

## A STUDY ON THE APPLICATIONS OF MACRO CYCLIC POLYMERS

**Sandeep**

*Asst Proff R.K.S.D. college Kaithal*

### **ABSTARCT**

*A broad variety of inorganic supports has been customized and is appropriate for diverse catalytic and chromatographic applications. Nevertheless they are restricted in their utilize as supported reagents for the reason that their drawbacks such as little loading capabilities, inemulsifiable in appropriate solvents, and also are dominate to natural and compound breakdown of the matrix. The effortlessness of chemical adjustment of a resin and the accomplishment in its relevance as a reagent or a catalyst depends on the corporal proprietorship of the resin itself. The majority of the effort concerning functional polymers has been earned out on cross linked polystyrene resins as polystyrene meets numerous of the necessities of a solid support. The current paper highlights the applications of macro cyclic polymers.*

### **Keywords:**

*Click chemistry, cyclic polymers, polymerization, ionic ring*

### **INTRODUCTION**

In malevolence of the broad extend exploit of polystyrene matrix as sustain, poly(methyl methacrylate) (PMMA) resins have freshly been equipped and chemically modified as

supports PMMA blob were primed by suspension polymerization technique. This support has the benefit of having a glacial disposition as well as functionality for straight correlation or production of a assortment of functional groups. Chloromethylation and bromination are the mainly usually conventional methods of chemical amendment of polystyrene. Lithiation is also used for chemical amendment Chloromethylation was conceded out via chloromethylmethyl ether (CMME) and a Lewis acid such as stannic chloride or zinc chloride.

Chloromethylated polystyrene referred to as Merrifield's resin has been used comprehensively both as a sustain in peptide synthesis and as a predecessor to frequent other functional polymers, in which a substrate is attach to the resin by nucleophilic dislodgment of chlorine. Lindeman et al urbanized a fresh technique for the production of CMME, via methoxy acetic acid. This technique is extremely secure as it fabricate CMME free from bis (chlorometho methyl)ether, a effective carcinogen that is created along with CMME by the customary technique. A supplementary topical technique was urbanized for preparing chloromethylaryl resin via methanesulphonychloride and Hunig's base. This is a straightforward and competent scheme for transforming hydroxymethylaryl-based resins to their equivalent chloromethylaryl plagiaristic via methane sulphonyl chloride and Hunig's base. Ring bromated polystyrene is furthermore a awfully flexible transitional in the research of various other polystyrene resins. The universal technique for the bromination of polystyrene was urbanized by Heitzana Michels and involves the reaction of polystyrene with bromine in the existence of ferric chloride medium.

Doubtless the most significant benefit of via a functionalized polymer as a reagent or a medium is the oversimplification of artifact work-up, division and segregation. With cross linked polymers, straightforward filtration can be used for seclusion, mechanization is possible here. Ultra filtration or selective precipitation removes soluble polymers. This enables one to exploit oversized overindulgence of polymeric reagent in sort to amplify the rejoinder speed and yields, deficient causing severance troubles. Cross linked polymers can be simply cleaned of soluble reactants and products. This permits the polymeric reagent to be used in either article or consignment process or it may be regenerated a number of times. Computerization is probable and the achievability of moving out reactions in flow reactors on a profitable level. They can be cast-off numerous epoch and thus expenditure is condensed the cross linked polymers are impenetrable and non-volatile. Thus, odorless and harmless polymers can be prepared by immobilizing noxious and malodoured chemicals on to impenetrable polymeric supports assembly the reactions environmentally more adequate. The compact polarity increases the shelf-life of the reagent, so that the supported analogues can be stored under normal conditions for a long epoch.

In accumulation to these factors, a figure of potentially significant reactivity alterations may be induced by the exploit of a functionalized polymer. This is known as the "polymer effect" which may improve the action of the reagent or medium by site segregation or on the contrail by accommodating effects of adjoining groups. The polymer acts as an immobilizing intermediate for the close species. The polymer matrix can be so preferred or custom-made to offer a detailed microenvironment that may

encourage some specificity at the rejoinder site. The reactivity of an unhinged reagent or medium may be attenuated when supported on a resin.

Side by side with these compensation, there are numerous downsides intrinsic with these polymer-backed reagents. The connection to or disconnection from the polymeric sustain desires expanded response instance and consequently somewhat pitiable yields. In the exploit of functionalized polymers, there exists the opportunity of side reactions within the polymer itself. An additional negative aspect is the inadequate convenience of the dynamic sites. The preponderance of the reactive sites are within a very glutinous cross linked polymer intermediate puffed-up with a solvent system. Conversely these shortcomings have been triumph over to a superior amount due to the regenerability and reusability of these supported varieties.

The appliance of functionalized polymers as a striking latest procedure for organic synthesis has acknowledged substantial concentration since the primary statement on solid-phase peptide synthesis by Merri field. The compensation of purposeful polymers in widespread unrefined chemistry for mutually introductory purposes and technical appliance have been described. Oxidation of alcohols to carbonyl compounds is a rejoinder of superlative significance in imitation organic chemistry and now significant concentration has been paying attention on the progress of expedient and economical oxidation techniques exclusive of reinstate to a stoichiometric quantity of metal reagents such as chromic acid and permanganate ion Cross linked polystyrene blob have habitually been used for the research of reagents and medium, although cross linked poly(vinyl pyrrolidone) or cross linked copolymers of styrene and vinyl pyridine have

established not as much of interest. This is payable to the complete accessibility and easiness of fictionalization of polystyrene. They also hold well controlled physical distinctiveness and are very straightforward for managing. Numerous polymeric reagents have found appliance in oxidizing alcohols to carbonyl compounds, epoxidation of olefins, oxidation of catechols and phenols, oxidation of thiols to disulphide's etc. The affection of the reagent occupation to the polymer back may be by way of ionic or covalent bonds.

## APPLICATIONS OF MACRO CYCLIC POLYMERS

### **Electrostatic-assembly-oriented tandem cyclization (backbiting and covalent fixation)**

In this method, electrostatic assembly occurs oriented by interaction between a quaternary ammonium cation and a carboxylic anion to form a cyclic ionic complex which further undergoes either substituted or covalent formation reactions to generate the cyclic polymers as shown in Figure 1. Cyclic polymers produced from this method also have been functionalized with  $-C\equiv CH$  and  $-N_3$  groups, and thus enable constructing topologically different cyclic polymer composites, such as bridged and spiro multicyclic topologies, via click cycloaddition reactions.

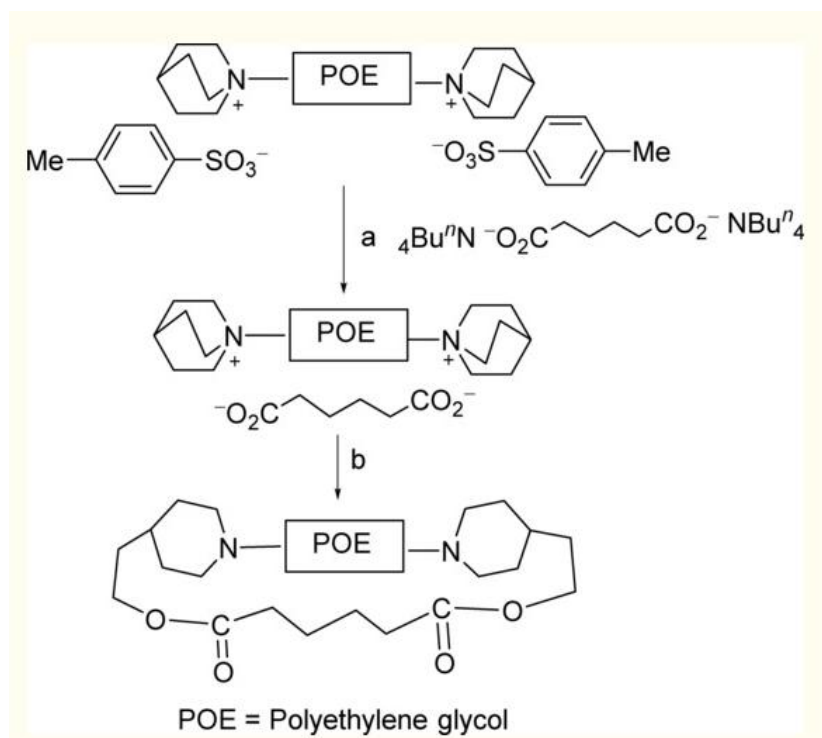


Figure 1: Cyclization via backbiting and covalent fixation. *Reagents and conditions:* a) acetone, 0°C, 0.5 h, 99%; b) toluene, reflux, 30 h, 100 %. Reproduced with permission

### Self-condensation

Intermolecular condensation of *N*-benzylated phenyl *p*-aminobenzoates in the presence of lithium bis(trimethylsilyl)amide (LiHMDS) could form a three-membered triangular cyclic amide. After deprotection of *N*-(*o*-alkoxybenzyl) protecting groups, cyclic tri(*p*-benzamide) was obtained. The macro cycle exhibited a highly ordered two-dimensional orientation on calcite surfaces.

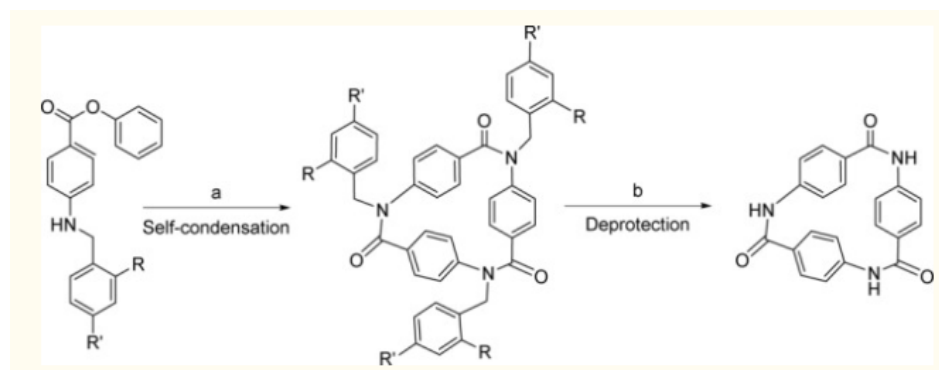


Figure 2: Condensation reaction to synthesize cyclic polymers. *Reagents and conditions:*  
a) lithium bis(trimethyl silyl)amide, tetrahydrofuran (THF), rt, 18 h, 33—52 %; b)  
trifluoroacetic acid, triisopropylsilane, 65 °C, 18 h, 43 %.

#### *Diels–Alder (D–A) addition ([4+2])*

Intramolecular [4+2] reaction of a linear  $\alpha$ -maleimide- $\omega$ -cyclopentadienyl-functionalized polymer results in a well-defined highly pure cyclic polymer upon heating at high dilution. The more convenient UV-induced [4+2] cycloaddition between end groups of photoenol and dithioester has also been reported, as shown in Figure 3. The method combined a reversible addition–fragmentation chain transfer (RAFT) polymerization and UV-induced Diels–Alder addition.

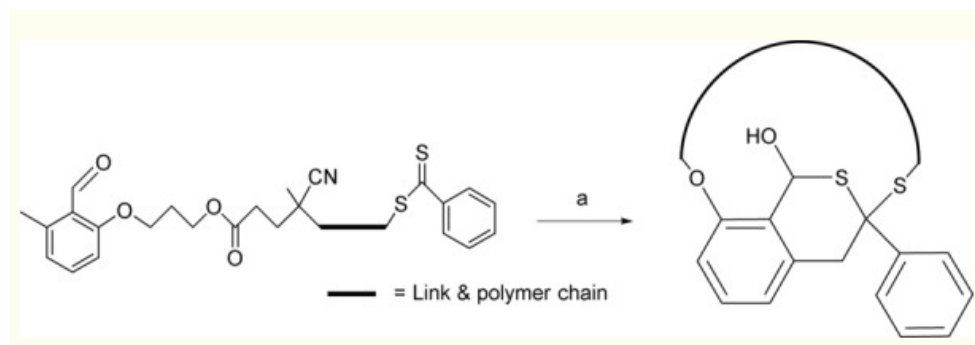


Figure 3: Light-induced D–A reactions to synthesize cyclic polymers.

### **Formation of the CO–NH bond**

The classical intramolecular amidation of a linear polymer with  $\text{-NH}_2$  and  $\text{-CO}_2\text{H}$  end groups leads to the formation of a cyclic peptide. Microwave irradiation has been used to promote formation of the CO–NH bonds. For example, microwave irradiation allows the efficient conversion of the amide of maleic acid to cyclic poly(aspartic acid), with a reaction efficiency of above 93 %.

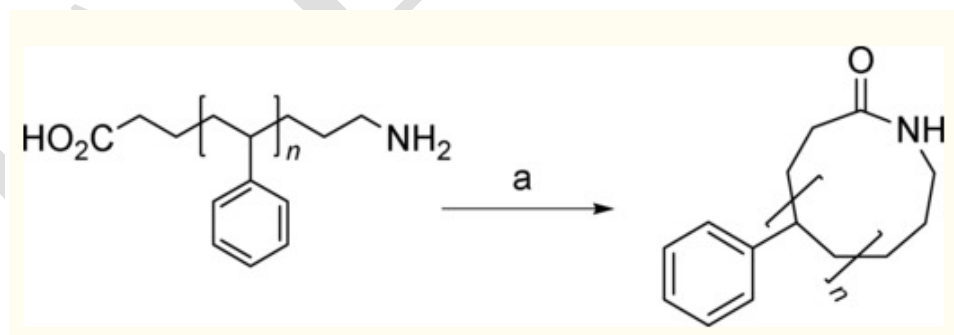
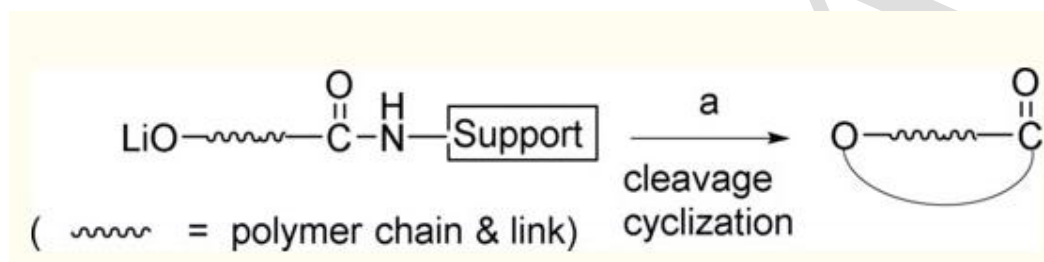


Figure 4: Formation of CO–NH bond for cyclization. *Reagents and conditions*



### *Cyclization-cleavage cyclization*

A polymer support enriched with functional groups such as  $-NH_2$  and  $-OH$  is commonly used in this method. After an intramolecular cyclization, the cyclic polymer can be released into the solution phase. However, due to other competing reactions, the obtained products require further purification.



**Figure 5:** Cyclization cleavage for cyclic polymer synthesis

### **DISCUSSION**

High-value applications of cyclic polymers urgently need investigation to begin more interesting research. Therefore, great efforts have been made to prepare unique and useful cyclic materials to broaden their applications. However, functionalization of cyclic polymers remains a big challenge compared with linear polymers due to the compatibility issues of some functional groups with cyclization methodology. In addition, for metal-complex-catalyzed cyclic polymerization, the remaining toxic metal species have to be removed from product mixtures, similar to linear polymers. This issue is critical for cyclic polymer applications before scale-up. Finally, it is highly desirable to discover new

applications for cyclic polymers, such as their use as additives for coating material and as macromonomers producing ultrahigh-molecular-weight linear polymers by ring-opening polymerization.

Two existing styles, namely ring-closing and ring-expanding polymerizations, are commonly used to prepare cyclic polymers. Between them, ring-expansion technology is recognized as more attractive and practical because it generally produces highly pure cyclic polymers from a relatively high concentration of monomers. Therefore, this protocol might be more suitable for industry processes. On the other hand, ring-closing polymerization usually needs to be carried out in an extremely dilute solution of monomers, which limits their scale-up capabilities. Recent reviews have summarized the two methods well. This review shortly summarizes the synthetic methodology by amending it with fresh reports and mainly focusing on special properties and potential applications.

The catalytic azide ( $N_3$ )-alkyne ( $-C\equiv CH$ ) 1,3-dipolar cycloaddition, commonly called the “click” reaction, usually occurs in mild reaction conditions with high yields and good functional group tolerance. It was first introduced to cyclic polymer chemistry by Laurent and Grayson in 2006. Significant achievements have been made following the introduction, and plenty of cyclic polymers have since been reported. The click reaction has also been applied to construct multiring complex topologies from azide-alkyne multifunctional cyclic polymers. Complex polymer structures such as bridged and spiro-tricyclic, tetracyclic, pentacyclic and heptacyclic topologies with 1,2,3-triazole links, as shown in Figure 6 a, have been synthesized. Alkynes and azides can also be conveniently

attached to linear nucleic acids to undergo click reactions to form cyclic mini-DNA duplexes and DNA catenane as described in Figure 6 b.

Nucleic acid ligations by click reaction have been well summarized in recent reviews and therefore, a similar detailed description in this report is repetitive and unwarranted. However, the inherent drawbacks, such as requirement of a highly dilute reaction medium and presence of  $\text{Cu}^I$  catalyst species during the reaction course, may limit its commercial applications such as in drug delivery or gene delivery.

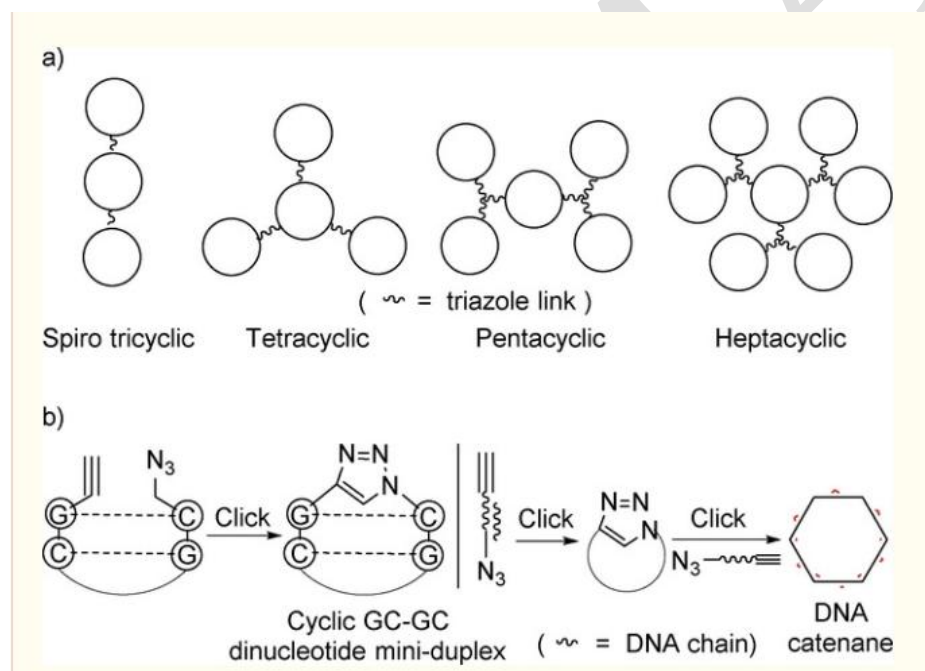


Figure 6: Multicyclic polymers prepared by click cyclo addition. 6 a reproduced with permission. 6 b reproduced with permission

## CONCLUSION

Significant achievements have been made in the synthetic technology of cyclic polymers.

Highly pure cyclic polymers could be produced from convenient ring-expansion

polymerization reactions, such as metathesis, click chemistry, and zwitterionic ring-opening polymerization (ROP). Cyclic polymers with various topologies such as mono- and multicyclic polymers have been reported and well characterized with advanced analytical technology. Introducing click chemistry in DNA synthesis has made it more convenient in preparing various cyclic DNA and related structures. Due to the inherent cellular toxicity of Cu<sup>I</sup>-based catalysts, in vivo applications of cyclic DNAs, produced from Cu-catalyzed click reactions, have not been fruitful. Therefore, removal of the Cu residue is highly desired.

Cyclic polymers always show unique properties in comparison with their linear counterparts due to well-known topology effects. More derived unique and useful properties are expected to be discovered in near future. In this regard, biomedical applications such as polymer–drug conjugates for drug delivery, applications in gel chemistry, and additives to tune linear polymer properties are likely to be discovered. In addition, cyclic polymers may also be used to prepare novel organic–inorganic hybrids, and the resulting materials could find further broad applications similar to linear polymer–inorganic hybrids, like catalyst supports.

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