



# Perfectly Alternating and Regioselective Copolymerization of Carbonyl Sulfide and Epoxides via Metal-free Lewis Pairs

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**Abstract:** The preparation of perfectly alternating and regioselective copolymers derived from the copolymerization of carbonyl sulfide (COS) and epoxides via metal-free Lewis pair catalysts composed of a Lewis base (amidine, guanidine, or quaternary onium salts) and a Lewis acid (triethyl borane) is described. Colorless and highly transparent copolymers of poly(monothiocarbonate) were successfully obtained with >99% tail-to-head content and high molecular weight (up to 92.5 kg/mol). In most instances, oxygen-sulfur exchange reactions (O/S ERs), which would generate random thiocarbonate and carbonate units, were effectively suppressed. The turnover frequencies (TOF) of these Lewis pairs catalyzed processes were as high as 119 h<sup>-1</sup> at ambient temperature.

## Introduction

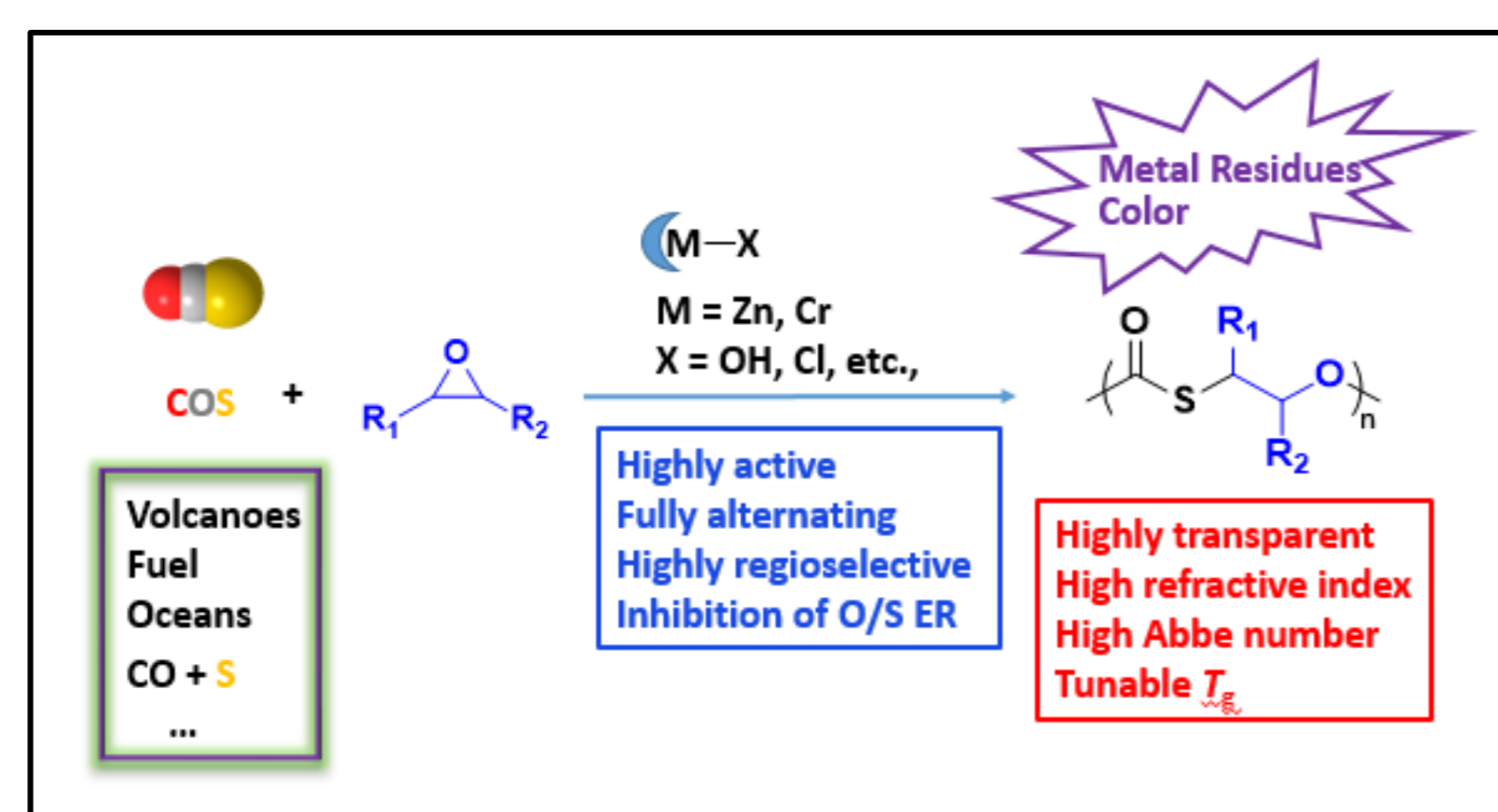


Fig. 1. Synthesis of poly(monothiocarbonate)s from COS/epoxide copolymerization (R<sub>1</sub> and R<sub>2</sub> represent substituted groups).

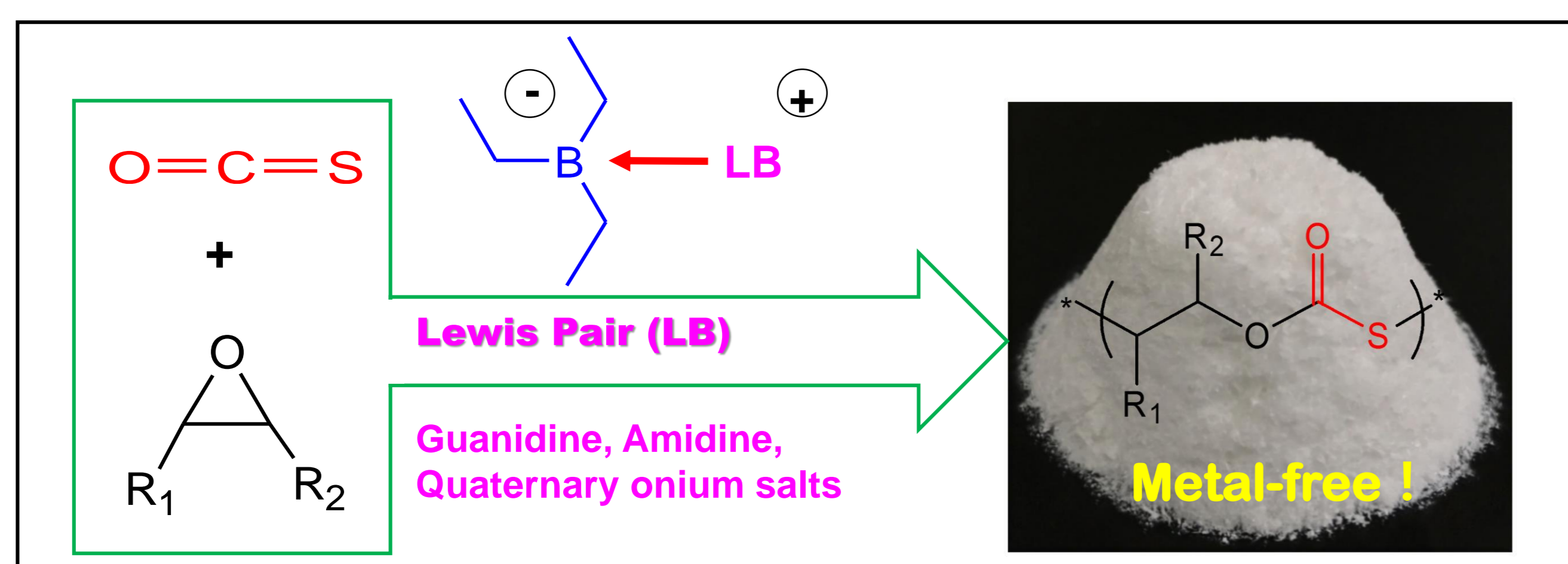


Fig. 2. poly(monothiocarbonate)s from the copolymerization of COS with epoxides mediated by metal-free catalyst.

Carbonyl sulfide (COS) is a sulfur-containing one-carbon (C1) building block which is derived from the burning of fossil fuels, coal gas, and many chemical processes. However, the releasing of COS into the environment causes formation of sulfur aerosols, fog, haze, acid rain, as well as damage of the ozoneosphere due to a series of photochemical processes. Concurrently, the utilization of COS can provide an atom-economic route upon copolymerization with epoxides to afford various functionalized copolymers. Presently, only metal catalysts have been shown to effectively promote the copolymerization of COS/epoxides, the residues of which impede the applications of these copolymers. Here we introduce a metal-free catalyst system, which can mediate the copolymerization of COS and epoxides effectively, affording colorless and highly transparent poly(monothiocarbonate)s.

## Active Lewis pairs for copolymerization

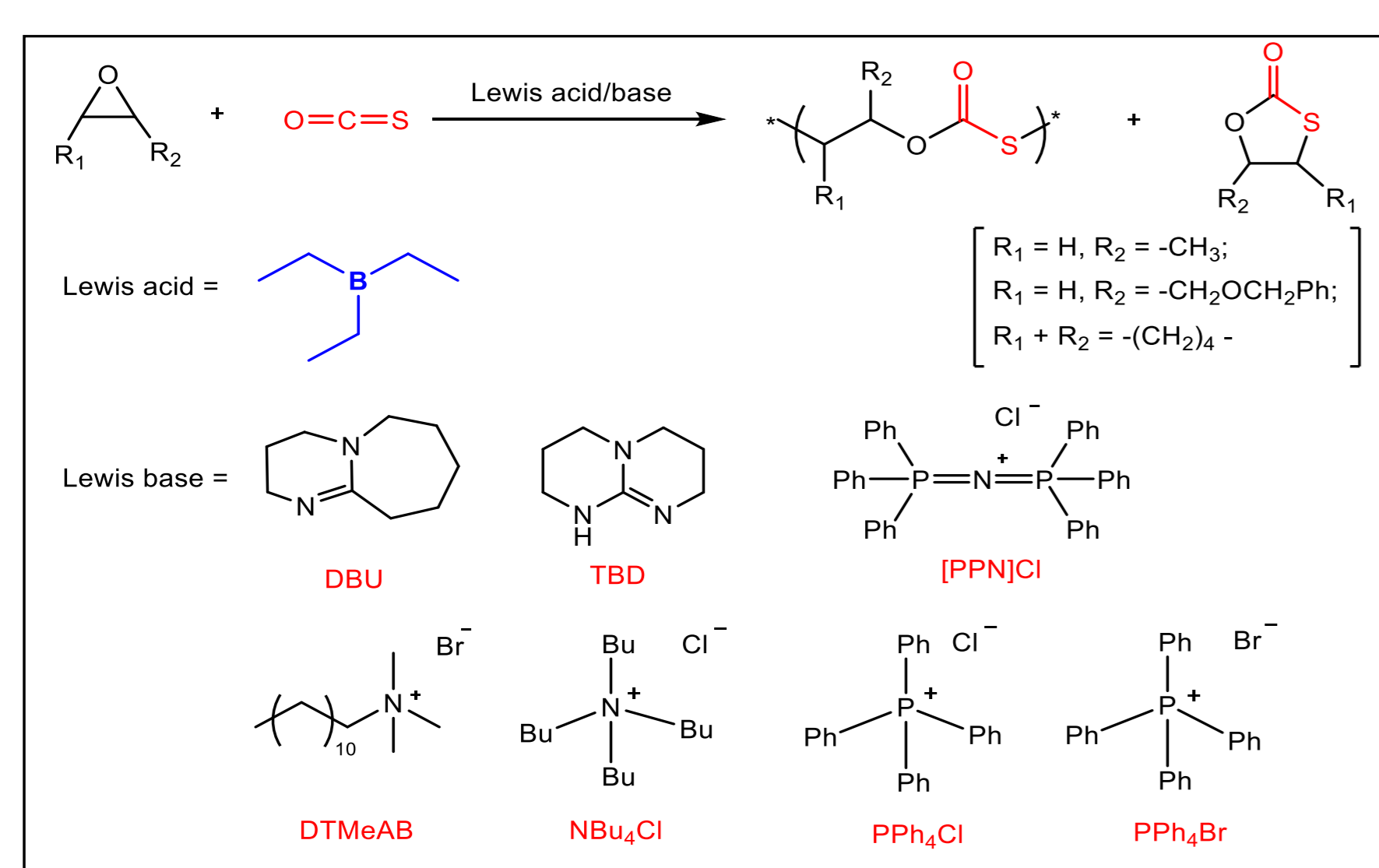


Fig. 3. Active Lewis pairs for the copolymerization of COS with epoxides.

TEB: triethylborane;  
DBU: 1,5-diazabicyclo[5.4.0]undec-5-ene;  
TBD: 1,5,7-Triazabicyclododecene;  
[PPN]Cl: Bis(triphenylphosphine)iminium chloride;  
DTMeAB: Dodecyltrimethylammonium bromide;  
NBu<sub>4</sub>Cl: Tetrabutylammonium chloride;  
PPh<sub>4</sub>Cl: Tetraphenyl phosphonium chloride;  
PPh<sub>4</sub>Br: Tetraphenyl phosphonium bromide;

Considering the similarity of Frustrated Lewis Pairs (FLPs) and binary metal/base catalyst systems, we attempted to find active Lewis Pairs for catalyzing the copolymerization of COS and epoxides. It turned out that the acidity of the Lewis acid, the nucleophilicity of the Lewis base, together with the steric effects of the Lewis pair are the deciding factors for effective metal-free catalysts. Then we developed a fully alternating and perfectly regioselective COS/epoxide copolymerization process catalyzed by the Lewis pair of TEB with various Lewis bases, including amidine, quinidine, quaternary onium salts to provide colorless and highly transparent well-defined poly(monothiocarbonate)s.

## Conclusions

We have described herein the synthesis of perfectly alternating and regioselective copolymers from COS and epoxides employing metal-free Lewis pairs as catalysts. The copolymerization processes were efficiently carried out at 25-80°C to afford poly(monothiocarbonate)s with >99% H-T linkages generally in the absence of oxygen/sulfur exchange processes. TOFs were as high as 119 h<sup>-1</sup> with M<sub>n</sub> values up to 92.5 kg/mol with a PDI of 1.2. Importantly, the use of Lewis pairs for the COS/epoxide copolymerization reactions avoids the shortcomings of the metal catalysts. That is, these copolymers are colorless and highly transparent which favor their applications as optical materials.

## Acknowledgement

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## Highly regioselectivity

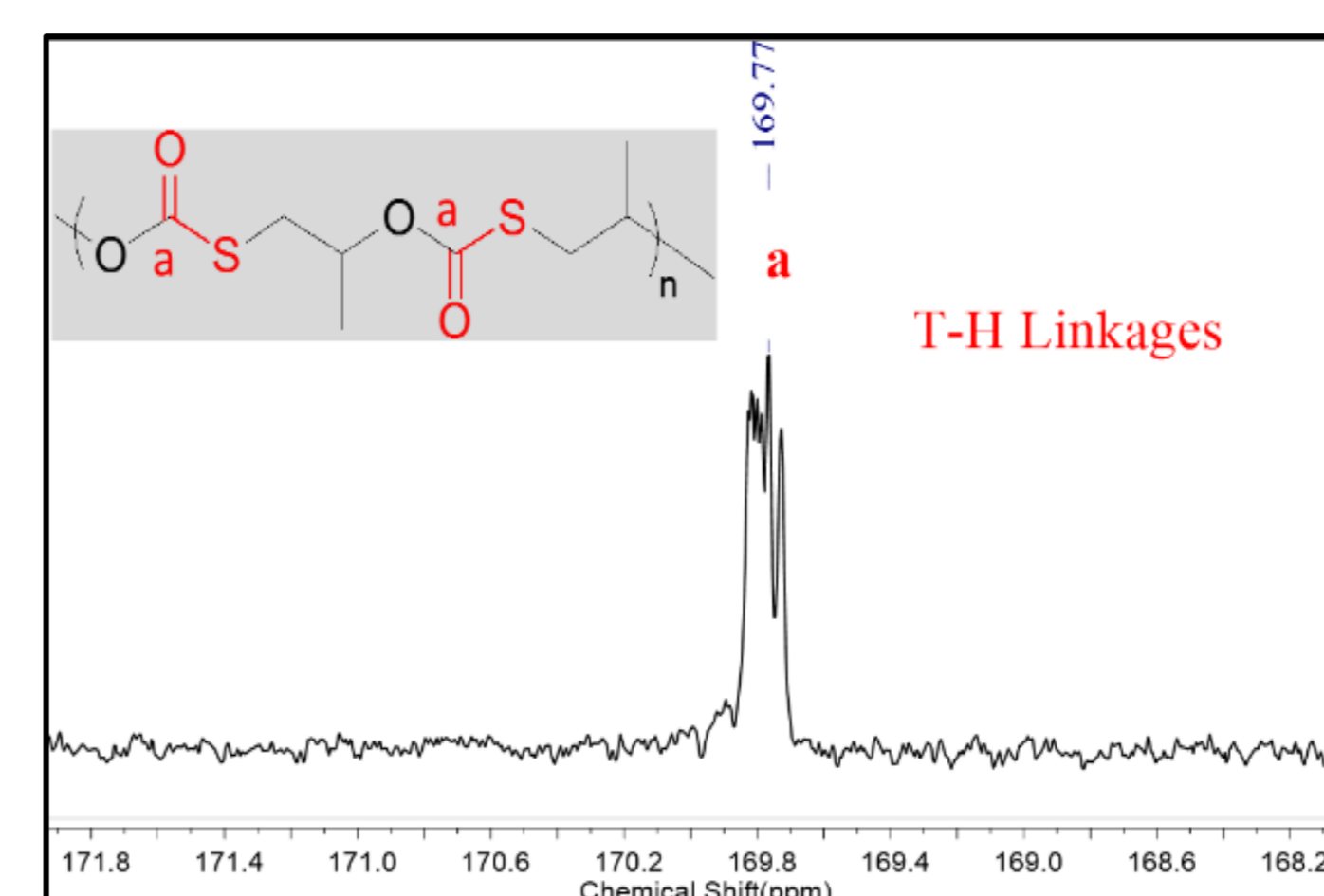


Fig. 4. Typical <sup>13</sup>C NMR spectrum of the COS/PO copolymer.

Regioselectivity is one of the two special problems involved in the copolymerization of COS and terminated epoxides, the possible coexistence of -SC(=O)O- and -OC(=S)O- units and their nucleophilic attack to CH<sub>2</sub> or CH of PO will result in four kinds of linkages. Up to >99% T-H linkages in the resultant copolymers showed -SC(=O)O- were the only active species and its attack to CH<sub>2</sub> were highly selectivity. The performance of Lewis pairs was superior than metal catalysts.

## Investigation of initiation mechanism

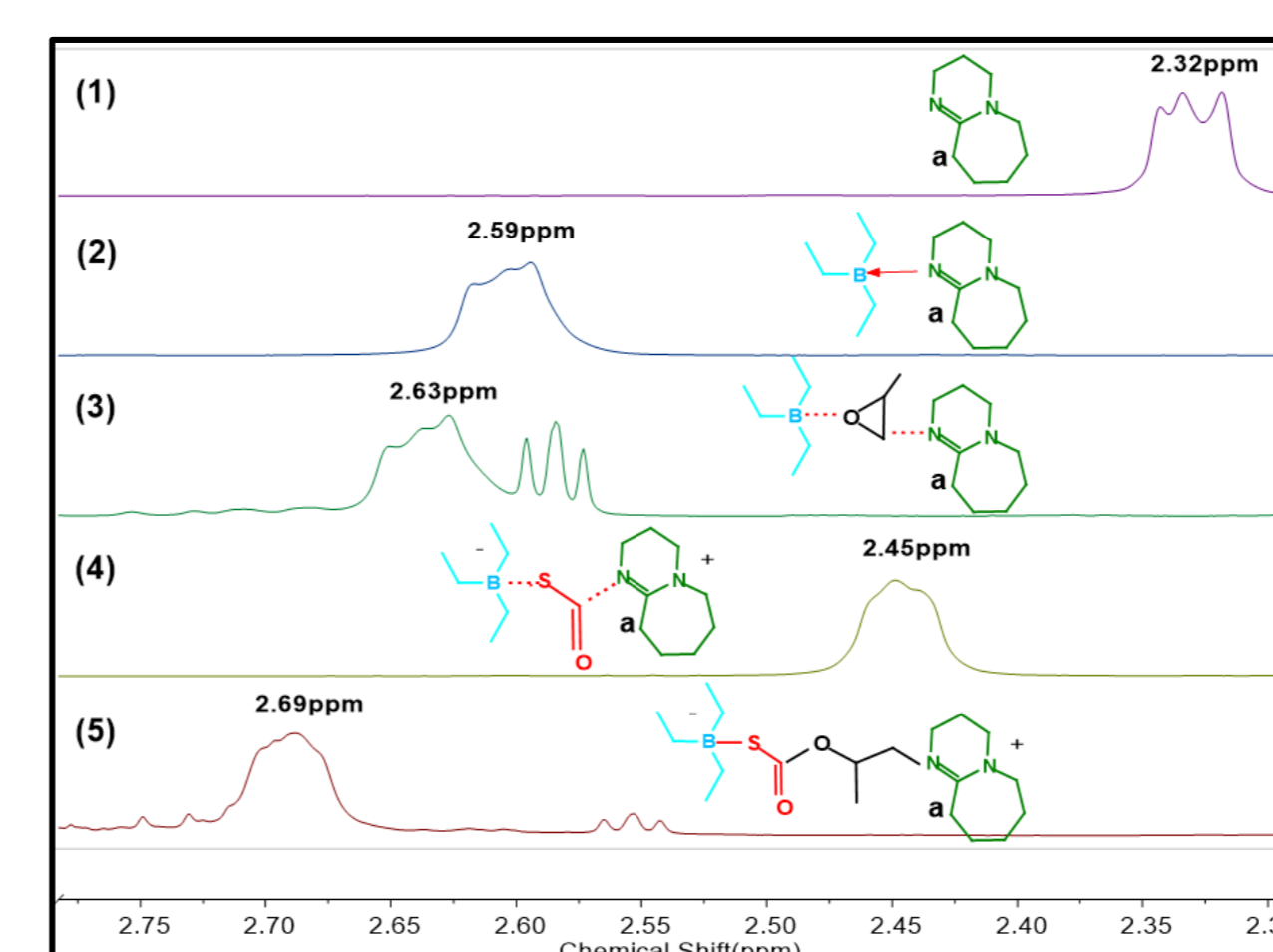


Fig. 5. <sup>1</sup>H NMR spectra of Lewis pairs with monomers.

In an effort to gain more insight into the initiation step for the latter process, a series of Lewis pairs in the presence of monomers were characterized by <sup>1</sup>H NMR spectroscopy. The formation of the TEB/DBU pair was clearly evident by the <sup>1</sup>H NMR spectra, when an equivalent of PO or excess COS was introduced, corresponding intermediates was formed respectively. Upon addition of both PO and excess COS into the TEB/DBU pair simultaneously, PO was likely ring-opened in the DBU-PO-COS-TEB adduct, and acts as the chain initiating species for propagation (Scheme 3).

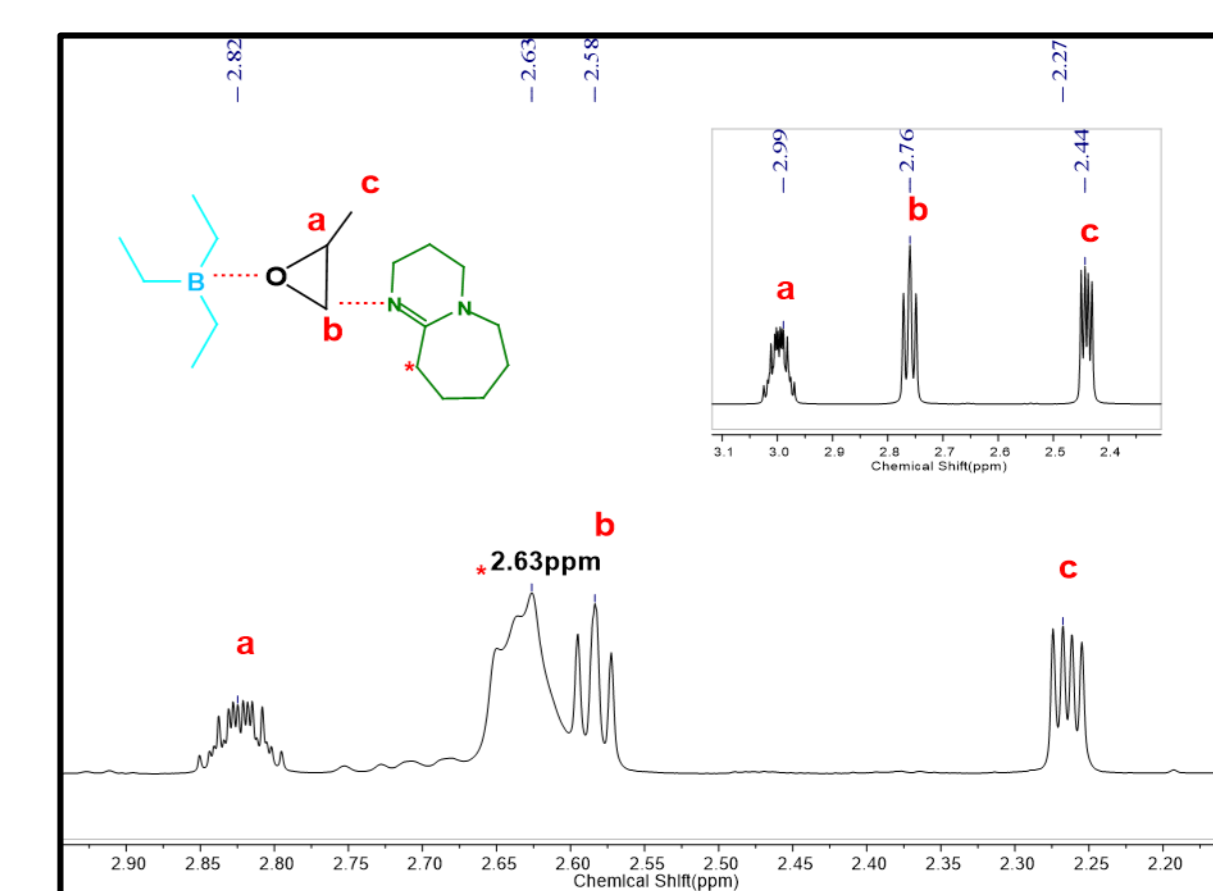


Fig. 6. The formation of intramolecular TEB/DBU pair for activating COS and PO.

## Proposed mechanism

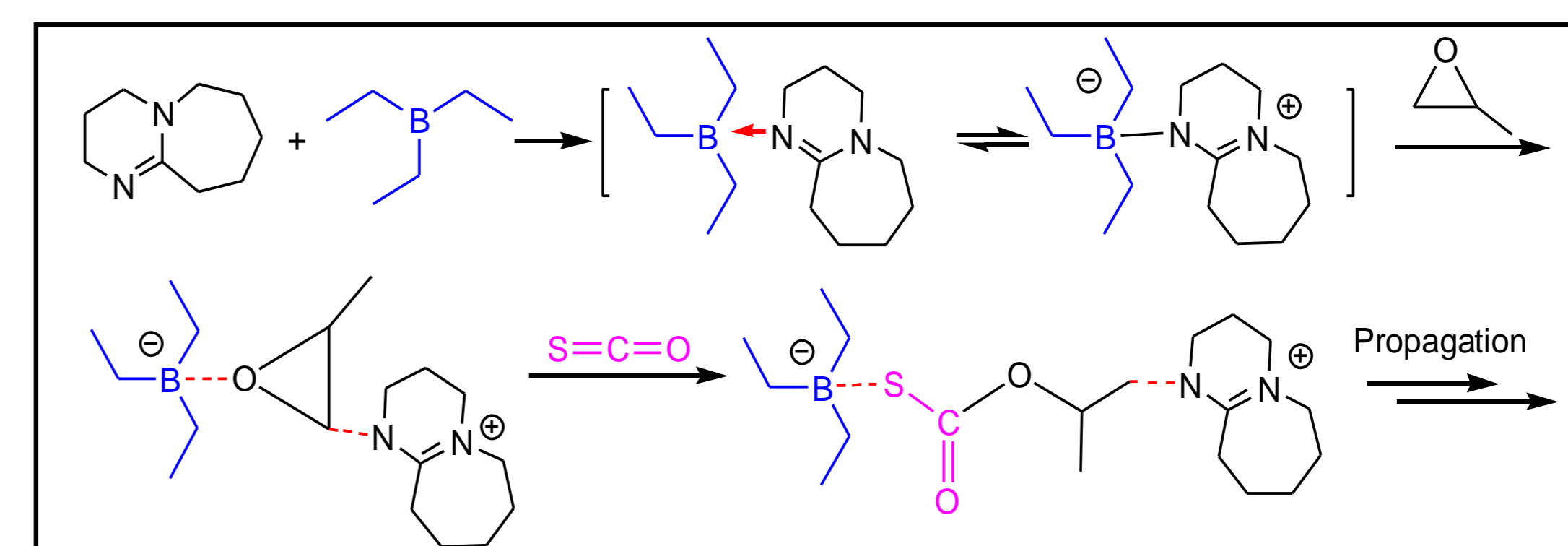


Fig. 7. The formation of intramolecular TEB/DBU pair for activating COS and PO.

The anionic tetrahedral boron moieties containing a coordinated bond to the oxirane are proposed as the initiating species in the copolymerization process. As indicated, such species are stabilized by the bulky cations, i.e., an intramolecular cation when DBU or TBD was used as LB and an intermolecular cation when quaternary onium salts was used.

## References

- [1] Yang J. L.; Wu H. L.; Zhang, X. H.; Darensbourg, D. J. Perfectly Alternating and Regioselective Copolymerization of Carbonyl Sulfide and Epoxides via Metal-free Lewis Pairs. (Accepted)
- [2] Luo, M.; Zhang, X.-H.; Darensbourg, D. J. Accounts of Chemical Research 2016, 49, 2209.