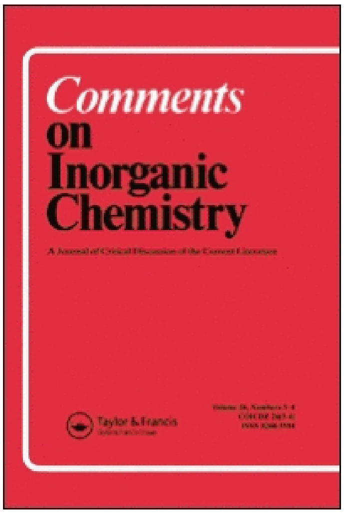

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POLYMERS FROM RENEWABLE RESOURCES: THE ROLE OF METAL ALKOXIDE CATALYSTS

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POLYMERS FROM RENEWABLE RESOURCES: THE ROLE OF METAL ALKOXIDE CATALYSTS

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RELATIONS WITH PROFESSOR F. G. A. STONE, CBE, FRS

My coming of age as a research chemist started in London in the 1960s where at Queen Mary College, QMC, I completed both my undergraduate and postgraduate degrees, the latter with Professor D. C. Bradley, FRS, who had recently returned from the University of Western Ontario. It so happened that both Professors Gordon Stone and Joe Chatt had spent short spells at QMC prior to taking up positions at Bristol and Sussex University, respectively. While this was my first knowledge of Gordon Stone, I did my undergraduate senior project with Dr. Alan G. Massey. Although I did not recognize this at the time, here was another connection with Gordon for one of the thousand or more compounds prepared in Gordon's lab is $B(C_6F_5)_3$, a compound prepared and reported by Massey, Park and Stone,[1] that later would become famous as a Lewis acid co-catalyst in single-site metal olefin polymerization.

Upon completion of my Ph.D. with Don Bradley, I moved to the University of Western Ontario where I worked with Professor H. C. Clark

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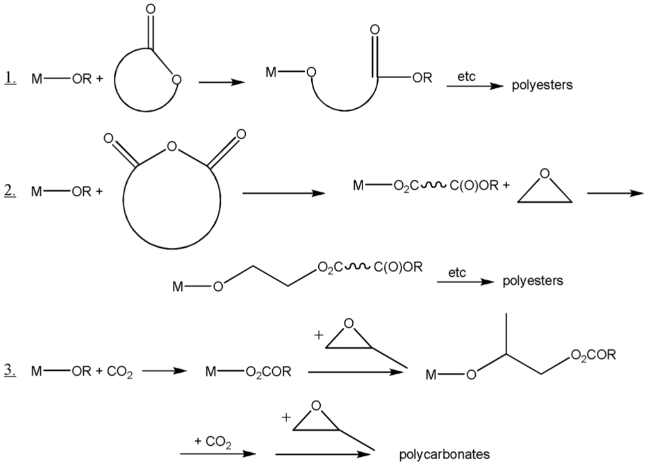
who was Don Bradley's successor. The move from London, England, to London, Ontario, brought about for me a change from working with mostly paramagnetic metal amides and alkoxides to the organometallic chemistry of platinum. At this time I began to realize the full influence of Gordon on the rapidly emerging field of organometallic chemistry. This interest in organometallic chemistry stayed with me when I moved to Princeton University to start my independent career. Looking back on the 1970s and 1980s I cannot help but recognize the strength of British organometallic chemistry. Professors Wilkinson at Imperial College, Lewis at Cambridge and Stone at Bristol each developed a "School of Organometallic Chemistry," which has left a considerable mark upon the contemporary landscape – not just because of the science that emerged from their labs but more because of the number of academic offspring they spawned that took up academic positions around the world. In terms of local influence I believe that Gordon Stone has left the greatest mark with regard to his department of chemistry.

In 1981, it was suggested that I submit my independent publications for consideration for a London University D.Sc. and the following year I was delighted to receive this honor and certificate. Shortly thereafter I was on a sabbatical leave in the UK at Cambridge University with Professor Sir Jack Lewis (now Lord Lewis) and visited Bristol University as a seminar speaker. It was at that time that I learned from Gordon that he had been the examiner for my D.Sc. Both he and his wife, Judy, were very gracious hosts to me and my wife, Cyndy, and it was from that time on I realized just how supportive Gordon was for younger chemists who were trying to establish their mark in academe. It is not unusual for senior Professors to support their own but much less common for them to support those who have no specific connection. Gordon is certainly amongst those who support talent when they recognize it and I am most grateful to Gordon for his support over the years. He is above all a chemist's chemist – one who lives his profession, demands the highest standards, is at times a hard task master and always one who inspires the younger chemists. He has, of course, left a remarkable legacy both in terms of the research from his group and the service he has given to the profession. It was, indeed, a great pleasure to be one of the co-organizers of this symposium in celebration of his career and on behalf of all those in attendance I thank Professor Patrick Farmer and his colleagues for extending such a warm Baylor welcome to their guests at this event.

INDUSTRIAL POLYMERS

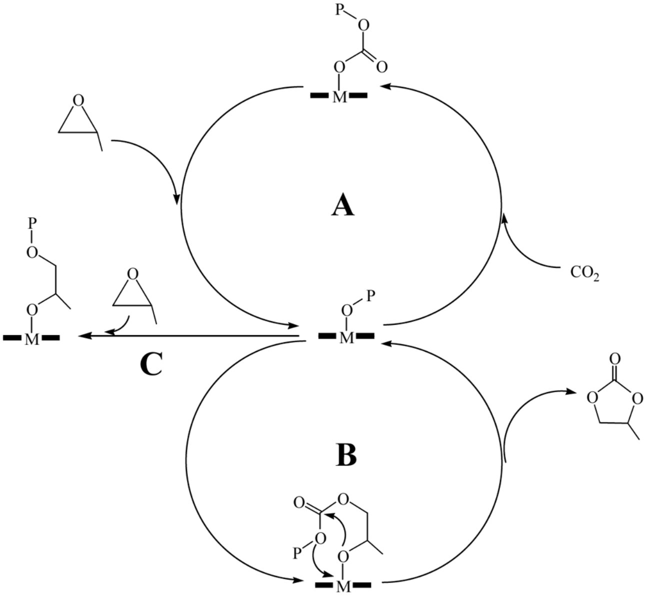
Of the four major industrial polymers, namely polyolefins, polyesters, polycarbonates and polyurethanes, each of which is produced in over 10^6 tonnes per year, only polyolefins are produced in what can be considered as an atom efficient manner. The others are produced by condensation polymerization and all of them are made from petrochemical feed stocks. It would be useful to develop synthetic routes that are atom efficient and employ chemical feedstocks that are from inexpensive abundant renewable resources. Routes to polyesters and polycarbonates indicated by equations (1) to (3) would comply with these green principles.



Each of these reactions employs metal-oxygen/alkoxide bonds just as olefin polymerization or hydroformylation employs metal-carbon/alkyl bonds. The employment of single-site catalysis is desirable both from a mechanistic and practical standpoint. It allows one to examine in detail the individual steps/reactions in the catalytic cycle and provides for the development of living polymerization wherein molecular weight and regio and stereo control may be achieved.

POLYCARBONATES

The industrial preparation of polycarbonates employs the condensation polymerization of a diol with phosgene or a derivative under basic conditions to neutralize the hydrochloric acid liberated. Following the pioneering work of Inoue[2] there has been considerable interest in the copolymerization of epoxides and carbon dioxide. Recent reviews by Darensbourg[3] and Coates[4] are available and provide excellent accounts of the development of this field. Amongst the most active catalyst systems are Schiff base derivatives of chromium (III) and cobalt (III), which in the copolymerization of propylene oxide, PO, and CO_2 to give polypropylenecarbonate, PPC, can achieve turn over frequencies (mols of monomer per mol of catalyst) of 10^2 to $10^3\,h^{-1}$. These polymerizations employ Lewis base cocatalysts such as N-atom bases (imidazoles or 4-dimethylaminopyridine) or soluble halide salts such as PPN^+Cl^-. In this catalysis there are really three competing reactions as shown in Scheme 1; namely polyether formation, polycarbonate formation and formation of the cyclic carbonate, propylenecarbonate. Our studies have primarily focused on the reactions of porphyrin metal(3 +) catalyst systems where the metal is Al, Cr or Co. These allow us to study the influence of the metal and its d^n configuration (d^0 Al, d^3 Cr and d^6 Co) together with the influence of the Lewis base co-catalyst and the substituents on the porphyrin.[5,6]



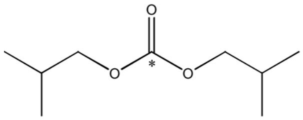
Scheme 1. Reactions competing with polycarbonate formation, path A, are cyclic carbonate formation, path B and polyether synthesis, path C.

Mechanistic Comments

For porphyrinaluminum initiators the rate of ring-opening of the epoxide by the Al-X bond follows the order OR $>O_2CR$ $\sim O_2COR$ but upon the addition of a Lewis base or PPN^+Cl (1 equiv) the order is reversed and the rate of ring-opening significantly enhanced. At 5 Bar CO_2 pressure the position of the equilibrium involving the insertion of CO_2:[Al]-OR $+CO_2 =$ [Al]-O_2COR is greatly influenced by the substituents on the porphyrin with electron donating groups favoring the alkylcarbonate. However, upon addition of a Lewis base this order is reversed with the alkylcarbonate being favored almost 100% for 5,10,15,20-tetrakispentafluorophenylporphyrin. The Lewis base co-catalyst thus promotes both CO_2 insertion and the ring-opening of the epoxide and the fluorinated porphyrin is more reactive than tetraphenylporphyryn in the production of PPC by a factor of 100.

Ring-opening of epoxides is well known to occur by an S_{N2} mechanism involving backside attack or by interactions with strong Lewis or Broensted acids, which initiate a carbonium ion chain reaction. The latter lead to low molecular weight polymers and cycles while the base promoted reactions lead to regioregular polymers via repeated ring-opening at the least sterically hindered/substituted carbon.

The reaction involving the porphyrin metal(3 +) complexes, like the SalenCr(3 +) complexes of Darensbourg[3] are unusual in showing 1st order kinetics in the metal complex during the copolymerization. This rules out a bimolecular mechanism involving epoxide activation at one metal center and attack from another metal bound alkylcarbonate ligand, though this mechanism is commonly invoked in the literature. With the planar porphyrin it seems that the epoxide and the alkylcarbonate must reside within the same hemisphere. It is perhaps as if the epoxide is entering into an interchange associative substitution reaction aided by the trans-effect of the Lewis base co-catalyst. With this epoxide coordination to the M(3 +) center positive charge is induced on the epoxide carbons which in turn enhances nucleophilic attack by the labilized alkylcarbonate ligand. It seems unlikely that the alkylcarbonate is dissociated since there is evidence that such a free anionic ligand would lead to cyclic carbonate formation, which is the thermodynamic product in contrast to the polycarbonate, the kinetic product.[3] Given this sort of incipient carbonium ion mechanism for the enchainment of the epoxide it is not surprising that there are often HH and TT junctions in addition to HT/TH for the carbonates. These are shown below. Furthermore in reactions involving rac-PO and *R* or *S*-PO it can be shown that the HH junctions are formed with varying degrees of retention and loss of stereochemistry depending upon the specific catalyst system.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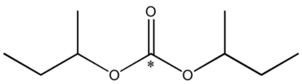
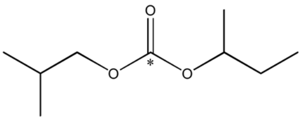
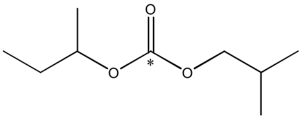

HH

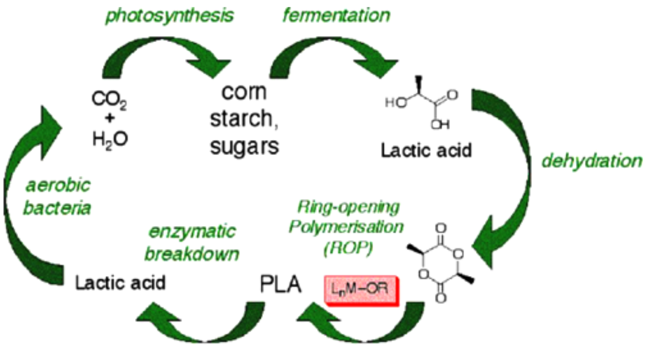

TH


HT

POLYESTERS

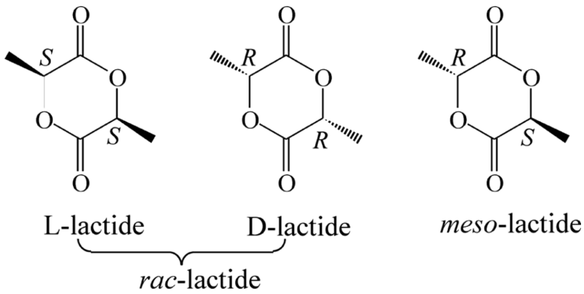
Poly-*L*-lactide is a rapidly emerging polyester that enjoys many uses as a clear packaging material with good thin film and fiber forming properties. It also finds uses in drug delivery, sutures, stints and as a polymer matrix in tissue engineering. It is a biocompatible, biodegradable polymer and is biobased with a life cycle shown in Scheme 2.

Common enzymatic degradation of starches and sugars yield *L*-lactide but new enzymatic processes are now producing *D*-lactide.



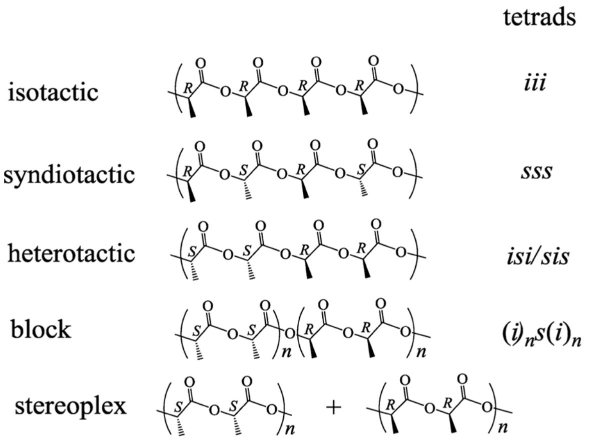
Scheme 2. Life cycle of poly-*L*-lactide. (Figure appears in color online.)

Epimerization of either of these will also yield *meso*-lactide and these three isomers are shown below. A mixture of 50:50 *L*- and *D*-lactide is called *rac*-lactide and within the past decade there has been considerable interest in the development of stereoselective polymerizations of *rac*-lactide[7] to give a stereoplex polymer (poly-*L* +poly-*D*-lactide), which has a higher $T_m \sim 220°C$ relative to poly L-lactide, $T_m \sim 180°C$.



The desired mechanism for the formation of PLAs is ring-opening polymerization and this can be brought about by enzymatic, organic and coordination catalysis.[8] The latter has attracted considerable academic attention with regard to the development of single-site metal catalysts with attendant ligands that may enforce or aid in stereoselective polymerizations. Catalysts are now known that will convert *rac*-LA to heterotactic-PLA wherein *L*- and *D*-lactide monomers are enchained alternately. In a polymerization of *meso*-LA it is also possible to form a syndiolactic polymer involving alternating *R* and *S* stereo centers. These stereosequences are shown in Scheme 3.

Commercially poly-*L*-LA is prepared using a Sn(II) carboxylate catalyst. This system is tolerant of water and does not induce epimization. Thus *L*-LA is converted to poly-*L*-LA or P*L*LA. The Sn(II) system is not highly active but a solvent free melt polymerization can be carried out. More active catalysts contain more polar metal-alkoxide bonds, $M^{\delta+}$–$OR^{\delta-}$ and so for divalent metals we find the reactivity order $Mg^{2+} > Zn^{2+} > Sn^{2+}$. Calcium alkoxides are even more reactive than magnesium but both metals are extremely labile to the Schlenk equilibrium: $2LMOR = LM + M(OR)_2$ and the $M(OR)_2$ compounds are clusters or aggregates $[M(OR)_2]_n$. The binding of ligands to the large Ca^{2+}, $r \sim 1.0$ Å, does not have any formal covalency or preferred directionality such as is found for transition metals, e.g., octahedral Co(3 +) or square planar Pt(2 +). There is therefore a considerable challenge to prepare



Scheme 3. Tetrads of polylactide showing the stereosequences iii, isi/sis, sss and stereoplex/blocking polymers.

single-site calcium alkoxide catalyst systems that are kinetically persistent and tolerant to impurities such as water. We have been working with functionalized tris-pyrazolylborate ligands that contain hemilabile ether appendages and a promising catalyst precursor is the 7-coordinate $HB(pz\text{-}3\text{-}CMe_2CH_2OMe)_3Ca(OC_6H_4\text{-}4\text{-}Me)$ shown in Figure 1.[10] This appears a promising catalyst system for ROP of cyclic esters and is tolerant of trace quantities of water.

Another promising route to polyesters that is atom efficient involves the ring-opening co-polymerization of epoxides and cyclic organic anhydrides. Recently, succinic acid has been heralded as a biobased molecule[11] and succinic anhydride, SA, can thus be similarly considered. As noted earlier in the ring-opening of epoxides by porphyrin M(3 +) complexes the M-X bond order is $M\text{-}O_2CR > M\text{-}OR$. It is thus possible to carry out a regioregular copolymerization of PO and SA to form polypropylenesuccinate PPSA.[12]

Ring-opening of styreneoxide, SO, is much more difficult by a coordinate catalyst mechanism and porphyrin Cr(3 +) catalysts systems give regioirregular polystyreneoxide. Attempted preparations of polystyrenecarbonate by the copolymerization of SO and CO_2 yielded styrenecarbonate and when *R*-SO was employed the styrenecarbonate was 30% *S*- and 70% *R*- implicating ring-opening by attack at both the methylene and methine carbons and furthermore that the latter was not stereoselective.

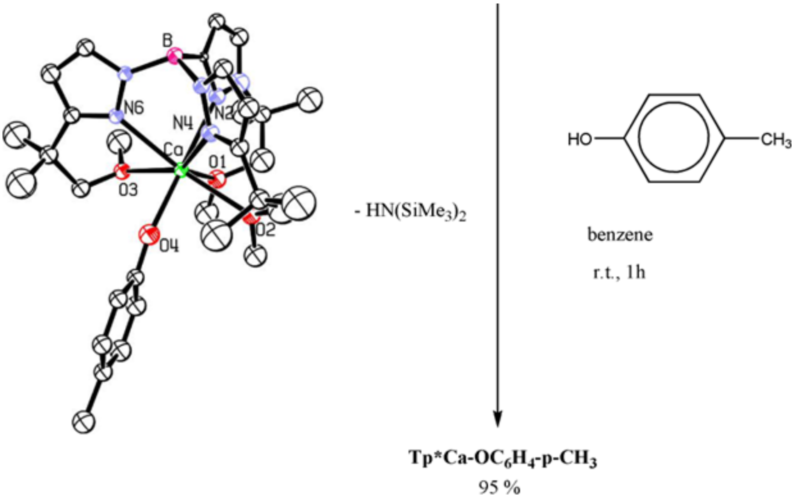
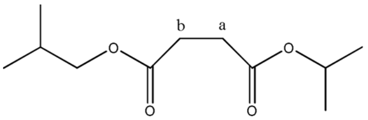


Figure 1. Preparation and structure of Tp*CaOC$_6$H$_4$-4-Me. (Figure appears in color online.)

However, again because of the order of ring-opening of epoxides M-O$_2$CR >M-O$_2$COR >M-OR it is possible to copolymerize SO and SA to give polystyrenesuccinate.[12] When this reaction is carried out at 80°C the TOF is $\sim 100\,h^{-1}$ and the polymer is regiorandom, again implicating regiorandom ring-opening of the SO molecule. This is clearly evident from the $^{13}C\{^1H\}$ signals of the succinate methylene carbons that appear as four signals of equal intensity due to the statistical distributions of HT, HH and TT junctions as shown below.



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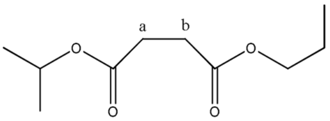

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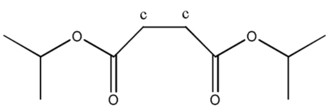
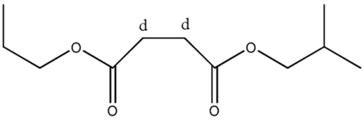


HH



TT

When reactions are carried out at lower temperatures some selectivity is observed but a perfectly regio regular (HT)n polymer has not been obtained in these reactions. Reactions employing substituted succinicanhydrides have been found to show stereoselectivity in the ring-opening of the anhydride, implying that the metal-alkoxide bond selectively attacks the least hindered or more activated anhydride carbonyl carbon.[12]

CONCLUDING REMARKS

It seems likely that polymers derived from renewable resources will find an increasing market share in the world of plastic materials. They will need to have physical properties comparable to (or better than) those currently derived from petrochemicals. Biodegradability and biocompatibility are two attractive features. The atom efficiency of ring-opening polymerizations or copolymerizations of the type exemplified by Eq. (1) to (3) is another, and this points to the direction for fertile future research.

ACKNOWLEDGEMENTS

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