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A REVIEW ON PREPARATION METHOD FOR DIFFERENT MALEIMIDE UNITS, THEIR HOMO AND CO-POLYMERS AND THEIR APPLICATIONS

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Abstract:

The classical vinyl polymers cannot be used at higher temperature as they degrade at elevated temperature. The incorporation of a rigid structural unit into a polymer backbone brings about enhancement of the glass transition temperature T_g. It has been found that N-substituted maleimide could polymerize with many vinyl monomers, therefore maleimides became interesting monomers to copolymerize with other monomers in order to obtain heat resistant resins. Therefore, synthesis of maleimide monomer units with different methods were studied in this article.

Introduction

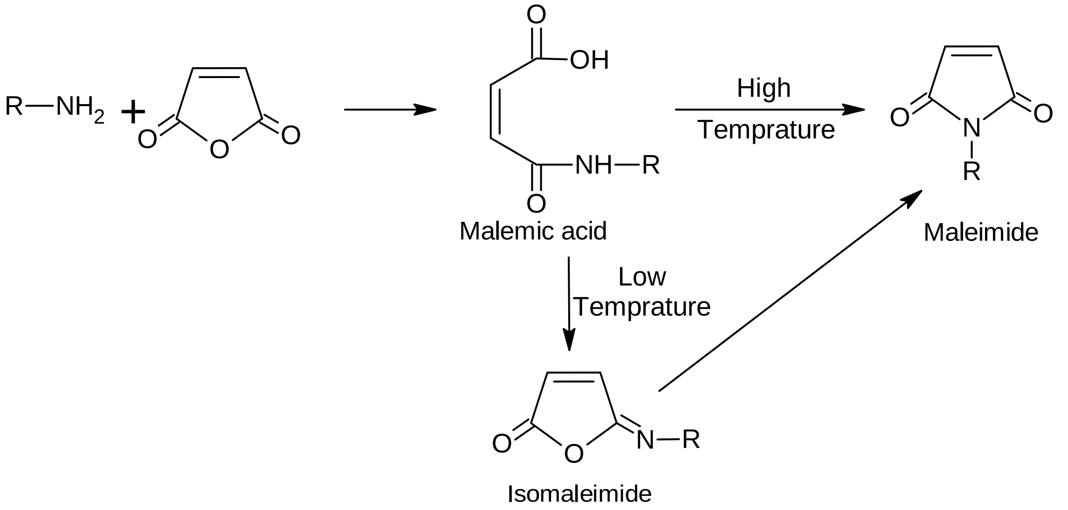
Polymers are widely used in several technological applications. Thermally stable and heat-resistant polymers are in great demand for use as insulators, varnishes, enamels, adhesives etc. **[1]**. A large percentage of such materials are used in modern military and civil aircraft. Reinforced plastics, based on high temperature resistant polymers are light in weight and even many times stronger than the metals.

Polyimide-related groups of plastics have some outstanding properties due to their high thermal stability. Polymaleimides are one of the most important classes of high-performance polymers because of their radiation resistance, high fire resistance, and thermal as well as stable dielectric properties at temperatures up to 200–250°C1 because of their minimal number of oxidizable hydrogen atoms and the high extent of conjugation **[2]**. There are so many methodologies reported for the preparation of maleimide and poly-maleimides.

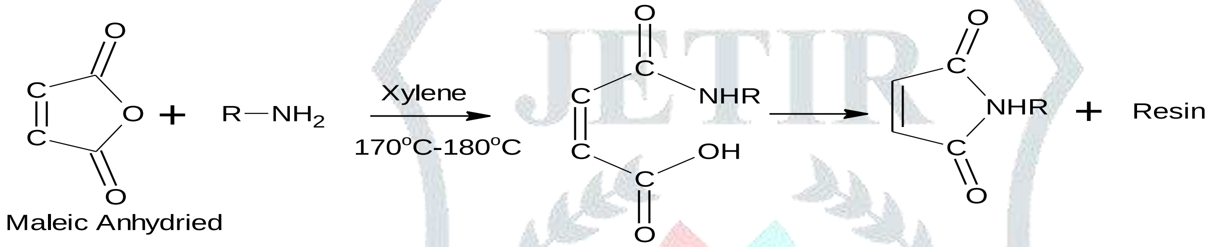
Some N-substituted maleimide monomers have greater reactivity than that of simple maleimide toward radical polymerization. In general, N-substituted maleimide monomers are prepared by direct substitution in maleimide, an imidization of maleamic anhydride, and a retro-Diels-Alder approach **[3]**. In this review, we describe the different ways to synthesize maleimide compounds and in a second part, we focus on their use as building blocks for material chemistry, owing to various reactions such as nucleophilic, radical, and cycloaddition reactions.

Synthesis of Maleimides

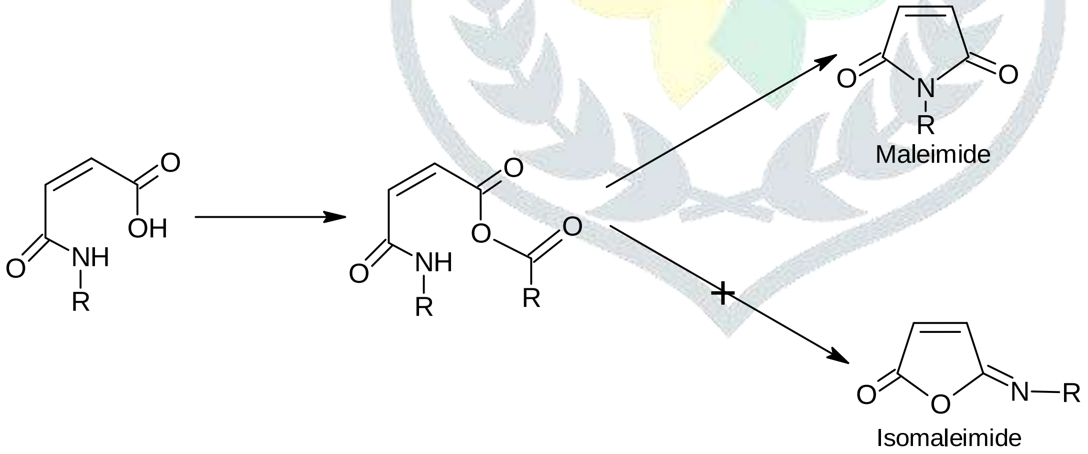
Several methods have been described for the preparation of Maleimides. The most highly developed synthetic route for imides is the classical two-step method, the first step being the synthesis of poly (amic acid) from the reaction of diamines and dianhydrides and the later step being subsequent thermal or chemical imidization of the poly (amic acid) **[2]**. Moreover, the nature of this last step enables to control of the ratio between the synthesized maleimide and the by-produced isomaleimide **[4]**.



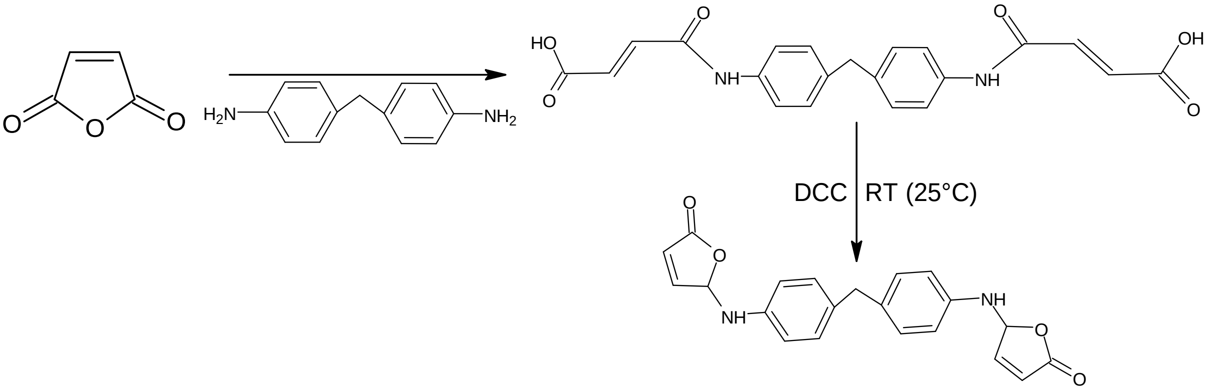
The ring closure is the most difficult step in the synthesis of Maleimides and is especially difficult to achieve where the parent amine is directly attached to an aliphatic backbone. Four N-alkyl (butyl, octyl, decyl and dodecyl) maleimides were prepared by reacting maleic anhydride with the appropriate amine in xylene at 170-180^{o}C **[29]**.



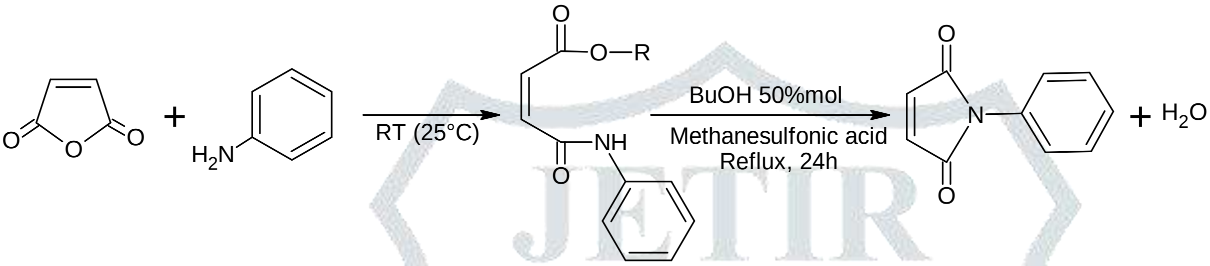
Mizori and co-workers suggest few methods have been reported to accomplish the ring-closure step. One method is through the reaction of the maleamic acid residue with acetic anhydride and sodium acetate.



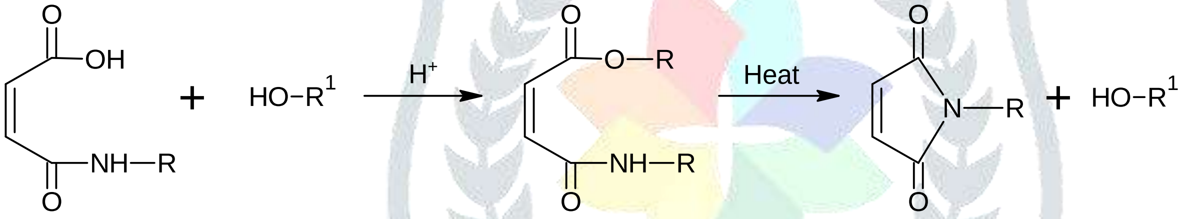
Another method used in the reaction of maleamic acid with another dehydrating agent such as DCC, with DCC alone, the product exists an isomaleimide but in the presence of a suitable isomerising agent, such as 1-hydroxybenzotriazole the maleimide is produced instead of the isomaleimide. Auvergne et al. **[5]** used the same method to synthesize polyether bismaleimide.



Method of cyclization can also be done by either esterification or amidification of the maleamic acid intermediate **[3]**.

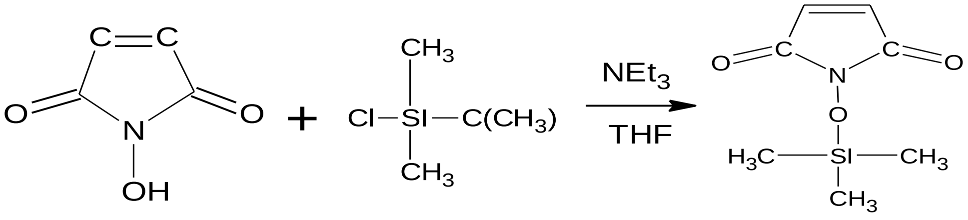


Another method that has been employed for ring closure involves thermal cyclodehydration of maleamic acid using an alcohol and acid catalyst combined with an azeotropic solvent **[3]**.



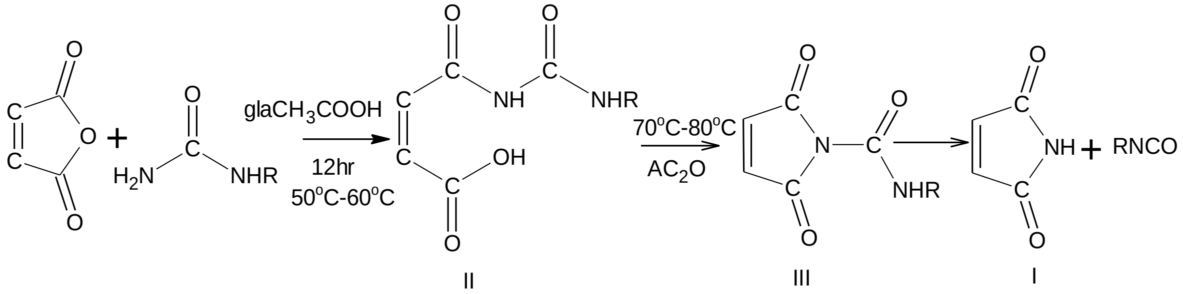
The thermal dehydration of aliphatic maleimides was reported by Syrett et al. **[6]** who synthesized maleimides in two steps. After protection of the reactive double bond of the maleic anhydride thanks to a Diels-Alder reaction with furan, the cyclo-dehydration is carried out by heating the mixture in the presence of triethylamine. Final maleimide is obtained after a heating step where the retro-Diels-Alder reaction occurs and furan is removed.

A new silicon-containing maleimide monomer, *N*-(*tert*-butyldimethylsilyloxy)-maleimide (SiOMI) has been synthesized **[30]**.



HOMI SiOMI

Tawney et al. **[31]**. conveniently synthesized maleimide by preparation and pyrolitic decomposition of 3,6-endo-methylene-Δ-tetrahydrophthalimide. A variety of N-substituted derivatives of maleimide were prepared.



IIa & IIIa. R = H
IIa & IIIa. R = C_6H_5
IIa & IIIa. R = n-C_4H_9
IIa & IIIa. R = $(CH_3)_3C$

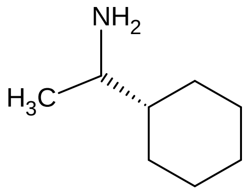
Polymerization of Maleimides

The reactivity of maleimides is mainly due to the vinyl bonds. Maleimides can polymerized owing as well as other monomers in three different ways: Anionic Polymerization, Diels-alder reaction (4+2) cyclo-addition, and free radical polymerization.

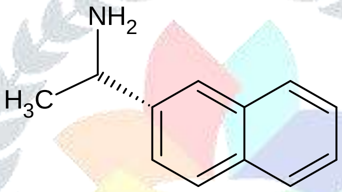
Anionic polymerization

Only a few studies have been conducted on the subject of anionic maleimide polymerization.

Optically active Polymaleimides can be synthesized by using chiral or achiral amine initiators **[7]**, *n*-BuLi, or Et_2Zn (Bnbox) chiral initiator **[8,9]**.



(S)-(+)-1-cyclohexylethylamine



(S)-1-(2-napthyl)ethylamine

Asymmetric polymaleimides are also synthesized by anionic polymerization using alkali-metal tert-butoxides **[10]** as initiator.

The anionic maleimide polymerization is mostly considered a side reaction that is initiated by basic initiators like alkali metal alkoxides and gives a cross-linked network. This polymerization is difficult to control and therefore hardly used in macromolecular chemistry.

Diels-Alder reaction [(4+2) cycloaddition reaction]

The DA reaction is a [4+2] cycloaddition reaction between a dienophile and a diene. The DA adduct can undergo dissociation by retro Diels-Alder reaction (rDA) under thermal treatment and convert back into the initial diene and dienophile. Moreover, maleimides are good dienophiles due to their conjugated double bond. Most of the time, DA reaction is performed between maleimides and furanic derivatives, which are very good dienes (blocked in cis-conformation).

H. Laita, S. Boufi, and A. Gandini **[11]** synthesized Mono- and Bis-maleimide by using two types of furan-containing polymers, namely polyurethanes and acrylic copolymers. Razvan C. Cioc and co-workers **[12]** show that poor electron-rich dienophiles such as furfuraldehyde and its derivatives can also directly engage in Diels–Alder couplings with maleimides.

An Ionic Liquid has been employed for the Diels-Alder reaction between anthrone and maleimide in which an external base was not required for the generation of the diene component and the faster reaction also suggested the role of hydrogen bonding of the Ionic Liquid with the dienophile component **[13]**.

Free radical Maleimide polymerization

maleimides have shown very attractive properties as monomers in radical co- or homo-polymerization. First, they can generate radicals under UV radiation and polymerize in an alternated system with electron-donor co-monomers. Second, they possess versatile structures that allow the introduction of various reactive substituents into highly stable polymers.

Co-polymers were synthesized from free radical co-polymerization of methyl methacrylate (MMA), styrene (ST), and acrylonitrile (AN) with N-(4-Azodiphenyl) maleimide (ADPMI), using AIBN as an initiator and DMF as a solvent at 70°C **[14]**.

Radical polymerizations of various N-substituted maleimides (RMIs) with AIBN in benzene at 60°C were carried out to elucidate the effect of the N-substituents on the polymerization reactivity **[15]**. The radical homo- and co-polymerizations of maleimide derivatives in the presence of chiral substances are also synthesized **[16]** such as Cobalt complexes **[17]**.

New maleimide-terminated oligomers of n-butyl acrylate can be synthesized by atom transfer radical polymerization, using functional initiators **[18]**. The copolymer of N-substituted maleimides with Styrene is prepared by an atom transfer radical polymerization (ATRP) mechanism and the general ATRP catalyst is composed of a simple alkyl halide as an initiator and a copper(I)-bipyridine complex as a catalyst **[19]**. A series of Alpha-functional maleimide polymethacrylates have been also prepared via copper-catalysed living radical polymerization (LRP) **[20]**. Polymaleimides (PMAI) was also synthesized by reacting polymaleic anhydride (PMA) with urea via a solvent-free reaction at 180 °C **[21]**.

Application

Thermally stable and heat resistance polymaleimides are in great demand for use as thermosetting binders in products for structural, electrical insulating, and instrumentation purposes and also used as bio-based thermosetting polymers **[22]**, making liquid crystal displays **[23]**, chelating agents in antimicrobial activities **[22]**, insecticidal and antifungal activities **[24]**, aerospace industries **[25]**, microelectronics **[14]**, and nanotechnologies **[26]**, etc.

The maleimides and acrylate-based functionalized polymers are applicable in targeted drug delivery, thermally responsive systems, hydrogels, and tissue engineering **[27]**.

Conclusion

Maleimide compounds are being increasingly studied, and their use in smart systems is increasingly reported. N-substituted Maleimides are generally synthesized from maleic anhydride and primary amines, urea, ammonia, etc. to form maleamic acid. The formation of maleimide from maleamic acid is quite difficult but by using different methods it is possible. The Homo and Co-polymerization of maleimide is done in three different ways: Anionic polymerization, Diels-Alder cycloaddition, and Free radical Polymerization using different initiators. Due to high heat resistance power and high thermal stability, Polymaleimides are widely used in various sectors.

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