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Review

Synthesis and Polymerizability of Atom-Bridged Bicyclic Monomers

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Abstract: The synthesis and polymerizability of atom-bridged bicyclic monomers was surveyed. The monomers included lactams, ureas, urethanes, lactones, carbonates, ethers, acetals, orthoesters, and amines. Despite widely-varying structures, they almost all polymerized to give polymers with monocyclic rings in the chain. The polymerizations are grouped by mechanism: uncoordinated anionic, coordinated anionic, and cationic.

Keywords: alicyclic ring-containing polymers; anti-Bredt monomers; atom-bridged bicyclic monomers; ring-opening polymerizations

1. Introduction

Ring-opening polymerizations, which convert cyclic monomers into linear polymers, are a major type of polymerization. A recent authoritative treatise [1] covered ring-opening polymerization of monocyclic monomers; this Review covers ring-opening polymerization of atom-bridged bicyclic monomers. “Atom-bridged” means all three chains connecting the bridgehead atoms contain at least one atom. Bicyclic compounds with bridgehead atoms directly attached to one another will not be considered here because they usually polymerize like monocyclics. Alkene metathesis of bicyclic monomers has been well-reviewed elsewhere and will not be included here.

The reactions are arranged below according to mechanism:

UNCOORDINATED ANIONIC POLYMERIZATIONS of lactams, ureas, and urethanes
COORDINATED ANIONIC POLYMERIZATIONS of lactones and carbonates
CATIONIC POLYMERIZATIONS of ethers, acetals, orthoesters and amines

Although these monomers may appear exotic, they are often synthesized rather easily. Hydrogenation of suitable benzene derivatives followed by cyclization has been used most often. This is easy for industrial research laboratories equipped with high pressure equipment but less so for academic laboratories, perhaps accounting for the limited data in this field.

All of the syntheses involve the possibility of forming linear polymer directly instead of bicyclic monomer. The synthesis conditions may have to be adjusted to favor the formation of bicyclic monomer. These include dilute solution, high temperature, and other factors.

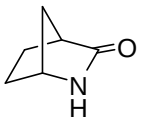
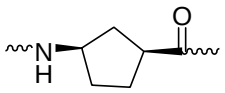
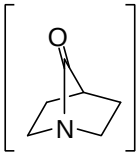
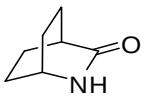
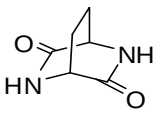
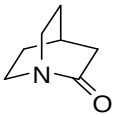
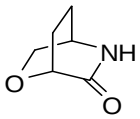
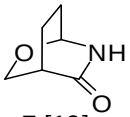
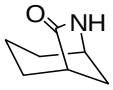
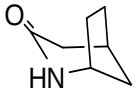
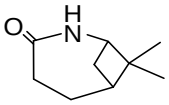
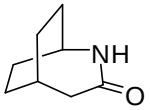
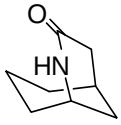
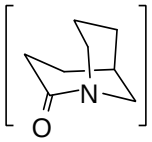
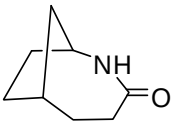
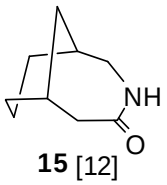
Since the polymer structure is usually obvious from the monomer structure, the polymer structure is only given below for the first example and in some later cases where more than one polymer structure is possible.

2. Discussion

*2.1. Lactams (**1–15**)*

Lactams dominate the group of bicyclic monomers which undergo uncoordinated anionic polymerization (Table 1).

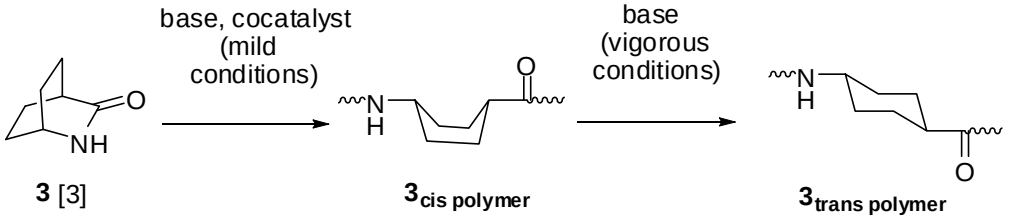
Table 1. Bicyclic lactam monomers **1–15** [2–13].

Bicyclo[2.2.1]heptanes				
 **1** [2]	 **1**$_{polymer}$		 **2** [3] (brackets = monomer has not been been isolated because the usual conditions for monomer synthesis give polymer)	
Bicyclo[2.2.2]octanes				
 **3** [3]	 **4** [4]	 **5** [5-8]	 **6** [9]	 **7** [10]
Bicyclo[3.2.1]octanes		Bicyclo[4.1.1]octane	Bicyclo[3.2.2]nonane	
 **8** [3]	 **9** [9-11]	 **10** [12]	 **11** [11]	
Bicyclo[3.3.1]nonanes		Bicyclo[4.2.1]nonane	Bicyclo[4.3.1]decane	
 **12** [11]	 **13** [13]	 **14** [11]	 **15** [12]	

Lactam synthesis usually involves removal of a small molecule from an amino acid derivative, often by simply heating the amino acid under vacuum to remove water. Cyclization of an aminoacyl chloride hydrochloride with triethylamine has also been employed. The polymerizations are catalyzed by the lactam anion, assisted by cocatalyst *N*-acyllactam. Bicyclic amides **1**–**15** shown below (except the one in brackets) have been converted to polymers; the polymer is shown for monomer **1** only.

When the carbonyl group is attached to the ring in the initial polymer, it may be epimerized by the strongly basic lactam anion (Scheme I).

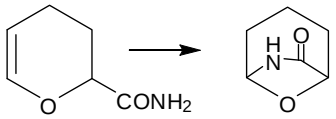
Scheme I. Ring-opening of bicyclic lactam **3** to give either cis or trans polymer [3].



3 [3] $\mathbf{3}_{\text{cis polymer}}$ $\mathbf{3}_{\text{trans polymer}}$

Oxabicyclic lactam **16** (Scheme II) and derivatives were synthesized from starting material $\mathbf{16}_{\mathbf{sm}}$ by internal addition of the carboxamide group to the dihydropyran group. Although monomer **16** is both a bicyclic lactam and a bicyclic ether, it has only been polymerized as the former by an anionic mechanism; cationic ether polymerization is excluded because of the basic amide group. This topic has been reviewed [14–16].

Scheme II. Synthesis of bicyclic lactam monomer **16**.



$\mathbf{16}_{\mathbf{sm}}$ **16**

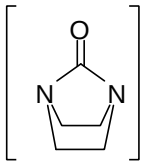
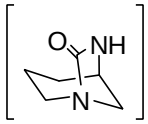
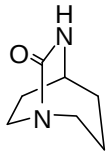
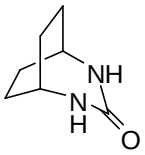
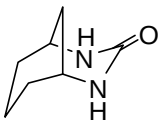
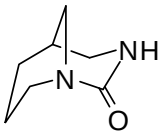
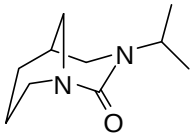
An especially interesting class of lactam and related *N*-containing monomers contains a bridgehead N next to a carbonyl group. These are greatly destabilized relative to normal amides because the usual N–CO resonance is absent according to Bredt's Rule, which forbids the occurrence of double bonds at bridgeheads as pointed out by Lukes [5]. Yakhontov also discussed this problem [6]. Pracejus [7] synthesized 1-aza-6,6-dimethylbicyclo[2.2.2]octan-2-one, while recent workers synthesized the parent structure as a salt by a nitrene insertion reaction; the free lactam could not be generated from the salt [8]. Although polymerization studies were not reported, these anti-Bredt lactams undoubtedly polymerize, being destabilized by their boat form as well as Bredt's Rule violation. The effect can be offset with an adjacent heteroatom, or in ureas and urethanes; the results of these studies are discussed below.

*2.2. Ureas (**17–23**)*

Bicyclic ureas (Table 2) are prepared by carbonylation of the corresponding diamine [3]. They polymerize anionically. The bicyclo[3.3.1]nonane-*N*-bridgehead ureas **22** and **23** were stable because

of electron donation to the carbonyl by the non-bridgehead N atom [17,18]. The molecules adopted a chair-boat conformation, as does bicyclo[3.3.1]non-1-ene.

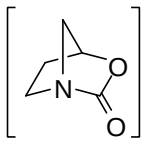
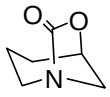
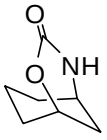
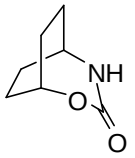
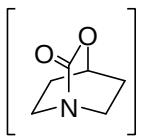
Table 2. Bicyclic urea monomers **17–29** [3,4,11,17,18].

Bicyclo[2.2.1]heptane	Bicyclo[3.2.1]octane			
				
17 [3]	**18** [18]			
Bicyclo[3.2.2]nonanes		Bicyclo[3.3.1]nonanes		
				
19 [11]	**20** [4]	**21** [3]	**22** [18]	**23** [17]

*2.3. Urethanes (**24–29**)*

Bicyclic urethanes (Table 3) are synthesized from amino alcohols with carbonylating agents such as phosgene and diphenyl carbonate [3]. Attempted cyclizations of 3-hydroxypyrrolidine and 4-hydroxypiperidine failed to yield bicyclic urethanes **24** and **29**, respectively. However, the *N*-bridgehead urethanes **25** and **27** were sufficiently stable to be isolated because of the resonance stabilization provided by electron donation from the oxygen adjacent to the carbonyl [19–21]. This topic has been reviewed [22].

Table 3. Bicyclic urethane monomers **24–29** [3,19–21].

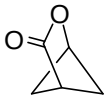
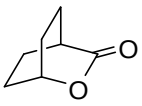
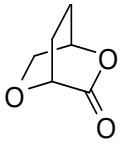
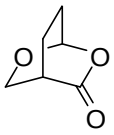
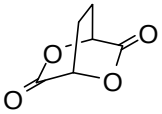
Bicyclo[2.2.1]heptane	Bicyclo[3.2.1]octane	Bicyclo[3.3.1]nonanes	
			
24 [19]	**25** [19,20]	**26** [3]	**27** [19,21]
Bicyclo[3.2.2]nonane	Bicyclo[2.2.2]octane		
			
28 [3]	**29** [19]		

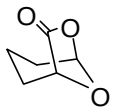
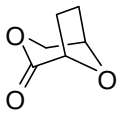
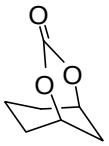
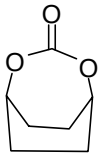
*2.4. Lactones (**30–37**) and Carbonates (**38–39**)*

Lactones (Table 4) can undergo "uncoordinated" anionic polymerization, but "coordinated" anionic polymerization, in which the addition of a Lewis acid of a metal like aluminum, tantalum, or titanium

provides simultaneous Lewis acid-base activation, is much more selective and does not lead to reshuffling of the polymer chains. The lactone monomers are synthesized by loss of small molecules from hydroxyacids or hydroxyesters. Also in this group are cyclic carbonates, prepared by carbonylation of alicyclic diols.

Table 4. Bicyclic lactone and carbonate monomers **30–39** [3,14,23–30].

Bicyclo[2.1.1]hexane	Bicyclo[2.2.2]octanes			
				
30 [23]	**31** [3,24]	**32** [25]	**33** [26,27]	**34** [28,29]

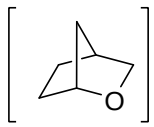
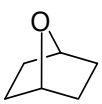
Bicyclo[3.2.1]octanes			Bicyclo[3.3.1]nonane	Bicyclo[3.2.2]nonane
				
35 [3]	**36** [14]	**37** [30]	**38** [3]	**39** [3]

The polymer from monomer **31** retains the cis form when the polymerization is carried out under mild conditions [3,24]. Monomer **33** readily gave high polymer while monomer **32** gave lower molecular weight polymer. Monomer **36** showed a propensity for macrocyclic oligomerization. The bicyclic oxalactone polymers, also stemming from dihydropyrans, have been reviewed [14–16].

*2.5. Ethers (**40–43**)*

Ethers (Table 5) comprise the first group of oxygen-containing monomers we will consider which undergo cationic polymerization. Their polymerization involves oxonium ion intermediates. This topic has been reviewed [31].

Table 5. Bicyclic ether monomers **40–43** [31–36].

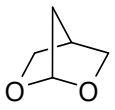
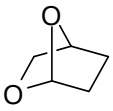
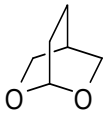
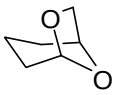
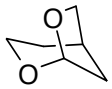
Bicyclo[2.2.1]heptanes		Bicyclo[2.2.2]octane	Bicyclo[3.2.2]heptane
			
40	**41** [31-34]	**42** [35]	**43** [36]

The stereochemistry of these polymerizations, involving nucleophilic displacement on the propagating oxonium ion, is trans. The isomeric 2-methyl-7-oxabicyclo[2.2.1]heptanes gave stereoregular polymers [32–34].

*2.6. Acetals (**44–52**)*

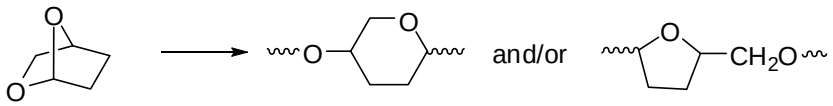
Unsubstituted acetal monomers (Table 6) were prepared by syntheses involving malonic ester alkylation followed by acid-catalyzed bicyclization with loss of methanol. Crucial to the success of these reactions was removal of the sensitive acetal by distillation under reduced pressure as it formed [37–40]. This topic has been reviewed [41–43].

Table 6. Bicyclic acetal monomers **44–49** [37–40,44,45].

Bicyclo[2.2.1]heptanes		Bicyclo[2.2.2]octane
		
44 [37,38]	**45** [37,38]	**46** [39]
Bicyclo[3.1.1]heptane		**Bicyclo[3.2.1]octanes**
		 
47		**48** [40] **49** [44,45]

Unsymmetrical acetals like **45** can cleave in either or both of two ways (Scheme III).

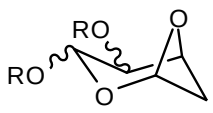
Scheme III. Ring-opening of an unsymmetrical acetal.



45

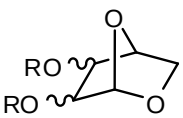
Although atom-bridged monomers have generally been unsubstituted, the acetals represent a marked exception. Numerous atom-bridged bicyclic acetals like **50**–**52** derived from sugars (Scheme IV) have been used to synthesize unnatural polysaccharides. Their hydroxyl groups are protected by benzylation or acylation before polymerization and can be removed after polymerization [46–49]. These substituents can produce stereoregularity in the oxacarbenium ion polymerization.

Scheme IV. Bicyclic acetal monomers **50–52** from sugars [46–59].



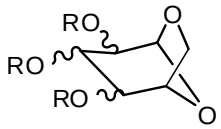
50 [46-49]

1,3-anhydropyranose
2,6-dioxabicyclo[3.1.1]heptanes



51 [50-54]

1,4-anhydropyranose
2,7-dioxabicyclo[2.2.1]heptanes



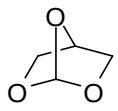
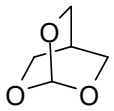
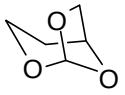
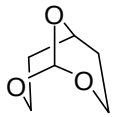
52 [55-59]

1,6-anhydropyranose
6,8-dioxabicyclo[3.2.1]octanes

*2.7. Orthoesters (**53–56**)*

Orthoesters (Table 7) are the third member of this oxygen group. They are synthesized from condensation of triols with ethyl orthoformate, again removing the bicyclic monomer as it forms [60–65]. This topic has been reviewed [41–43,66].

Table 7. Bicyclic orthoester monomers **53–56** [60–65,67].

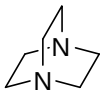
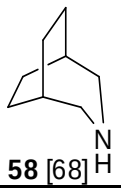
Bicyclo[2.2.1]heptane		Bicyclo[3.2.1]octane	Bicyclo[3.3.1]nonane
			
53 [60-62,67]	**54** [63]	**55** [64,65]	**56** [64]

For the bicyclic acetals and orthoesters, oxonium ion propagation is still predominant. However, for these monomers, cleavage of the oxonium ion to oxacarbenium ion can lead to loss of stereoregularity [66]. Moreover, in the many sugar-derived monomers, neighboring group participation by adjacent benzoate or benzyloxy groups plays a role in determining polymer stereochemistry.

*2.8. Amines (**57–58**)*

Finally, bicyclic amines **57** and **58** (Table 8) have also been polymerized cationically via S_N2 displacements on ammonium ion intermediates [66]. 1,4-Diazabicyclo[2.2.2]octane (**57**), widely used as a catalyst, is now seen to be a monomer itself.

Table 8. Bicyclic amine monomers **57–58** [68].

Bicyclo[2.2.2]octane	Bicyclo[3.2.2]nonane
	
57 [68]	**58** [68]

2.9. Attempted Correlations with Monomer Properties

2.9.1. Infrared

Carbonyl groups in small rings absorb infrared radiation at much higher frequencies than carbonyls in open chain analogs. However, we determined that the carbonyl absorption did not correlate with polymerizability of monocyclic monomers [69]. This also proved true for bicyclic monomers [70]. The higher carbonyl absorption frequency in small rings is attributed to orbital hybridization effects.

2.9.2. Saponification Rates

We tried and failed to correlate saponification rates with polymerizability for monocyclic monomers [71]. Our thought was that strain relief in polymerization might parallel strain relief in

saponification reactions. However, no parallel was found [70]. The same was true for bicyclic monomers [72]. The reason is that formation of tetrahedral intermediates, not ring opening, is the rate-determining step.

2.9.3. Dipole Moments

We noticed that lactones possess much higher dipole moments than their open-chain analogs and wondered whether this factor might be related to polymerization. However, this proved not to be the case [73]. For example, γ-butyrolactone and δ-valerolactone both have high dipole moments, yet only the latter polymerizes.

2.9.4. Polymer Properties and Uses

The physical properties of the polymers described herein have not been investigated to any great extent. Ring-opening polymerization of an atom-bridged-bicyclic monomer gives a linear polymer containing a ring in the chain. This often imparts desirable physical properties to the polymer, including increased melting point and glass transition temperature [74,75]. Polymerization of bicyclic ether **41** gives a crystalline polymer melting at 250 °C. while the polymer from tetrahydrofuran melts at 50 °C [31]. Given that the polymerization mechanisms for the bicyclic and monocyclic monomers are the same, the synthesis of new copolymers can be anticipated.

The polymers from bicyclic acetals, after deprotection, have been intensively studied as synthetic polysaccharides [76]. The polymeric orthoesters have been examined as bioerodible materials [66].

3. Conclusions

The polymerizabilities of the atom-bridged bicyclic compounds in this review are listed in Table 9. They almost all polymerize! The sole exceptions are bicyclo[3.3.1]nonanes; even here, *N*-bridgehead anti-Bredt lactams do polymerize.

Table 9. Polymerizability of bicyclic monomers in this review.

Monomer Structure	Polymerizability
Bicyclohexane [2.1.1]	+
Bicycloheptane [2.2.1]	+
Bicyclooctanes [2.2.2]	+
[3.2.1]	+
[4.1.1]	+
Bicyclononanes [3.3.1]	±
[3.2.2]	+
[4.2.1]	+
Bicyclodecane [4.3.1]	+

This surprising generalization requires explanation. For the small ring sizes (three and four members), angle strain and eclipsing interactions are important. For the common ring sizes (five to seven members), eclipsing interactions dominate. Often the six-membered rings in bicyclic monomers are locked into either boat or chair forms (the boat forms of cyclohexane are destabilized by about

8 kcal/mole relative to the chair forms). For larger rings, transannular hydrogen crowding as well as entropic considerations come into play. The monomers described possess combined 5- and 6-membered rings. Although no significant angle strain occurs, ring fusion causes eclipsing H–H repulsions. The cyclohexane rings in many of the monomers are locked into boat forms with strain energies of ~8 kcal/mole. The non-polymerizability of bicyclo[3.3.1]nonanes possessing two stable chair forms supports this line of thought. Second, amide and ester bridges are forced into energetically unfavorable cis conformations. Third, entropic considerations favor polymerization; chain polymers have many more available conformations than the rigid bicyclic monomers. Fourth, the bridgehead N–C=O structure present in the anti-Bredt monomers described above is a powerful driving force for polymerization. Fifth, isomerization of an initially formed *cis*-disubstituted ring to a thermodynamically favored *trans*-disubstituted ring is another driving force in cases where the carbonyl group is attached to the ring and epimerization is permitted. Bicyclic monomers possess these attributes to varying degrees, but the sum is almost always sufficient to cause polymerization.

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