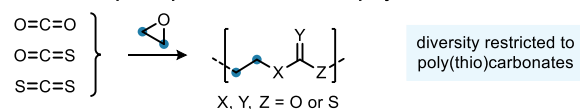
ABSTRACT: Aryl isocyanates are introduced as comonomers for ring opening copolymerization (ROCOP) with epoxides. Informed by studies of reaction kinetics, we show that divergent sequence selectivity for AB- and ABB-type copolymers can be achieved with a single dimagnesium catalyst. The resulting materials respectively constitute a new class of polyurethane (PU) and a new class of material featuring an unprecedented backbone structure, the polyallophanate (PA). The successful use of isocyanate comonomers in this way marks a new direction for the field of ROCOP, while providing distinct opportunities for expansion of PU structural diversity. Specifically, the methodology reported herein delivers PUs featuring fully substituted (tertiary) carbamyl nitrogen atoms, a structural motif that is almost inaccessible via extant polymerization strategies. Thus, in one step from commercially available comonomers, our methodology expands the scope of ROCOP and gives access to diverse materials featuring both privileged (PU) and unexplored (PA) microstructures.

Controlled ring opening copolymerization (ROCOP) involving epoxide comonomers represents a significant accomplishment in the fields of catalysis and materials chemistry. By overcoming the synthetic challenges associated with selective alternate copolymerization, readily-available comonomers such as carbon dioxide,¹⁻³ its sulfur-analogs⁴⁻¹⁵ or cyclic anhydrides¹⁶ can be converted directly to valuable, biodegradable plastics such as poly(thio)carbonates (Scheme 1A) and polyesters.¹⁷ Perhaps most notably, ROCOP strategies offer atom-economic access to materials with properties that can be readily tuned by varying *both* comonomers. While this advantage is regularly exploited in epoxide/cyclic anhydride ROCOP,¹⁸ the same cannot be said for epoxide/heteroallene ROCOP where the scope with respect to heteroallene comonomers has remained limited to carbon dithiocarbonates (CO₂, COS or CS₂). All materials synthesized via epoxide/heteroallene copolymerization must therefore be based on the (thio)carbonate linkage. Methods employing isocyanates as the heteroallene component would overcome this limitation^{19,20} and provide concise access to polyurethanes (PUs), an iconic class of material with a market value predicted to exceed \$79bn in 2023.^{21,22}

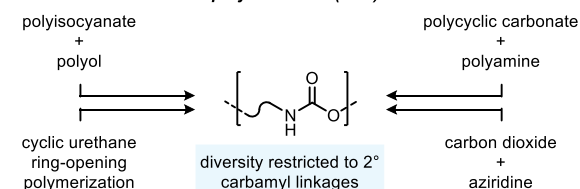
Current routes to PUs - including industrially ubiquitous copolymerization of diisocyanates with polyols - give secondary (NH) carbamyl linkages (Scheme 1B). There exists no general method for the direct synthesis of PUs featuring tertiary carbamyl linkages.^{17a-c,22-25} Challenging post-polymerization N-H functionalization is thus necessary if all vectors of the PU chain are to be exploited.

Scheme 1. Context and Strategic Blueprint for Copolymerization of Epoxides and Heteroallenes

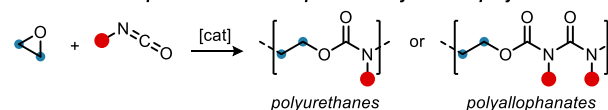
A. current scope of epoxide/heteroallene copolymerization



B. conventional routes to polyurethanes (PUs)



C. this work: sequence-controlled epoxide/isocyanate copolymerization



- direct access to 3° carbamyl linkages from diverse monoisocyanates
- access to synthetically-challenging class of polyurethane microstructure
- new polymer class: polyallophanates

In contrast, epoxide/isocyanate copolymerization represents a fundamentally new approach to PUs that addresses this limitation, providing direct access to tertiary carbamate linkages in which all nitrogen vectors are substituted (Scheme 1C). Within this manifold, variation of the *N*-pendant functionality is achieved simply by choosing from the plethora of commercially available monoisocyanates.²⁶

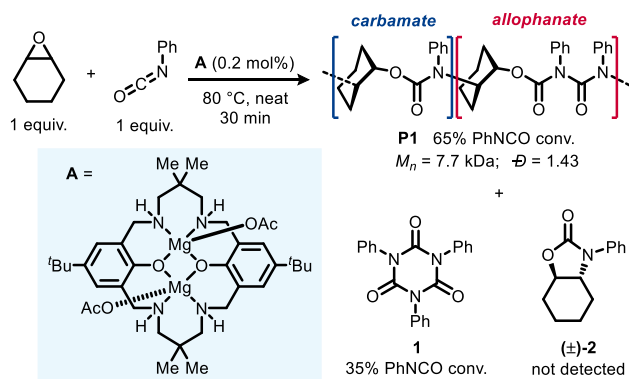
The key hurdle to realizing this strategy is the high and varied reactivity of isocyanates, particularly in combination with epoxides. In the presence of either Lewis basic or Lewis acidic additives, isocyanates readily undergo homo-oligomerization²⁷⁻³¹ to

uretidones, allophanates and isocyanurates, or react with epoxides to form oxazolidinones.³²⁻³⁶ This contrasts with the stability of heteroallenes currently employed in copolymerization with epoxides; indeed CO₂ and CS₂ are so stable that they are used as solvents.

Herein we report, for the first time, that the innate reactivity of isocyanates and epoxides can be harnessed for productive and selective copolymerization. Informed by studies of reaction kinetics, we demonstrate that this copolymerization affords not only a new class of PUs, but also a new class of material featuring an unprecedented backbone structure, polyallophanates (PAs). Both classes of material are accessed with excellent sequence control using the same precatalyst. The resulting PUs feature microstructures that are otherwise challenging to access via direct polymerization strategies.^{23,37} The corresponding PAs are inaccessible through any other means and represent a rare opportunity to enter unexplored materials space.

Within our screening study,³⁸ Williams' dimagnesium complex **A**³⁹ was uniquely active in the copolymerization of cyclohexene oxide (CHO) and phenyl isocyanate (PhNCO) (Scheme 2). Complete conversion of PhNCO to copolymer **P1** and triphenyl isocyanurate **1** occurred in 30 mins at 80 °C; oxazolidinone **2** was not detected. The unprecedented selectivity exhibited by precatalyst **A** stands in stark contrast to the myriad Lewis acid catalysts that yield oxazolidinones with high efficiency.³²⁻³⁶

Scheme 2. Copolymerization of Cyclohexene Oxide (CHO) and Phenyl Isocyanate (PhNCO)



GPC analysis confirmed the polymeric nature of **P1**. However, ¹H NMR spectroscopy indicated it to be microstructurally heterogeneous: enrichment in PhNCO relative to CHO implied the presence of linkages featuring urea-type moieties in addition to carbamate moieties. Further analysis³⁸ by ¹³C{¹H} NMR spectroscopy and hydrolysis experiments revealed that the linkages containing these urea moieties are constructed from just two consecutive PhNCO monomers, forming an allophanate linkage (red brackets, Scheme 2).⁴⁰ This microstructural assignment was confirmed following subsequent studies of constitutionally pure materials (*vide infra*).⁴¹

Identification of two distinct structural sub-units in **P1** indicated that this reactivity manifold promises access to not only a

Table 1. Selectivity of CHO/PhNCO Copolymerization^a

new class of polyurethanes (AB copolymers, blue brackets, Scheme 2) but also to previously inaccessible polyallophanates (ABB copolymer, red brackets, Scheme 2). To realize the synthesis of each of these new copolymers, we sought to understand the kinetic origin of the partitioning between the carbamate and allophanate sub-units.

The urethane sub-units within **P1** comprise a single, A-B (carbamate) linkage, whereas the allophanate sub-units comprise linkages featuring both A-B (carbamate) and B-B (urea) components. Given that isocyanurate **1** comprises entirely B-B linkages, we hypothesized that the kinetics of formation of this cyclic trimer would be representative of the kinetics of formation of the B-B linkages within the allophanate sub-units. On this basis we proposed that insight into this cyclotrimerization could be used to develop a *de facto* kinetic description of the formation of A-B linkages

Cyclotrimerization of PhNCO to isocyanurate **1** was monitored by *in situ* IR spectroscopy, and a kinetic model (eq. 1) was developed that could reproduce the observed reaction profiles (Fig. 1, left).³⁸ This model for B-B linkage formation allowed an analogous term for formation of the A-B linkages to be developed (eq. 2). Combination of the terms gives an empirical rate law (eq. 3) that models the combined cyclotrimerization and copolymerization processes across a range of practical comonomer stoichiometries (Fig. 1, right).

$$\frac{-d[\text{PhNCO}]}{dt} \approx \frac{k_1 k_2 [\text{cat}] [\text{PhNCO}]^2}{k_{-1} + k_2 [\text{PhNCO}]} \quad (1)$$

$$\frac{-d[\text{PhNCO}]}{dt} \approx k_4 [\text{cat}] [\text{CHO}] \quad (2)$$

$$\frac{-d[\text{PhNCO}]}{dt} \approx \frac{k_1 k_2 [\text{cat}] [\text{PhNCO}]^2}{k_{-1} + k_2 [\text{PhNCO}]} + k_4 [\text{cat}] [\text{CHO}] \quad (3)$$

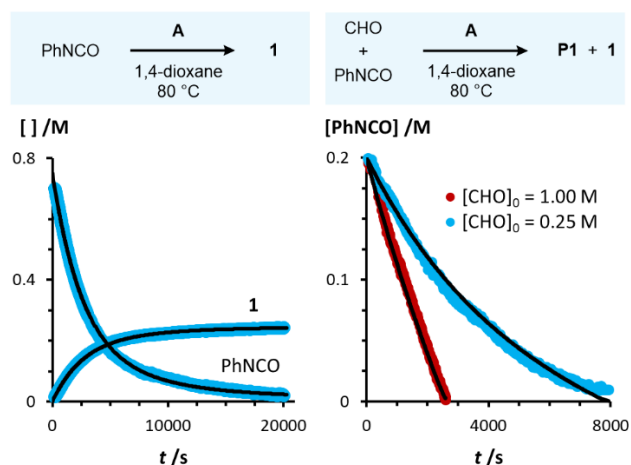
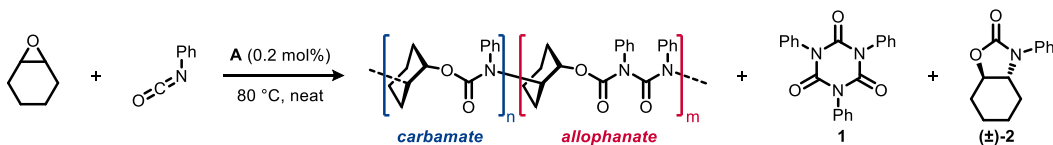


Figure 1. Representative kinetic profiles for isocyanate cyclotrimerization (left; $[\text{A}]_0 = 4.90$ mM, $[\text{PhNCO}]_0 = 0.75$ M), and combined copolymerization/cyclotrimerization (right; $[\text{A}]_0 = 3.50$ mM, $[\text{PhNCO}]_0 = 0.20$ M). Simulated data shown as solid black lines are calculated using equations 1 (left) and 3 (right).



entry	PhNCO:CHO molar ratio	PhNCO addition time	reaction time after PhNCO addition complete (min)	n:m ^b	% PhNCO conversion to 1 ^c	(±)- 2 ^c	M _n (kDa) ^d	D ^d
1 PI	1:1	<5 s	30	12:88	35	n.d.	7.7	1.43
2 PI'	1:5	<5 s	30	25:75	11	n.d.	8.2	1.63
3 PU1	1:5	6 h	60	>95:5	n.d.	5	4.8	1.32
4 PA1	3:1	<5 s	60	5:>95	68	n.d.	3.0	1.66

^aConditions: PhNCO added to 0.2 mol% precatalyst **A** in CHO at 80 °C; stir at 80 °C for the time indicated. ^bDetermined by ¹H NMR spectroscopy and hydrolysis studies.³⁸ ^cDetermined by calibrated HPLC and ¹H NMR spectroscopic analyses (*vs* internal standard).³⁸ ^dDetermined by GPC in THF (calibrated *vs* polystyrene standards). n.d., not detected.

Inspection of equation 3 reveals that, while the rate of formation of B-B linkages depends on the concentration of PhNCO and not CHO, the converse is true of A-B linkage formation. Conditions that limit the instantaneous concentration of PhNCO should therefore suppress the formation of B-B linkages, providing sequence-selective access to materials composed solely of A-B linkages. While using CHO in excess afforded only a slight increase in selectivity (Table 1, entry 1 *vs* entry 2), combining this with syringe-pump addition of PhNCO over 6 hours gave polyurethane **PU1** with high constitutional purity and restricted isocyanurate formation to amounts that could not be detected by ¹H NMR or HPLC analyses (entry 3). The sequence selectivity for this polymerization (>95% carbamate linkages) was supported by NMR spectroscopy and confirmed by hydrolysis experiments.³⁸

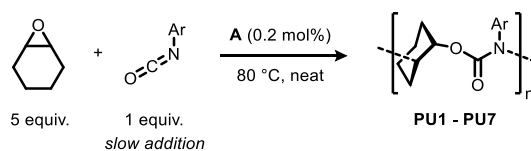
Conversely, equation 3 indicates that conditions of high PhNCO concentration should favor the formation of B-B linkages, affording both isocyanurate **1** and polymeric material composed of allophanate (ABB) sub-units. In practice, rapid addition of excess PhNCO in a single portion afforded polymeric material with >95% selectivity for ABB linkages (Table 1, entry 4) albeit in only 36% conversion based on limiting CHO.

Having demonstrated that PUs and PAs can both be accessed with high constitutional purity, we sought to diversify the library of materials by varying the *N*-pendant substituent. While introduction of substituents at this position *via* extant strategies would necessitate challenging post-polymerization functionalization or lengthy stepwise procedures,³⁷ our chemistry simply requires that a different aryl isocyanate comonomer is used (Tables 2 and 3).

While the methodology cannot be extended to alkyl isocyanates, electron-poor, electron-rich and sterically hindered aryl isocyanates all afford PUs with sequence selectivities in excess

of 95% (Table 2). In all cases, the polymers are isolated in high yield⁴² with oxazolidinone formation limited to trace quantities.^{38,43} Given the widespread availability of diverse monoisocyanates, this initial scope is particularly promising for future applications of the methodology.

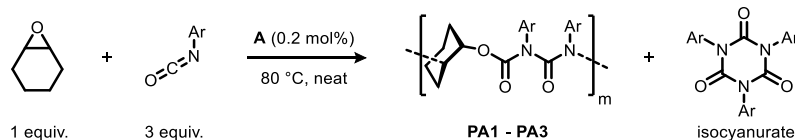
Table 2. Scope of Polyurethane Synthesis^{a,b,c}



entry	Ar	M _n (kDa) ^d	D ^d	% yield ^e
1 PU1	Ph	4.8	1.32	83
2 PU2	<i>p</i> -Me-C ₆ H ₄	3.1	1.28	96
3 PU3	<i>m</i> -Me-C ₆ H ₄	3.8	1.57	90
4 PU4	<i>p</i> -CF ₃ -C ₆ H ₄	4.2	1.43	72
5 PU5	<i>p</i> -F-C ₆ H ₄	3.9	1.32	71
6 PU6	<i>p</i> -MeO-C ₆ H ₄	3.3	1.37	71
7 PU7	<i>o</i> -Me-C ₆ H ₄	3.0	1.37	85

^aConditions: 1 equiv. ArNCO added over 6 h to 0.2 mol% precatalyst **A** in 5 equiv. CHO at 80 °C, then stir at 80 °C, 60 min. ^bAs determined following hydrolysis of the isolated materials, all polymers consisted of >95:5 carbamate:allophanate linkages.³⁸ ^cAs determined by ¹H NMR spectroscopic analysis (*vs* internal standard) and analogy to **PU1**, oxazolidinone side-products accounted for ≤5% of ArNCO.³⁸ ^dDetermined by GPC in THF (calibrated *vs* polystyrene standards). ^eYields are of isolated, purified material and are calculated based on limiting ArNCO and the mass of the repeat unit.

Table 3. Scope and Selectivity of Polyallophanate Synthesis^a



entry	Ar	n:m ^b	% ArNCO converted to isocyanurate ^c	% ArNCO unreacted ^c	M _n (kDa) ^d	D ^d	% yield ^e
1 PA1	Ph	>95:5	68%	5.5%	3.0	1.66	36%

2	PA2	<i>p</i> -Me-C ₆ H ₄	>95:5	83%	6.5%	4.5	1.66	10%
3	PA3	<i>m</i> -Me-C ₆ H ₄	91:9	59%	21.5%	8.3	1.54	15%

^aConditions: 3 equiv. ArNCO added rapidly to precatalyst **A** (0.2 mol%) in 1 equiv. CHO; stir at 80 °C, 60 min. ^bLinkage quantification determined by hydrolysis of the purified polymer (*vs* internal standard).³⁸ ^cDetermined by calibrated HPLC and/or ¹H NMR spectroscopic analyses (*vs* internal standard). ^dDetermined by GPC in THF (calibrated *vs* polystyrene standards). ^eYields are of isolated, purified material and are calculated based on limiting CHO and the mass of the repeat unit.

A consequence of the slow addition protocol is that PUs **PU1-PU7** feature relatively low molar mass and high *D* (Table 2), presumably because chain transfer competes effectively with chain growth during the extended reaction periods.⁴⁴ Whilst higher *M_n* can be achieved by increasing the rate of isocyanate addition (*cf.* **P1'**, Table 1, entry 2), this is at the expense of sequence selectivity.

Synthesis of PAs via a single addition of excess isocyanate proved less general (Table 3). Formation of isocyanurate out-competed polymerization for electron-poor aryl isocyanates.⁴⁵ However, electron-rich and -neutral aryl isocyanates afforded the expected polyallophanates with excellent constitutional purity.

NMR spectroscopy was conducted at 90 °C to reduce signal broadening.^{38,46} ¹H NMR spectra of both classes of material are resolved into the aromatic, methine and the methylene regions, each of which integrate as expected. ¹³C{¹H} NMR spectra of the PUs show a single signal between 152 and 157 ppm, corresponding to the carbonyl environment within the carbamate moiety. ¹³C{¹H} NMR spectra of PAs display two signals between 150 and 155 ppm, corresponding to the two distinct carbonyl environments within the allophanate moiety.

IR spectra of the PUs display a single strong band at ≈1700 cm⁻¹ corresponding to the stretching frequency of the carbonyl group. IR spectra of the PAs display two strong bands at ≈1690 cm⁻¹ and ≈1725 cm⁻¹ corresponding to the two distinct carbonyl groups within the allophanate moiety.

Thermal decomposition of the PUs and PAs commences between 180 to 210 °C, and affords non-volatile small-molecule products.³⁸ While **PU5** exhibits a glass transition at 181 °C, the remaining polymers all initiate decomposition prior to the occurrence of any thermal events.

In conclusion, we have achieved productive copolymerization of epoxides and isocyanates for the first time. By overcoming the innate reactivity of each comonomer, we have fulfilled a missing link in epoxide/heteroallene copolymerization. Insight from kinetic models allows this new reactivity to be diverted towards the selective synthesis of either a new class of polyurethanes or polyallophanates, a material featuring a previously unprecedented microstructure. The ability to use isocyanates as comonomers enables the synthesis of diverse and tunable materials that cannot be accessed via other ROCOP strategies, or via conventional routes to PUs. We envisage that the diverse, modular materials reported herein will augment the privileged position that PUs hold as structural materials, and will expand their applicability into the field of functional materials.

ASSOCIATED CONTENT

Supporting Information

Additional discussion, experimental procedures, kinetic data and simulations, and characterization data (hydrolysis studies, NMR spectra, GPC traces and DSC traces). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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(41) Notably, other plausible linkage types – such as ethers or arylimido carbonates (ref. 19) – were not detected (see SI, figure S27 and associated discussion). Furthermore, control experiments indicate that no reaction occurs when precatalyst **A** is heated with CHO at 80 °C in the absence of PhNCO, indicating that the dimagnesium Robson-type complex is incapable of promoting (poly)ether formation.

(42) The isolation procedure involves washing the polymers with hexanes and methanol to remove trace oxazolidinone. This process results in material loss that attenuates the isolated yield of **PU4-6**.

(43) Adding PhNCO over 2 h instead of over 6 h reduces the formation of oxazolidinone to 1.5% from 5%. Conversely, increasing the heating time after PhNCO addition is complete has no effect on oxazolidinone formation: leaving the reaction to heat for 13 h instead of 1 h results in a negligible 0.04% increase of oxazolidinone formation. These observations suggest oxazolidinone formation takes place only on the growing polymer chain and not on already-formed polymer chains.

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(46) Even at 90 °C, the NMR spectra do not allow quantitative assertions to be made regarding polymer purity. Therefore, we performed detailed hydrolysis studies that quantitatively convert each linkage type into small molecule products that provide sharp signals in the NMR spectra. Integration of these signals relative to an internal standard allowed us to unambiguously quantify the carbamate and allophanate linkages within each polymer. See Section S4 in the SI for details.

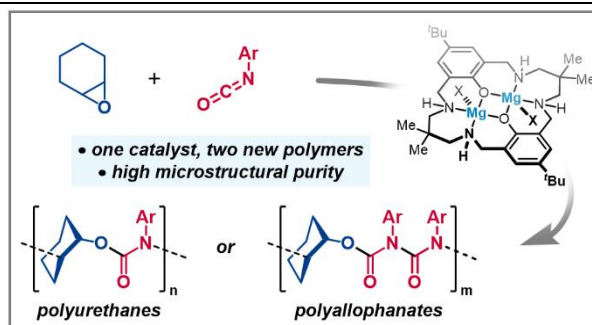


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