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An Introduction to Entropically-driven Ring-opening Polymerizations

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Summary: This mini-review outlines the principles of entropically-driven ring-opening polymerizations (ED-ROPs), a relatively new approach to the synthesis of condensation polymers. The various features of ED-ROPs are noted and examples of applications to polymer synthesis, polymer processing and polymer recycling are discussed.

Keywords: cyclodepolymerization; flow systems; polymer processing; polymer recycling; polymer synthesis

Introduction

The polymerization of vinyl compounds has been developed enormously in the last 20 years and this has resulted in several useful types of 'living' polymerizations, the syntheses of many types of vinyl polymers with narrow dispersities, and syntheses of polymers with novel architectures. Similarly, the 'living' ring-opening polymerizations of, for example, *strained* cyclic ethers, esters and olefins have been developed greatly. In contrast relatively little attention has been paid to the synthesis of condensation polymers, despite the fact that many commercial polymers, such as polyesters, polyamides and high performance polymers, are of this type and that many condensation polymers are potentially biodegradable. This mini-review is concerned with a relatively new approach to the synthesis of condensation polymers, namely entropically-driven ring-opening polymerization: ED-ROP. The subject has been reviewed before,[1–3] but it is an active field and there have been many recent developments. Due to space limitations this review cannot be comprehensive and it contents reflect the content of the lecture.

In this mini-review the principles of ED-ROPs are presented, then their applications in three areas are discussed. These are (i) selected examples of polymer synthesis, (ii) some applications in polymer processing, and (iii) the potential use in polymer re-cycling.

Principles of ED-ROPs

ED-ROPs are based on classical ring:chain equilibria (RCE) and the feedstocks are macrocyclic monomers or oligomers (MCOs): see Scheme 1. RCE are the equilibria that, in the presence of a suitable catalyst to facilitate making and breaking the linkages between the repeat units, exist between a condensation polymer and the corresponding family of homologous cyclic oligomers.[4,5] A key point about RCE is that the position of the equilibria depends crucially on the concentration. At low concentrations, typically $< 3\%$ w/v, the equilibria lie heavily on the side of the MCOs, whilst at high concentrations, ideally neat conditions, they lie heavily in favour of the polymers. Typically under *neat conditions* the equilibrated mixture contains ca. 98% polymer and ca. 2%

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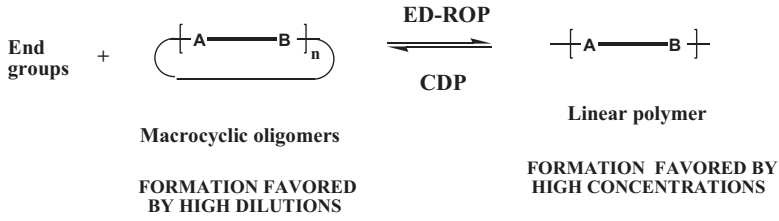

Scheme 1.
Ring-chain equilibria. ED-ROP = entropically-driven ring-opening polymerization. CDP = cyclo-depolymerization.

MCOs. Accordingly, ED-ROPs involve taking an MCO, or family of MCOs, at *high concentration* and establishing the equilibrium. This results in the MCOs being transformed into polymer in high yield. Generally ca. 2% of MCOs remains but, since these are usually much more soluble than the polymer, they can simply be removed from the final reaction mixture by precipitating the product into an appropriate non-solvent for the polymer.

It should be stressed that the principals outlined here are general and that ED-ROPs can be achieved using many types of reaction such as transesterification, transamidation, nucleophilic aromatic substitution and olefin metathesis. The examples given here include all these types.

Because the macrocycles used are *strainless*, or virtually so, ΔH for polymerization is close to zero and the polymerizations are driven by entropy. Thus, under the neat reaction conditions both the MCOs and the polymer have limited translational entropies, and the conformations available to the MCOs are limited. The latter increase significantly on ring opening.

The polymerization mechanism will have some similarities to the ROP of, for example, lactones.[6] Thus, the active ends of linear chains, which may include the catalyst, will react with MCOs to give chain growth. At the same time the active ends of the linear chains can also react with linkages in other chains, so shuffling the chain lengths. In 'living' ROPs the former process is usually much more important than the latter: in ED-ROP both processes are equally important.

Some Features of ED-ROPs

ED-ROPs have the following interesting features.

(i) ED-ROPs permit the polymerization of large strainless rings, not just small strained rings. This greatly increases the scope of ROPs.
(ii) As the reactions just involve a shuffling of the linkages between repeat units, no small molecules, and hence no volatiles, are emitted during the polymerization.
(iii) As most, if not all, the macrocycles in an homologous family of MCOs are strainless, little or no heat is evolved.
(iv) The MCOs have no end groups: but obviously end groups are required to produce linear polymers: see Scheme 1. Thus, the final molecular weight of the polymer depends, at least in part, on the number of end groups present in the system. It should be noted here that the catalyst used to bring about the equilibration may well be a source of end groups. Clearly minimizing the number of end groups brings the possibility of obtaining polymers with unusually high molecular weights.
(v) In cases where the macrocycles contain two types of repeat unit, each macrocycle automatically contains a perfect stoichiometric balance of the two types of repeat unit. Accordingly stoichiometric balance is not an issue. This, therefore, allows very small scale polymer syntheses, say 50 mg, to be carried out very successfully.

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(vi) As it is highly desirable to have a neat reaction mixture, it is often convenient to carry out polymerizations without solvent and without stirring.

(vii) If full equilibration is to be achieved there must be mobility in the system. This is even needs to be the case when the mixture consists of >95% polymer. Hence with a neat reaction mixture, even if only relatively briefly, the polymerization temperature should exceed the T_g of the product and possibly also the T_m.

(viii) Since ED-ROP is an equilibration process, the polydispersity index (PDI) of the product is expected to be 2.0, i.e. the same as that expected for all classical step growth polymerizations.

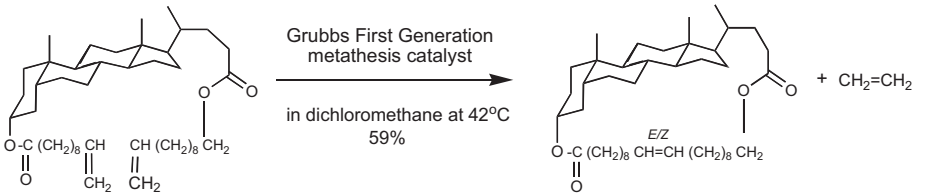
(ix) Since ED-ROP is an equilibration process, if two monomers are used the final co-polymer should have the thermodynamically most probable structure. Thus, if the equilibrating linkages in the two monomers are in a similar structural environment the final product is expected to be a random copolymer.

Synthesis of Macrocyclic Oligomers

There are four main synthetic approaches that can be used to obtain MCOs. It should be noted that when the product of a synthesis is an homologous family of cyclic oligomers, it is not necessary to isolate specific macrocycles from the mixture as all the homologs have the same repeat units and so will react to give the same polymer.

The most obvious way to prepare MCOs is by *classical high-dilution syntheses*, i.e to carry out condensation reactions between the end groups of linear species at sufficiently low concentrations that intramolecular reactions are greatly favoured over intermolecular reactions. The reactants are added as slowly as is necessary to keep the concentrations of the reacting groups low. An example is the synthesis of MCOs **1** by ring-closing metathesis of α, ω-bisolefins (Reaction 1).[7]

Reaction 1.[7]



(**1**)

Classical high-dilution methods are obviously only suitable for the synthesis of relatively small quantities of MCOs especially as isolating them may require chromatography. If, however, rapid non-reversible reactions are used to form the linkages between repeat units and the reactants are added sufficiently slowly that the actual reacting species are kept at very low concentrations, the concentrations of the MCO products can rise to high levels. This is the very important *pseudo-high-dilution method*. An example is the synthesis of cyclic-oligoamide **2**: Reaction 2.[8] Interesting and valuable techniques have been developed by Daniel Brunelle's research group at General Electric. These allow the synthesis of cyclic oligomers **3** (see Reaction 3)[9] and various macrocyclic esters, such as cyclic oligo(butylene terephthalate)s **4** (see Reaction 4),[10] to be prepared easily in multi-kilogram, and possibly even larger, quantities. Reaction 5 allows MCOs **5** to be prepared easily.[11]

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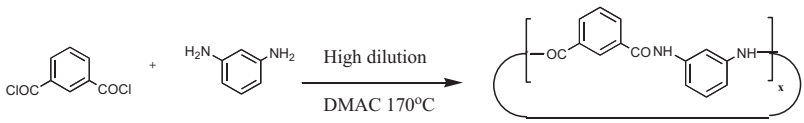
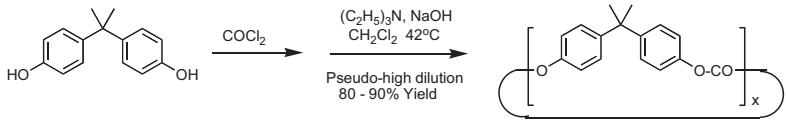
Reaction 2.[8]



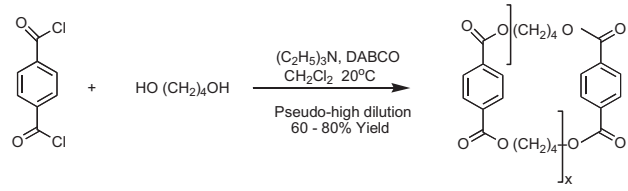
(**2**)

Reaction 3.[9]



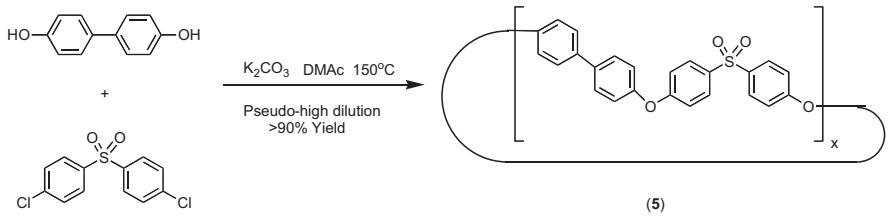
(**3**)

Reaction 4.[10]



(**4**)

Reaction 5.[11]



(**5**)

A third method of MCO synthesis is *polymer-supported cyclo-oligomerization*: see Scheme 2. This is suitable when the repeat units are of the A-B type and only small quantities of MCOs are required, as, for example, in the preparation of polymer libraries.[12] With this method the starting material is attached to the polymer support via just one type of end group. A supported cyclization reaction then creates the MCOs and, since they have no end groups, they are released into solution: all linear species remain attached via one end group and so are easily separated from the MCOs. This approach has been used to prepare many macrocyclic esters that include both hydrocarbon- and olig(ethylene oxide)-based rings.[13,14] Since the support is generally chloromethylated crosslinked polystyrene beads, peptides can first be synthesized on the support by standard methods, then capped with a hydroxy acid prior to cyclization.[14,15] Some products from this method of synthesis are shown in Scheme 2. Others are shown in formulae **6** and **7**. Macro-

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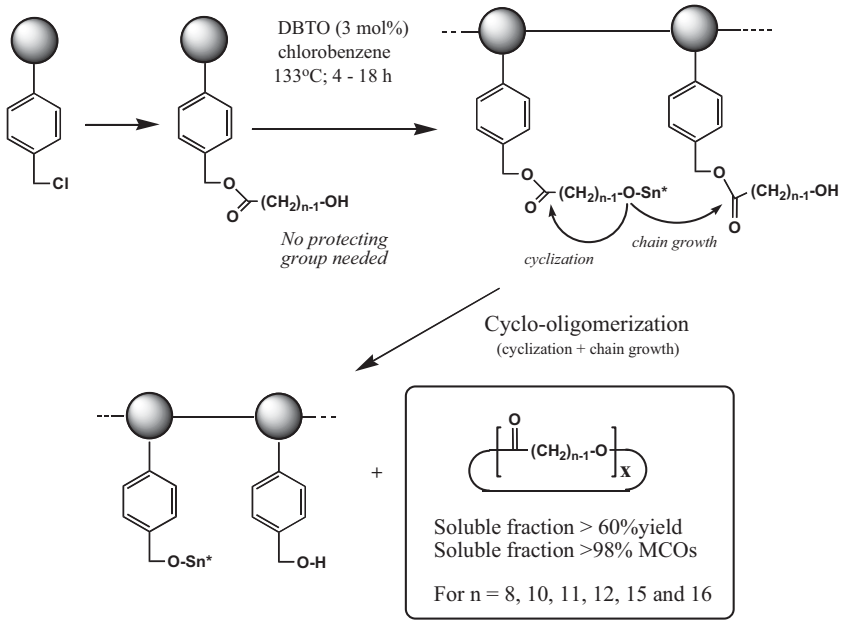
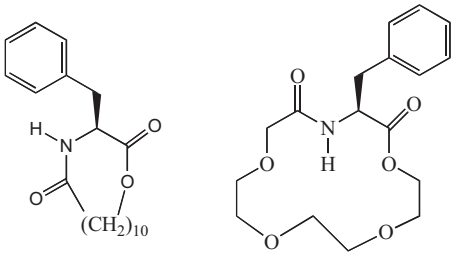
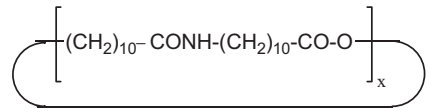


Scheme 2.
Synthesis of MCOs by polymer-supported cyclo-oligomerization.[13]

cycles **8** have also been prepared using amide bond formation.[13,16] tion shifts to give an homologous family of MCOs in high yield. Few linear species are



(**6**) (**7**)



(**8**)

The fourth method of MCO synthesis is cyclo-depolymerization (CDP). This method is essentially just the reverse of ED-ROP: see Scheme 1. It involves taking a *dilute* solution, typically <3% w/v, of the appropriate polymer and establishing the RCE. Due to the low concentration, the equilibrium position shifts to give an homologous family of MCOs in high yield. Few linear species are formed as the only end groups present in the system derive from the starting polymer and, possibly, the catalyst. CDP often allows the synthesis of, say, 25g of MCOs in one step from a readily available polymer. Examples of MCOs prepared by CDP are shown in Reactions 6 – 8.[11,17,18]

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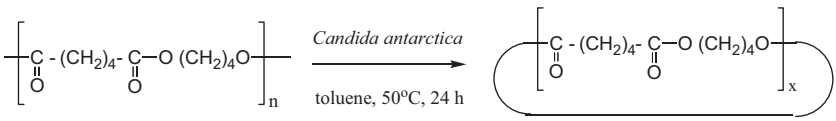
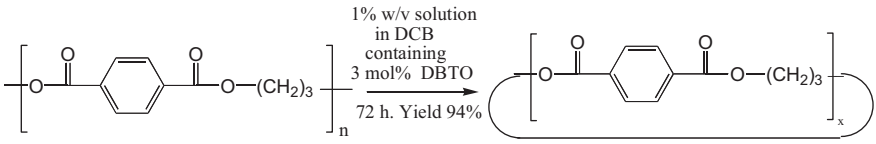
Reaction 6.[17]



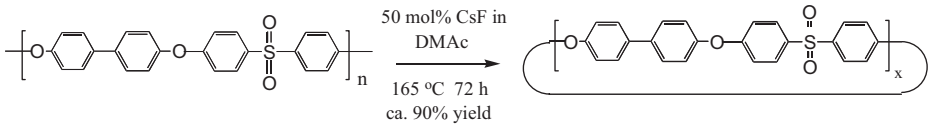
(**9**)

Reaction 7.[18]



(**10**)

Reaction 8.[11]



(**11**)

Selected Examples of Polymer Synthesis Using ED-ROPs

Many ED-ROPs have been reported in recent years.[1–3] The examples given here are chosen on the basis that they involve a range of different linking groups between the repeat units, so illustrating the generality of this method of synthesis, and/or because they illustrate a particular feature of ED-ROPs, such as giving products with unusually high molecular weights. Though the formation of unusually high molecular weight polymers is common, it does not always occur.

Reactions 9 – 12 are examples of ED-ROPs that proceed via transesterifications. It will be noted that all these examples afford products with unusually high molecular weights and PDIs that are close to 2.

Reaction 9 affords poly(bisphenol carbonate) (**12**) whilst Reaction 10 affords poly(butylene terephthalate) (**13**). Both of these polymers are important commercial polymers. Monomer **14** can be polymerized to give polymer **15** similarly, as can many other polyesters. By reacting mixtures of different MCOs together copolyesters are formed. Indeed, libraries of random copolyesters can be prepared easily this way on a ca. 100 mg scale.[20] Reaction 12 is of interest because it is catalyzed by an enzyme and so the final product **17** will necessarily be free of any metal residues.[17]

In Reaction 13 equilibration is achieved by transamidations.[8] Again the molecular weight is unusually high. Reaction 14 proceeds via nucleophilic aromatic substitutions,[11] and is one of many examples of such reactions being used to synthesize high performance aromatic ether-ketones or ether-sulfones.[1,2]

Reactions 15 and 16 proceed by olefin metathesis.[7,21] Both reactions afford products with very high molecular weights. A novel feature of Reaction 15 is that the reaction was carried using a film of the monomer cast on a microscope slide. The final product was a self-standing film.[21] Subsequent work has shown that a dilute dichloromethane solution of monomer **20** plus catalyst was stable for a week.[22] When

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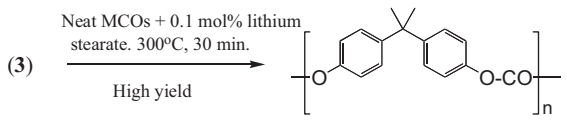
the solution was applied dropwise to a microscope slide, as the solvent evaporated and the monomer concentration increased, the position of the RCE shifted and polymer **21** was formed. After 30 min a self-standing the polymer film was formed with Mn 73,000 g/mol. Thus, the polymerization mixture can be stored if the solution is dilute and the polymerization is then ''initiated'' by allowing the solvent to evaporate so that the concentration rises.

expected to be biodegradable. The polymer has interesting mechanical properties that are very similar to those of skin.[7,23]

Applications of ED-ROPs in Polymer Processing

The facts that ED-ROPs take place without the emission of any volatiles, or indeed any small molecules, and that liquid MCOs are

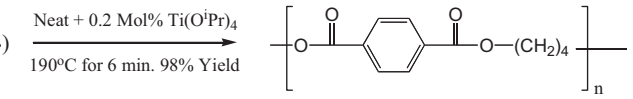
Reaction 9.[9]



Mn 125,000 g/mol; PDI 2.4

(**12**)

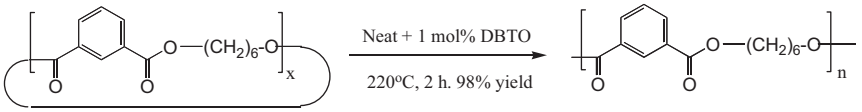
Reaction 10.[10]



Mn 54,800 g/mol; PDI 2.1

(**13**)

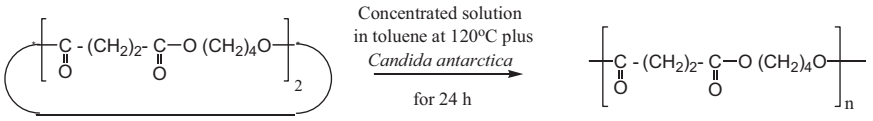
Reaction 11.[19]



Mn 40,000 g/mol; PDI 2.0

(**14**) (**15**)

Reaction 12.[17]



Mn 81,200 g/mol; PDI 1.6

(**16**) (**17**)

Reaction 16 also illustrates how the ability to polymerize macrocycles allows large moieties to be incorporated into the polymer.[7] In this case the final polymer is generally lower melting and substantially less viscous than the corresponding polymers under similar conditions makes ED-ROPs potentially useful in processing. The

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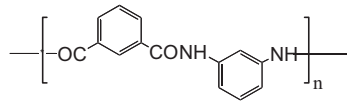
Reaction 13.[8]

(**2**) → 4 Mol% sodium hydride reacted with a 25%w/v solution in DMSO; containing 8% w/v lithium chloride at 170°C

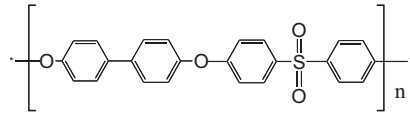


Mn 23,000 g/mol; PDI 2.0

(**18**)

Reaction 14.[11]

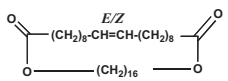
(**11**) → 2 Mol% cesium benzophenone-4-thiolate; 320°C 5 min



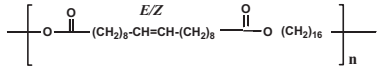
Mn 26,000 g/mol; PDI 5.8

(**19**)

Reaction 15.[21]



(**20**) → Neat monomer plus 1 Mol% of Grubbs Second Generation catalyst. Heat at 40°C 10 min

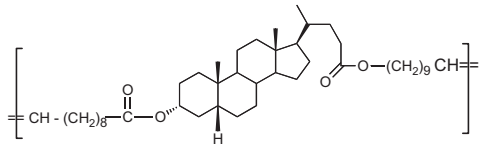


Mn 94,000 g/mol; PDI 1.9

(**21**)

Reaction 16.[7]

(**1**) → Concentrated solution in dichloromethane plus Grubbs' Second Generation catalyst; 20°C 3 h.



H-H, T-T and H-T arrangements expected. Mn 146,000 g/mol; PDI 1.9

(**22**)

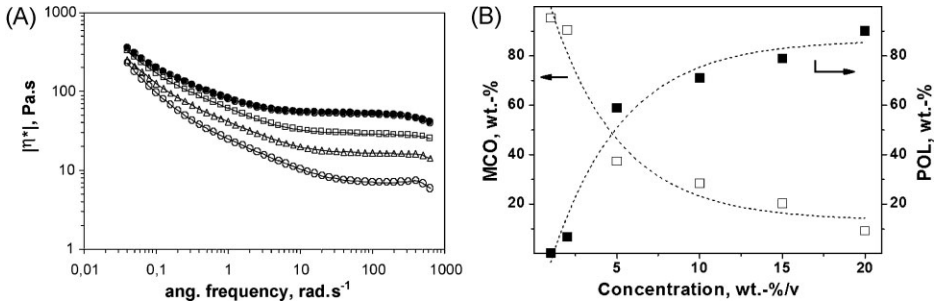


Figure 1.

(A) Melt viscosities of polymer **26** and mixtures with MCOs **25** at 280°C. *Solid circle* = pure polymer **26**; *Squares* = **26** + 5 wt% of MCOs **25**; *Triangles* = PET + 10 wt% of MCOs **25**; *Open circles* = **26** + 20 wt% MCOs **25**. (B) Proportions of polymer **26** and MCOs **25** in equilibrated mixtures. Equilibrations started with pure polymer.

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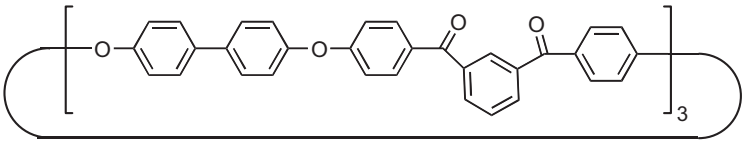
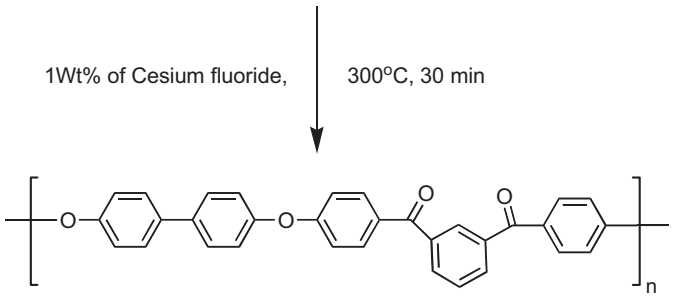
former point means that no voids are created during polymerization: the latter points mean that the MCOs can flow easily into confined spaces and to do this more easily than the molten polymer can.

One example is the preparation of a composite by the ED-ROP of the cyclic trimer **23** in the presence of a woven stainless steel 150μm mesh cloth.[24] The composite was formed much more satisfactorily than that obtained by heating polymer **24** in the presence of the cloth.

Potentially the use of 100% MCOs in polymer synthesis requires large amounts of the MCOs, and for many applications this unattractive. A potential alternative is to process a mixture of MCOs and the corresponding polymer. The presence of the MCOs would be expected to lower the melt viscosity of the polymer. In agreement with this it was found that the presence of 10% w/w of MCOs **11** in Radel™ **19** lowered the melt viscosity at 320 °C and 1.0 radians.sec^{-1} by approximately a factor of 5.[26] To demonstrate that the MCOs **11**



(**23**)



(**24**)

A second example is the preparation of 200-400 nm diameter fibrils or tubes of high performance polymer.[25] This was achieved by placing a disc of MCOs **11** plus initiator on top of a 1.0 μ alumina Anodisc™ filter: see Scheme 3. On heating the MCOs flowed down into the pores of the filter and high performance polymer **19** was formed. On treatment with aqueous sodium hydroxide the alumina disc dissolved to leave the fibrils or tubes. By coating the interior of the Anodisc™ with cesium fluoride, polymerization only occurred within the pores of the disc. By using a monomer prepared by linking together two macrocycles, crosslinked high performance polymeric fibrils or tubes could be prepared.[25]

in the mixture would satisfactorily undergo conversion into polymer, the mixture was treated with 3.5 mol% of the cesium salt of 4-hydroxybenzophenone for 35 min at 330 °C. The MCOs satisfactorily underwent ED-ROP in situ to give a final polymer **19** with Mn 34,000 g/mol and Mw 79,500 g/mol. In these experiments the required 90:10 mixture was obtained by solution blending. However, the proportions of polymer and MCOs produced in the synthesis of the polymer is determined by the concentration of the monomers in the reaction mixture: the more dilute the reaction mixture the more MCOs are present. By diluting the reactant concentration used for the synthesis of the polymer approximately two-fold the required 90:10 mixture was obtained directly.[26]

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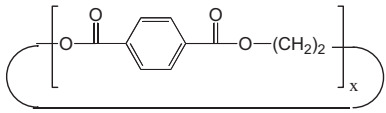
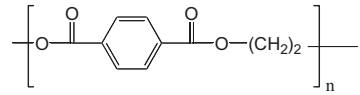


(25)

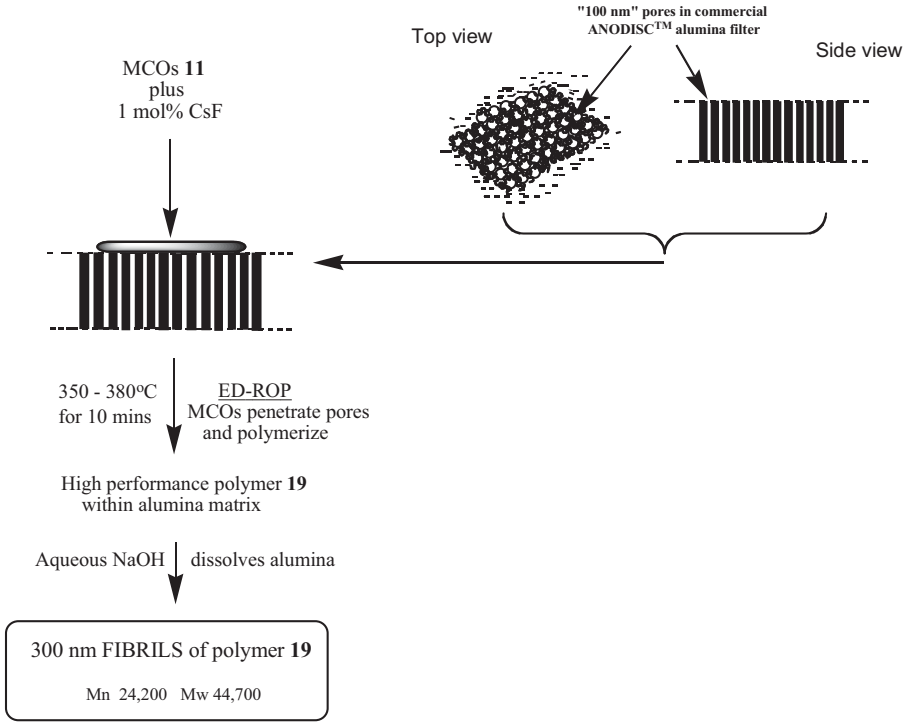


(26)

A second system studied was that of MCOs **25** and the corresponding polymer **26**.[27] Figure 1A shows a plot of the melt viscosities at various proportions of **25** and **26**. It is evident that at 280 °C and 10 radians.sec^{-1} the melt viscosity of polymer **26** fell by a factor of 6 in the presence of 20% of MCOs **25**. For the subsequent in situ ED-ROP it was not necessary in this case to add any catalyst: heating to 300 °C proved to be sufficient. The final polymer **26** had Mn 40,700. As before the required mixture of polymer and MCOs can be obtained directly. Figure 1B shows the proportions of **25** and **26** as a function of concentration. It is evident that establishing the RCE at about 12%w/v gives the 80:20 mixture of **26** and **25** directly.[27]

Potential Use of ED-ROPs in Polymer re-Cycling

The obvious approach to the chemical re-cycling of condensation polymers is to convert them back to their monomers, or closely related compounds, by hydrolysis, methanolysis, aminolysis, or whatever.[28] Re-forming the polymer from these compounds then requires the careful and highly efficient removal of the condensate. A potential alternative approach would be



Scheme 3.
Procedure for formation of polymeric fibrils or tubes.[25]

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to convert the recovered polymer to MCOs by CDP. The attraction here is that the MCOs can be converted back into polymer much more easily.

A major problem with CDP is the need for dilute solutions. However, this need not necessarily be such a serious problem. For instance, as we have seen (Figure 1B) modest dilutions can produce a mixture containing, say, 15% of MCOs. If the MCOs can be removed efficiently whilst the RCE is re-established, eventually all the polymer will be converted into MCOs. Indeed, this approach was used by Spanagel and Carothers more than 70 years ago.[29] Thus, they treated, for example, poly-(hexamethylene sebacate) with stannous chloride at 270 °C under vacuum and continuously distilled out the cyclic monomer (18 ring atoms). The yield in 4 h was 73%.[29] An alternative possibility would be to use a membrane that is permeable to the MCOs but not the polymer. Both of these approaches would allow the CDP to be carried out in a continuous process.

Finally, another interesting possibility is to achieve CDP by passing a solution of the polymer down a column of polymer-supported enzyme. Thus, Matsumura's research group have successfully achieved the CDP of poly(butylene adipate) (**9**) in high yield by passing a solution in toluene down a column of polymer-supported *Candida antarctica* at 40 °C.[30] The author's research group has similarly achieved the efficient conversion of polyundecanoate to cyclic oligoundecanoates and a polymer closely related to **22** to the corresponding cyclic monomer.[31]

Conclusion

This mini-review has outlined the principles of ED-ROPs, a relatively new method for the synthesis of condensation polymers. One of the most attractive features of this method is that it allows very large strainless macrocycles to be polymerized successfully. This means that the repeat units can contain, in-chain, substantial functionalities, such as steroids. Accordingly this significantly expands the scope of ROP. ED-ROPs often afford products of unusually high molecular weights, they do not emit volatiles and they can be carried out easily on a small scale. These features make it attractive for the synthesis of a range of polymers, for certain types of processing and potentially for recycling.

Abbreviations

DABCO	1,4-diazabicyclo[2,2,2]octane
DBTO	di-n-butyltin oxide
DCB	1,2-dichlorobenzene
DCM	dichloromethane
DMAc	N,N-dimethylacetamide
DMSO	dimethyl sulfoxide.

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