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CYCLIC IMINO ETHERS (Ring-Opening Polymerization of 1,3-Oxazo Monomers)

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Previous reviews by Kobayashi et al., Rivas, and Seeliger et al. have described the monomer preparation and properties, polymerization, catalysis, spectral properties, and reactions of polymers derived from 1,3-oxazo compounds.[1–5] Less-studied 1,3-oxazo monomers are discussed in more detail in these previous reviews. This contribution attempts to provide an updated review of the synthesis, properties, and emerging applications of polymers derived from 1,3-oxazo monomers, with an emphasis on the commonly studied 2-oxazolines and 2-oxazines.

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PREPARATION AND PROPERTIES

Monomer Synthesis

The most commonly studied cyclic imino ethers are the oxazolines, followed by the oxazines. These compounds can be prepared by many methods. The reaction between amino alcohols and nitriles is a very convenient and practical method.[6] The reaction is catalyzed by Lewis acids (such as $ZnCl_2$, $ZnAc_2$, and $CdAc_2$), and aromatic or aliphatic nitriles can be used (**Structure 1**).

Commonly used laboratory preparations are often produced by ring closure of ω-halo amides under basic conditions (**Structure 2**).[7–11]

Other preparations of 2-oxazolines and 2-oxazines include the reaction of carboxylic acids with amino alcohols,[12,13] and dehydration of N-(ω-hydroxyalkyl) amides with reagents such as thionyl chloride,[14] sulfuric acid,[15] phosphorotriazolides,[16] and Mitsunobu conditions.[17]

The synthesis of oxazolines and oxazines with no substitution in the 2-position can be accomplished by the cyclization of hydroxyalkyl isocyanides (**Structure 3**)[18–20] or by the reaction of aminoalcohols with isocyanides (**Structure 4**).[21,22]

Of particular interest is the synthesis of difunctional monomers, which have an oxazoline moiety. For example, 2-isopropenyl-2-oxazoline has been prepared and was once commercially available.[23–25] Also, 2-p-styryl-2-oxazoline has been made via the reaction of ethanol amine with p-cyanostyrene.[26]

Polymerization

Both 2-oxazines, and in particular 2-oxazolines, have drawn a great deal of interest for several reasons. First, oxazines and oxazolines are homopolymerized with cationic initiators, which can include alkylating agents. Second, the polymerization is pseudoliving; thus block copolymers and chain-end functionalized macromers can be readily prepared. Third, physical properties can be varied greatly by choice of substitution in the 2-position.

Unlike most ring-opening polymerizations, the driving force is not release of ring strain, nor is there a great entropic gain, as seen in the ring opening of macrocycles. Rather, the driving force in oxazoline and oxazine polymerizations is the formation of the more thermodynamically favored amide functionality. The general polymerization is shown in **Structure 5**.

The polymerization is initiated most commonly by Lewis acids or alkylating agents. It is also common to use the isolated alkylated salt of the monomer as the initiator. In addition to the original work by Bassiri et al.[27] and Levy and Litt,[15] other examples are: Tsubokawa et al.,[28] Kagiya and Matsuda,[23] Kobayashi et al.,[29–39] and Han et al.[40] Trimethylsilyl compounds have been found to initiate by a slightly different mechanism as shown in **Scheme I**.[41]

Saegusa et al.[42–45] found that propagation in homopolymerizations of oxazolines can proceed via two mechanisms. If the counter ion is nonnucleophilic the propagating chain end is ionic (**Structure 6**).

However, if the counter ion is nucleophilic the propagation consists of a covalent chain end (**Structure 7**).

Extensive work has been done investigating oxazine and oxazoline polymerization mechanisms, and some of this work is tabulated in **Table 1** (see Kobayashi et al. review).[2]

The polymerization of 5-methyl-2-oxazoline is an interesting case because it shows both ionic and covalent character when initiated with methyl iodide.[46,47] This ionic mechanism becomes more prevalent in polar solvents. An interesting use and demonstration of the different mechanisms is the polymerization of 2-pyrolidino-2-oxazoline. With methyl triflate initiation the polymerization is ionic and the standard polyoxazoline is formed. However, with methyl-iodide initiation the covalent chain end is formed which recyclizes to form a different propagating species (see **Scheme II**).[48]

Termination

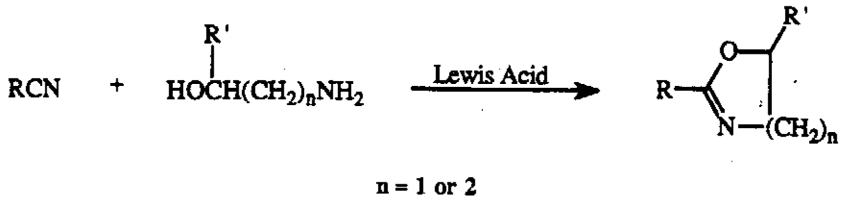
Little work has been done to investigate termination in these polymerizations. Litt et al. found evidence that 2-alkyl-2-oxazolines undergo chain transfer, and the resulting chain end can form branches (**Structure 8**).[49]

Practical Aspects

Although oxazoline and oxazine polymerizations are more robust than other cationic polymerizations, they are still sensitive to impurities. Oxazolines are usually polymerized between 100 °C and 150 °C, whereas oxazines often require temperatures of 150 °C or higher.[50] The reactivity of the chain end governs the polymerization rate, so stronger electron withdrawing substituents in the 2-position polymerize faster.[51] Also, increasing size of the 2-position substituent decreases monomer nucleophilicity and therefore slows the rate of polymerization. Substitution on the other positions of the rings generally have the effect of slowing the polymerization.[9] When possible, the polymerizations are done without solvents. When solvents must be used, polar aprotic solvents are usually the best choice (i.e., DMF, acetonitrile, nitromethane). Protic solvents and sulfoxides (DMSO) should not be used.[10]

Copolymerization

The attractive features of oxazoline and oxazine polymerizations include the ease with which alternating, block, graft, and random copolymers can be produced.



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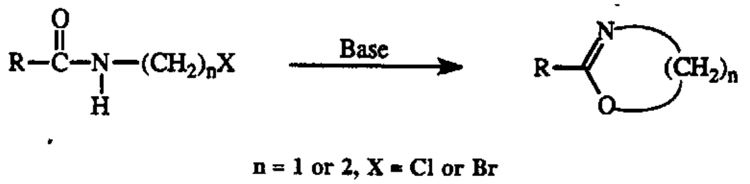

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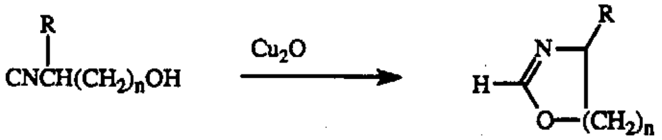

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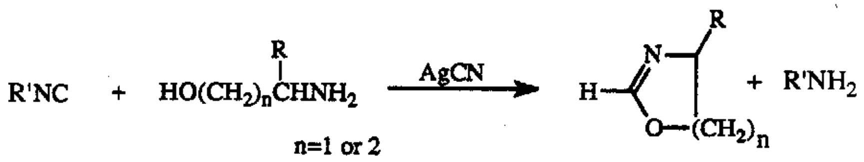

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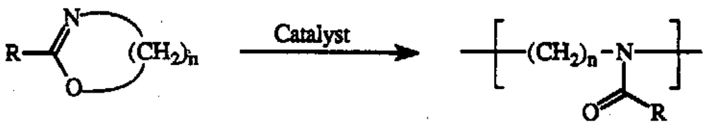

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Alternating/Zwitterionic

Oxazolines and oxazines react with acrylic monomers (acrylic acid,[43,44,52–54] α-halo acrylic acids,[55,56] ω-hydroxyalkyl acrylates,[57] and acrylamide[58]) to form alternating copolymers without an initiator. These polymers often have low molecular weights. A report by Balakrishnan[59] that methacrylic acid works in these polymerizations has been contested.[60] These polymerizations proceed by formation of a Zwitterionic adduct followed by proton transfer (**Structure 9**).

Kagiya et al. have produced alternating copolymers from bis(2-oxazoline)s and diacids (**Structure 10**).[61]

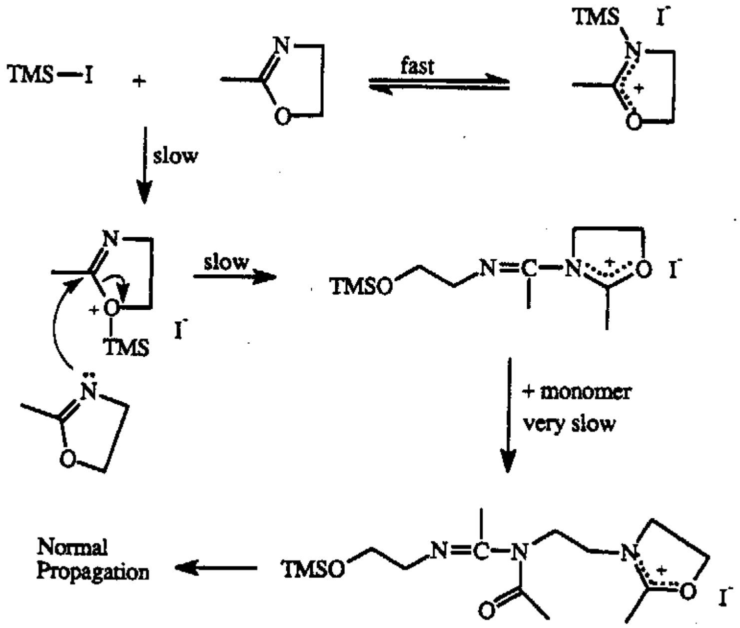
Gunatillake et al.[62,63] and Odian and Shi[64] found that thiol-containing monomers polymerize in a similar manner, with typical monomer structures shown in **Structure 11.**

Copolymerization of 2-oxazoline with β-propiolactone gives 1:1 alternating copolymer via the same intermediate as for the copolymerization of 2-oxazoline and acrylic acid.[65] γ-Propanesultone also gives a 1:1 alternating copolymer.[66] More often, the polymerization of oxazolines with lactones and cyclic anhydrides gives statistical copolymers or polymers rich in the cyclic anhydrides or lactones.[67–76]

Also, 2-oxazolines form copolymers with electron-accepting monomers, such as tetracyanoethylene, and 7,7,8,8-tetracyanoquinodimethane,[77,78] various maleimides,[79–87] and β-methylhydrogen itaconate.[88,89] These polymerizations generally yield polymers that are rich in electron-deficient monomers (**Structure 12**). Reported molecular weights are typically low.

Block

Oxazolines have been used to produce both AB and ABA block copolymers, as well as star polymers. (For an example of star polymers see Percec and Dworak).[90,91] Oxazoline–oxazoline or oxazoline–oxazine block copolymers are produced by homopolymerization of the first monomer. When the first monomer is consumed, the monomer for the second block is added and the polymerization continues (**Structure 13**).



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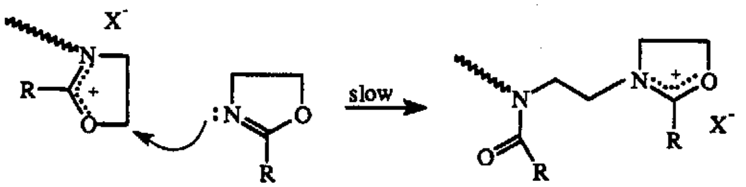

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Both di- and tri-copolymers have been produced in this manner. Usually the oxazoline copolymers are made with mixtures of hydrophobic and hydrophilic blocks for use as surfactants.[92–96]

Several styrene block copolymers with 2-methyl-2-oxazoline have been reported. For the synthesis of oxazoline-vinyl-oxazoline triblocks styrene, 2-vinylnaphthalene, and 9-vinylphenanthrene have been used.[97–99] These triblocks are prepared via sodium naphthalene polymerization of styrene, followed by quenching the dianion with dihaloalkanes or ethylene oxide. The halo-alkane terminated polymers initiate 2-methyl-2-oxazoline polymerization to form the oxazoline blocks directly (KI is added as a catalyst). The ethylene-oxide terminated styrenic must first be converted to the ditosylate, which initiates oxazoline polymerization. Similarly, Ishizu[100] studied the use of monohydroxy-terminated polystyrene to produce diblock and triblock (styrene–tetrahydrofuran–oxazoline) copolymers. Iodine-initiated polystyrene has also been used to produce diblock copolymers.[101] Some of these block copolymers have been hydrolyzed to give ethyleneimine blocks. α,ω-Hydroxy-terminated polybutadiene and hydroxyl-terminated polyisobutylene star polymers have both been used to make block copolymers of 2-methyl-2-oxazoline by way of the tosylate.[102] These polymers were also hydrolyzed to the polyethyleneimine. Iodine and HI/chloroethylvinyl-ether-initiated vinyl ether macromers also initiate the polymerization of 2-methyl-2-oxazoline to give oxazoline-vinyl ether diblocks.[103–106]

Triblock copolymers of the structure oxazoline-polyethylene oxide (PEG)-oxazoline have been made by the synthesis of the ditosylate PEG macroinitiator.[107,108] Also, the dichloroformate and the tosyl derivatives of PEG

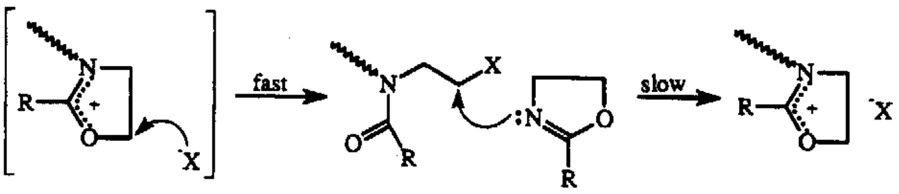

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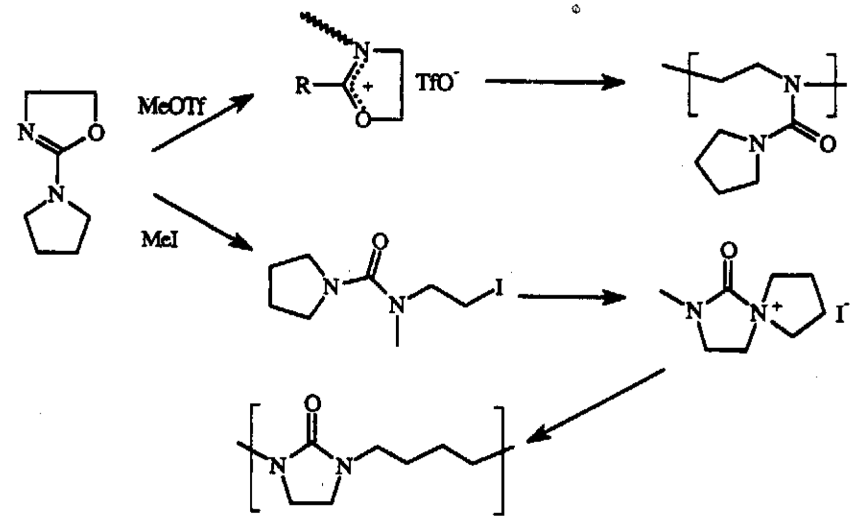
TABLE 1. Kinetic Data for the Polymerization of 2-oxazolines in CH_3CN at 40 °C

2-Oxazoline monomer	Initiator	$k_p \times 10^4$, L/mole·s	ΔE_p kJ/mole	$A\dagger_p$ L/mole·s	Chain end character
Unsubstituted	MeOTs[2]	19	105	7.5×10^{14}	Ionic
Unsubstituted	MeI[b]	0.18	56.5	5.0×10^{4}	Covalent
2-methyl	MeOTs[a]	1.17	79.9	1.9×10^{9}	Ionic
2-methyl	MeI[b]	1.14	72.8	1.7×10^{8}	Ionic
2-methyl	Benzyl Cl[c]	0.03[3]	61.9	6.5×10^{4}	Covalent
2-phenyl	MeOTs[a]	0.02[d]	98.3	7.2×10^{10}	Ionic
5-methyl	MeOTs[a]	0.09[d]	59.8	6.6×10^{5}	Ionic
5-methyl	MeI[b]	0.04[d]	67.4	4.9×10^{6}	Ionic and Covalent

[a] Methyl-p-toluenesulfonate.
[b] Methyl iodide.
[c] Benzyl chloride.
[d] Values extrapolated to 40 °C.
Source: Reference 2. With permission.



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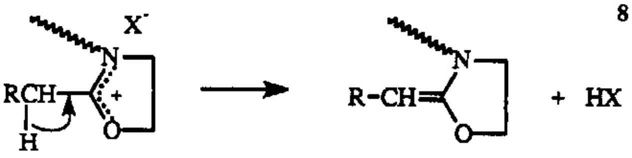
adipate have been used.[101,109,110] Hsiue has prepared multiblock copolymers by the method shown in **Structure 14**).[111]

Block copolymers with siloxanes,[112–114] ϵ-caprolactone,[115] and styrene oxide[116] have also been synthesized.

Graft

Four methods have been used to synthesize polymers that have oxazoline grafts. One method is the production of macromonomers by the initiation method. In this procedure the polymerization of an oxazoline is initiated by compounds containing a vinyl group. Initiators that have been used are *p*-halomethylstyrenes,[30,117–119] 3-methyl-2-p-styryl-2-oxazolinium salts,[120] and vinyl iodoacetate.[121,122] Resulting macromers are then radically polymerized. The second method is macromonomer synthesis by the termination method, which involves terminating an oxazoline polymerization with a compound that contains a polymerizable moiety. The favored terminating compounds used are acrylates[123–126] and methacrylates,[127] but styrenic compounds[119] or diethanol amine[29] have also been used. The styrene and acrylate macromers are then polymerized radically, whereas the diethanol-amine terminated macromer is copolymerized with polycaprolactone diol and MDI. The third popular method for making graft copolymers is the polymerization of oxazolines from polymers containing alkylating groups. For example, Saegusa et al. used macroreticular poly(4-chloromethylstyrene) to polymerize 2-methyl-2-oxazoline.[128] Other polymeric initiators



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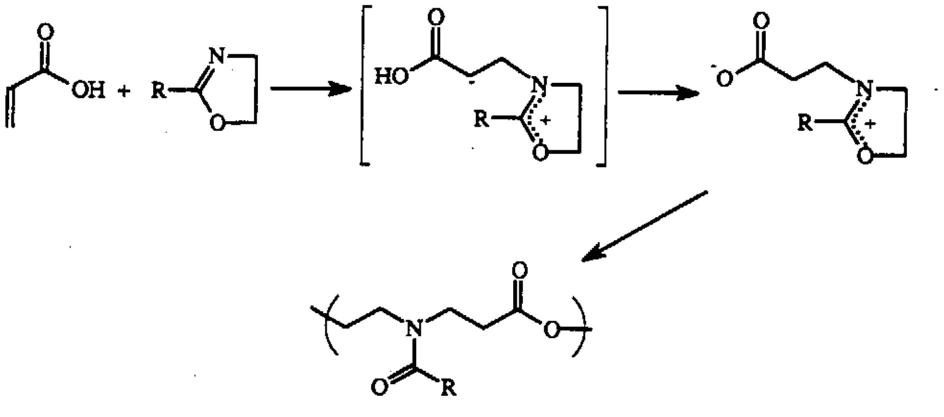

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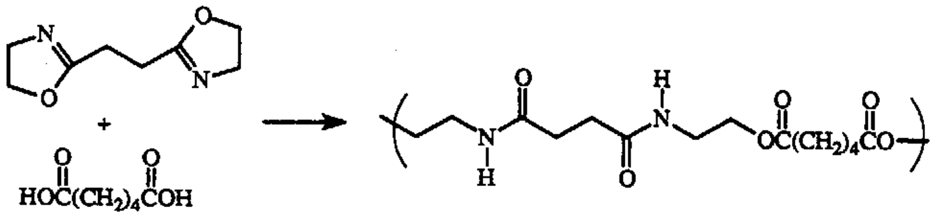

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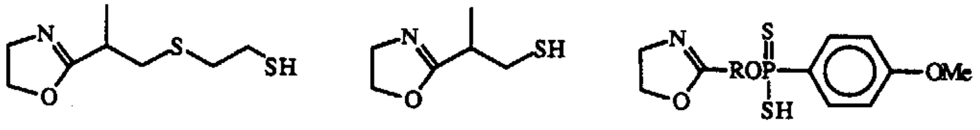

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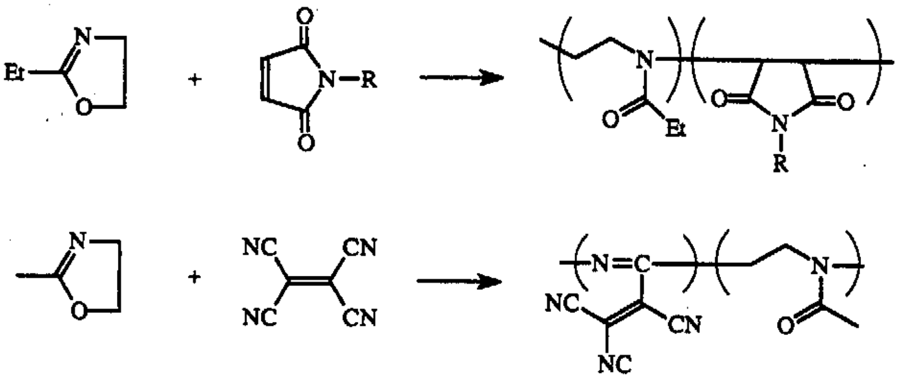
that have been used are: poly(2,6-dimethyl-1,4-phenylene oxide) containing CH_2Br groups,[117] polyvinylchloride-containing allyl chloride groups,[129] sulfonated cellulose,[130] poly-(2-isopropenyl-2-oxazolinium) salt/acrylate copolymers,[131] poly(vinyl alcohol) derivatives,[132] alkyl chloro polyethers,[133] poly(vinylsulfonates),[134] and acrylate derivatives.[135,136] The fourth method is the grafting of an existing polymer onto another polymer. Poly(2-methyl-2-oxazoline) initiated by allyl tosylate was catalytically coupled to polysiloxanes containing Si-H units.[137] There are a couple of special cases that deserve mention. First, Tomalia has made comb-burst dendrimer polymers by the grafting of poly(2-ethyl-2-oxazoline) oligomers onto poly(ethylene imine).[138] After hydrolysis this grafting is repeated. Second, there are two reports by Kobayashi detailing the synthesis of poly(oxazoline) backbones having poly(ethylene oxide) grafts.[46,139]

Random

Random copolymerizations of oxazolines and oxazines have not been thoroughly studied. Presumably, oxazolines



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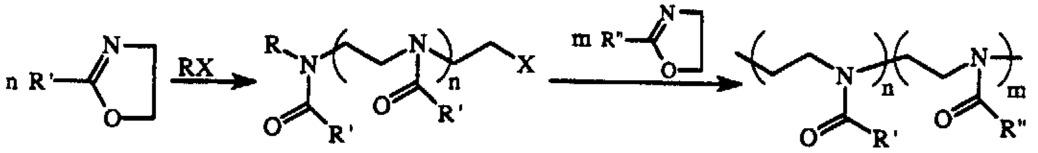

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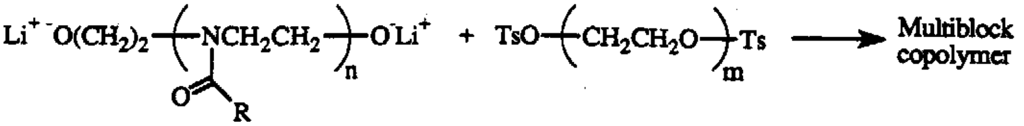

$Li^+ {}^-O(CH_2)_2\text{-}(NCH_2CH_2)_n\text{-}O^-Li^+ + TsO\text{-}(CH_2CH_2O)_m\text{-}Ts \longrightarrow$ Multiblock copolymer

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or oxazines of similar reactivities will copolymerize randomly.[140,141]

Linear Polyamines

The only way to synthesize linear polyamines of the structure $-(CH_2)_n$-NH- is by hydrolysis of poly(2-oxazoline)s[142–144] and poly(2-oxazine)s.[22,44,45] The hydrolysis has been done using either acid or base. Homopolymer polyamines are always hygroscopic, and their melt temperature increases with water content. Polyethyleneimine has a crystalline melt at 58.5 °C and is soluble in hot water. Polytrimethyleneimine is insoluble in water, but soluble in methanol or ethanol: for a polymer containing 9.3 wt% water the T_m=75 °C. Both chiral and racemic poly(propyleneimine) have been prepared (see **Structure 15**).[45–145] Saegusa has also prepared polymeric tertiary amines by the reduction of various oxazolines with $LiAlH_4$ or AlH_3.[146] And Tanaka prepared poly(*N*-methyl ethyleneimine) and poly(*N*-methyl trimethyleneimine by formalin/formic acid reductions of the polyamines or poly(2-oxazoline) and poly(2-oxazine).[147]

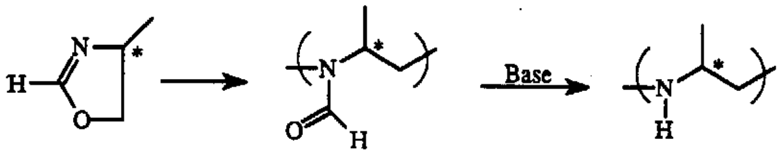
POLYMER APPLICATIONS

Recycling

The degradative thermal and hydrolytic effects of processing recycled poly(ethylene terephthalate) (PET) and polyamides can be compensated by chain extending these polymers with bisoxazolines.[148–150] The addition reaction of bisoxazolines with acid or hydroxyl end groups results in higher molecular weights and lower end-group concentrations. The reaction can be accomplished directly in an extruder and could result in a broader use of recycled PET and nylons. Akkapeddi conducted comparisons of various chain extenders for PET and polyamides under normal extruder-processing conditions.[151] Sano reported additional side reactions of an oxazoline with an amide group catalyzed by phosphites.[152] These reactions could lead to crosslinking in polyesters and polyamides. Nishikubo explored the addition reactions of pendant cyclic iminoethers for the synthesis of functionalized or crosslinked polymers.[153–155] Reactivities of the various pendant cyclic iminoethers and reactants were explored, including thiols, carboxylic, thiocarboxylic, and sulfinic acids. A novel, self-curing copolymer containing pendant cyclic iminoethers and carboxylic acid groups was also described. There is extensive worldwide patent literature on using the addition reactions of cyclic iminoethers for thermosetting resins, adhesives, and reaction injection molding (RIM) applications.

Hybrid Organic/Inorganic Composites

Hybrid organic polymer–inorganic composites were made using polyoxazolines.[156,157] These materials were made by blending or reacting polyoxazolines via standard sol–gel techniques to produce novel organic–inorganic composites. Saegusa synthesized triethoxysilyl-terminated polyoxazoline which effectively acted as a silane coupling agent.[158,159] When used as a reactant during the polymerization of tetraethoxylsilane by sol–gel methods, intimately mixed transparent composite materials were made. David and Scherer reported similar results for non-functionalized poly(ethyloxazoline).[160] These hybrid materials appear to approach molecular composite dimensions. Subsequent pyrolysis of the organic phase at 600 °C produced porous silicas with surface areas up to 800 m^2/g and pore volumes of 0.5 cm^3/g. Pore sizes ranging from 10 to 20 angstroms were reported. Starburst dendrimers of similar structure were also found to give transparent gels with silica gel. Excellent agreement was found between the calculated



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radius of the dendrimer and measured average pore size after pyrolysis.

Composite Resins

Kagiya et al. have investigated the addition reactions of bisoxazoline with dicarboxylic acids to give poly(ester amide) resins with high mechanical properties.[61] Culbertson et al. have extended this chemistry to bisoxazoline–phenolic resins and conducted evaluations for aerospace composite applications.[161,162]

Surfactants

Block copolymers have been widely exploited as surfactants in both aqueous and nonaqueous emulsion polymerizations. The living nature of the polymerization of oxazolines and oxazines has been used to synthesize a wide variety of nonionic surfactants with excellent surfactant properties. Copolymers with AB and ABA block copolymer structures containing both hydrophilic and hydrophobic chains show good surfactant properties. In addition to standard methods for producing block copolymers, two distinct methods have been developed for the synthesis of surfactants based on oxazolines. These are known as the initiator and terminator methods. For surfactants containing a hydrophilic polyoxazoline segment and a hydrophobic group, the hydrophobic group can be introduced as an initiator or terminator for the polymerization of oxazoline or oxazine monomers. The effectiveness of these surfactants has been explored in detail by Litt et al., Kobayashi et al., and Miyamoto.[3,31–33,36,48,163–165]

These nonionic surfactants displayed surface tensions in the range of 15–45 dyn/cm and, in some instances, very low values of critical micelle concentration. The surface-active properties of these polymers have also been explored in applications such as inverse emulsification,[166,167] compatibilization in polymer blends,[133,168] adhesion,[140,141,169,170] phase-transfer catalysis,[171] anti-electrostatics,[172] and Langmuir–Blodgett films.[173]

Chelators

Polyamines derived from the hydrolysis of linear and branched polyoxazolines were prepared and studied as chelators for heavy metal ions. They were also prepared as graft polymers onto resins and functionalized with a variety of functional groups. Stable complexes were formed with metals as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and UO_2^{2+}.[128,174–176]

Hydrogels

Hydrogels have found applications in a number of different fields, such as packaging, drying agents, medical devices, and controlled-release agents. In recent years, nonionic hydrogels based on crosslinked polyoxazolines have begun to be explored.[177] These are prepared by ring-opening polymerizing an oxazoline monomer with a bisoxazoline crosslinker. Alternatively, a polyoxazoline is partially hydrolyzed, or controllably terminated, to form secondary amines that are subsequently crosslinked using agents such as diisocyanates.[178–180] The hydrophilicity of the gels can be systematically tailored by the characteristics of the 2–alkyl substituent of the oxazoline monomer. Gels produced from lower alkyl-2-oxazolines form stable hydrogels with relatively high swelling properties in both water and 5% aqueous NaCl solutions. Gels from higher alkyl-2-oxazolines form lipogels and those gels made from intermediate alkyl-2-oxazolines form amphigels, which exhibit good swelling characteristics in both water and organic solvents.[181] Applications for these materials will likely be developed as research in this area continues.

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