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RING-OPENING POLYMERIZATION OF BICYCLIC ETHERS

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Abstract - The ring-opening polymerization of bond-bridged and atom-bridged bicyclic ethers containing the oxacyclopentane ring (THF) is comprehensively reviewed. The discussion of the thermodynamics reveal that an indispensable requirement for the first type to polymerize is a trans configuration at the bond bridge. In the second type varying substituents with respect to kind, number and position on the parent structure are tolerated owing to the common, strained 1,4 oxygen linked cyclohexane boat form. Structure examinations of the polyethers by NMR in connection with suitable model compounds in all instances allow the direction of the ring-opening to be deduced, including examples of bicyclic ethers containing larger oxacycloalkanes. Recent high resolution ^{13}C NMR analyses of the polyethers of the trans bond-bridged monomers reveal detailed microstructures indicating no stereochemical selection in the propagation. The kinetic investigations have cast light on the factors governing especially the propagation reactions. Whereas the atom-bridged monomers generally suffer from termination, the bond-bridged monomers are only influenced by two kinds of transfer reactions retaining the reactivity of the oxonium ions. The complete mechanistic interpretation of the polymerization of the bond-bridged monomers is discussed in relation to similar findings recently emerging for the oxacyclopentane polymerization.

INTRODUCTION

In general, polymerization of bicyclic monomers is an excellent tool in the design of new polymers containing rings in the polymer backbone. This provides the possibility of extending the range of polymers with particular backbones, with the aim of obtaining desirable properties with respect to thermal and mechanical behaviour of the polymers.

The fact that bicyclic ethers can be converted by a ring-opening reaction, initiated by cationic species, into polymeric materials has been known for two decades. During the later years numerous contributions have appeared reporting detailed information about various aspects of the polymerization of bicyclic ethers. We wish here to present a review of this work in the light of our most recent results and also in connection with the consideration of recently published work on the polymerization of oxacyclopentane (THF). We will essentially restrict the review of the thermodynamics, kinetics and mechanisms of the polymerizations to bicyclic ethers which contain the oxacyclopentane ring as part of the structure, and only brief mention will be made of compounds containing larger oxacycloalkane rings as well. Even with this limitation the number of possible modes of substitution as of actually investigated monomers is large, however, a convenient subdivision is provided by the possible structural forms. The bicyclic ethers to be discussed may be considered as disubstituted oxacyclopentanes:

1) spiro compounds (disubstitution on same carbon),
2) bond-bridged (substituents separated by a bond),
3) atom-bridged (rings have one or more atoms in common).

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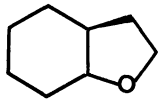
Compounds of the first type although interesting in connection with polymerization with expansion in volume will not be considered in this review.

Compounds of the bond-bridged type which will be reviewed are the following trans-7-oxabicyclo[4.3.0]nonane (1), trans-8-oxabicyclo[4.3.0]nonane (2), trans-2-oxabicyclo[3.3.0]octane (3) and trans-3-oxabicyclo[3.3.0]octane (4), (as racemates). Also, the bicyclic ethers with the corresponding cis structures will be mentioned, however, the comprehesive discussion of the behaviour of the four trans monomers is the main subject of this review.



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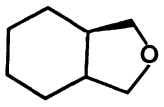

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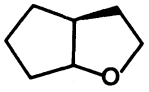

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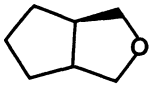

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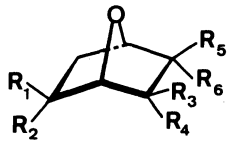
The atom-bridged bicyclic compounds which will be considered are indicated by the structure below and the following derivatives will be considered (as racemates where it applies):



5: 7-oxabicyclo[2.2.1]heptane (7-OBCH) (R_1=R_2=R_3=R_4=R_5=R_6=H)
6: exo-2-methyl-7-OBCH (R_1=CH_3,R_2=R_3=R_4=R_5=R_6=H)
7: endo-2-methyl-7-OBCH (R_2=CH_3,R_1=R_3=R_4=R_5=R_6=H)
8: exo-2-tert.-butyl-7-OBCH (R_1=$C(CH_3)_3$,R_2=R_3=R_4=R_5=R_6=H)
9: endo-2-tert.-butyl-7-OBCH (R_2=$C(CH_3)_3$,R_1=R_3=R_4=R_5=R_6=H)
10: exo-2-chloro-7-OBCH (R_1=Cl,R_2=R_3=R_4=R_5=R_6=H)
11: exo,exo-2,6-dimethyl-7-OBCH (R_1=R_3=CH_3,R_2=R_4=R_5=R_6=H)
12 endo,exo-2,6-dimethyl-7-OBCH (R_2=R_3=CH_3,R_1=R_4=R_5=R_6=H)
13: exo,exo-2,3-dimethyl-7-OBCH (R_3=R_5=CH_3,R_1=R_2=R_4=R_6=H)
14: endo,exo-2,3-dimethyl-7-OBCH (R_4=R_5=CH_3,R_1=R_2=R_3=R_6=H)
15: endo,endo-2,3-dimethyl-7-OBCH (R_4=R_6=CH_3,R_1=R_2=R_3=R_5=H)
16: exo,exo-2,5-dimethyl-7-OBCH (R_1=R_5=CH_3,R_2=R_3=R_4=R_6=H)
17: endo,exo-2,5-dimethyl-7-OBCH (R_2=R_5=CH_3,R_1=R_3=R_4=R_6=H)
18: endo,endo-2,5-dimethyl-7-OBCH (R_2=R_6=CH_3,R_1=R_3=R_4=R_5=H)

THERMODYNAMICS OF POLYMERIZATION

One of the basic requirements of a potential monomer is a favourable thermodynamics of polymerization i.e. the conversion of monomer should be accompanied by a sizeable decrease in free energy. In connection with the bicyclic monomers of this article the substitutional effects on the thermodynamics of polymerization of the oxacyclopentanes should be considered.

The thermodynamic concepts of ring-opening polymerization have been comprehensively discussed by Sawada (1). In general substitution of a cyclic compound reduces the free energy of polymerization of the substituted compound compared to that of the unsubstituted one. The introduction of substituents will raise the internal energy of the open chain polymer due to steric repulsions of the substituents. In addition, repulsion between the substituents, which changes the internal monomer angles, also makes the ring-opening less favourable. The overall effect of substitution will be a smaller enthalpy of polymerization of the substituted cyclic monomer compared to that of an unsubstituted analogue. The entropy of polymerization on the other hand is raised (larger negative value) by introduction of substituents on the rings mainly due to restricted rotation in the substituted polymer.

The effects of substitution are particularly important in the case of oxacyclopentane owing to the relatively small strain energy present in this molecule, 12.1 kJ·mol^{-1} (ref. 2). As a result, monosubstituted oxacyclopentanes cannot be converted into high polymers. The 3-methyl derivative forms low molecular weight polymers (ref. 3), the 2-methyl analogue can be obtained as oligomers (DP≈3) (ref. 4) and 2-chloromethyloxacyclopentane is inconvertible to any polymeric material (ref. 5).

Polymerizability and thermodynamics of bond-bridged monomers

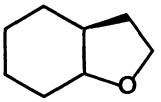
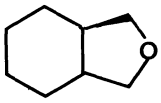
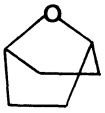
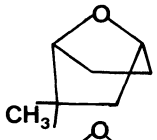
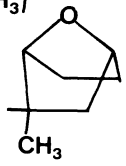
The effects of configuration in those monomers in which the oxacyclopentane ring is fused with five or six membered rings is remarkable. The striking feature is the decisive influence on polymerizability of whether the ring fusion corresponds to a cis or a trans substitution of the oxacyclopentane ring (structures 1 to 4). The polymerization investigations of the series of cis bicyclic ethers unequivocally report no formation of homopolymers whereas the corresponding trans monomers all can be converted into polymers (ref. 6-9). The conspicuous trend to be derived from these facts is in line with the predictions of the sensitivity of the enthalpy and entropy of ring-opening polymerization upon substitution. The fusion of the rings in the trans ethers introduces enough strain into the bicyclic structures to compensate for the substitutional effect on the enthalpy value and to counteract the unfavourable entropy contribution.

The few quantitative data available, presented in Table 1 indicate for monomers 1 and 2 an increased entropy of polymerization as compared to the unsubstituted parent compound. The particular set of data for oxacyclopentane in the Table has been selected from many other published and often quite scattered values because for these data allowance was made for the nonideality of the bulk system (ref. 10). In the case of trans-7-OBCN (1) the increased entropy of polymerization is seen to amount to around 15 J·mol^{-1}·K^{-1} as compared to oxacyclopentane. It appears to be a reliable measure of the order of magnitude of the substitution effects on the entropy of the ring-opening polymerization of cyclic ethers since the determinations were accomplished in the same manner. The small increase in enthalpy of polymerization of trans-7-OBCN again compared to oxacyclopentane corresponds to a somewhat higher strain in the bicyclic monomer. The data for trans-8-OBCN (2) are obtained for a solution system on the basis of the equilibrium concentration of monomer in methylene dichloride with the assumption of ideal behaviour and not taking solvent interactions into account (ref. 11). The values for this system cannot be compared with those above, since the interaction with solvent may have great influence on the thermodynamic parameters as recently pointed out by Penczek (ref. 12) and it is also seen that in this case a very low standard ceiling temperature (1 mol.l^{-1}) is found (T_c^o = -51°C).

Thermodynamic parameters for polymerization of the bond-bridged monomers trans-2-OBCO (3) and trans-3-OBCO (4) have not been determined. However, reliable indications of a high level of strain built into these structures are obtained from determinations of combustion enthalpies (ref. 13) for all four oxabicyclo[3.3.0]octanes. By this method a difference of ~20 kJ·mol^{-1} was found for the 2-oxabicyclo[3.3.0]octanes and up to 60 kJ·mol^{-1} in the 3-series. The differences were attributed to severe angular tensions in the trans isomers. These tensions are released by the transformation of the rigid and strained bicyclic structure to an essentially strainless linear macromolecule resulting in probable enthalpies of polymerizations of the order of 20-60 kJ·mol^{-1}. Previously (ref. 14), we have found in connection with a kinetic study of the polymerization of 3 and 4, that the conversion levels off in case of 3 but not in case of 4 indicating equilibrium conditions for the trans-2-OBCO. The equilibrium concentrations in methylene dichloride in the temperature range -20 to 0°C were 0.45 to 0.63 mol.l^{-1}.

The number of bond-bridged bicyclic ethers containing the oxacyclopentane ring as potential candidates for polymerization seems to be restricted to the trans compounds with a 5- or 6-membered alicyclic ring as discussed here. Preparations of trans compounds fused with smaller alicyclic rings have not been re-

TABLE 1. Thermodynamic parameters for polymerization of bicyclic ethers in comparison with the parent compound.

Monomer	$-\Delta H_p^o$ kJ·mol^{-1}	$-\Delta S_p^o$ J·mol^{-1}·K^{-1}	T_c °C	Ref.
	12.6 (lc)	41.0 (lc)	80	10
 1	14.0 (lc)	55.7 (lc)	12	7
 2	10.6 (ss)	48.6 (ss)	-51[a]	11
 5	44.3 (lc)	75.3 (lc)	320	18
 6	49.7 (lc)	96.2 (lc)	240	18
 7	45.4 (lc)	96.2 (lc)	200	18

(lc) denotes liquid monomer → condensed polymer (bulk polymerizations).
(ss) denotes monomer in solution → polymer in solution (methylene dichloride).
a T_c^o (at 1 mol·l^{-1}).

ported which is quite understandable since tremendous angle distortions would be required in these hypothetical compounds as indicated by molecular models. The corresponding cis compounds have been prepared in which the oxacyclopentane ring is fused either with a cyclobutane ring, 3-oxabicyclo[3.2.0]heptane (ref. 15) or a cyclopropane ring, 3-oxabicyclo[3.1.0]hexane (ref. 16). However, these will not undergo polymerization and therefore bicyclic ethers of the bond-bridged type with a cis structure will not undergo polymerization. Studies of molecular models of higher homologues where the alicyclic rings contain 7 or more members reveal rather strainless structures. Based on this and the knowledge of the thermodynamic parameters of trans-7- and trans-8-OBCN it is concluded that higher homologues will not gain sufficient strain to be able to polymerize.

Polymerizability and thermodynamics of atom-bridged monomers.

A striking feature of the atom-bridged oxacyclopentanes is the willingness to polymerize owing to the strain present in these structures. The many different examples (structures 5 to 18) of atom-bridged oxacyclopentanes all have the rigid skeleton of 7-oxabicyclo[2.2.1]heptane (7-OBCH) in common. With reference to the original chosen subdivision of the monomers to be discussed, these structures can also be described as 2,5-disubstituted oxacyclopentanes. The parent rigid structure is seen to be composed of a cyclohexane permanently

locked into a boat conformation by a 1,4-linked oxygen-bridge with no possibility of interconversion in the monomeric form.

A variety of substituents on the parent 7-OBCH will allow the monomers to be polymerized including not only methyl substituents but even the very bulky tert-butyl and the more polar substituent chlorine (ref. 17). In this connection the apparent insensitivity to the configurational arrangement of the substituents with regard to polymerizability should be noted. This is in marked contrast to the conditions existing in the bond-bridged oxacyclopentanes as already accounted for, however, for these, the configurational effects are related to the part of the molecules which are incorporated into the polymer in connection with the ring-opening reaction. In case of the substituted 7-OBCH's the inherent strain in the bicyclic structure is such that compounds containing two methyl substituents in different positions and configurations generally is able to undergo polymerization. It should be noted that such monomers are expected to suffer from a very unfavourable entropy change upon polymerization.

The enthalpies of polymerization of 7-OBCH, exo-2-methyl-7-OBCH, and endo-2-methyl-7-OBCH have been derived from enthalpies of combustion of liquid monomers and corresponding polymers (ref. 18). The parallel entropies of polymerization also listed in Table 1 were estimated by group additivity relations. The enthalpies of polymerization of these monomers, 44-50 $kJ \cdot mol^{-1}$, are much higher than those of the bond-bridged oxacyclopentanes and oxacyclopentane as seen in the Table. The data also show that the methyl substituent only influences the enthalpy of polymerization to a very small extent although in both instances result in a small increase. This proves the anticipated predominance of the strain relieved by the opening of the rigid skeleton being almost exclusively responsible for the polymerization as the driving force.

The estimated entropies of polymerization are on the other hand increased considerably in the two substituted 7-OBCH's as compared to 7-OBCH, obviously caused by the substituent on the parent structure, and they all show marked increases compared to the bond-bridged oxacyclopentanes and oxacyclopentane. The consequence of the resulting high ceiling temperatures computed as indicated in Table 1 is an extremely small concentration of monomer in equilibrium with polymer at $0^{o}C$ and below. This is in good agreement with the observation (ref. 19) that no exo-2-methyl-7-OBCH could be detected in a depolymerization experiment at $-20^{o}C$ after 96 hours.

DIRECTION OF THE RING-OPENING

Ring-opening of bond-bridged monomers.

The polymerizations of the four trans bicyclic ethers (1 to 4) can be effected by initiators typical for cationic ring-opening polymerization without the use of coinitiators or promotors. Generally phosphorous pentafluoride is an excellent initiator for the polymerization of these monomers. The use of triethyloxonium hexafluorophosphate as initiator for most of these monomers, trans-8-OBCN, trans-2-OBCO, and trans-3-OBCO, has been carefully investigated (ref. 11, 14). The polymerization of trans-3-OBCO has been initiated by boron trifluoride·tetrahydrofuran as well (ref. 9). Although the actual initiation process for cyclic ethers still seems to be debatable with the Lewis acid initiators just mentioned, the propagation is evidenced in all cases to proceed by oxonium ions.

Detailed knowledge of the direction of the ring-opening in the propagation reactions has been obtained by ^{13}C-NMR analyses of the polymers (ref. 9, 20, 21). Spectra of poly(trans-3-OBCO) and poly(trans-7-OBCN) are shown in Fig. 1 and 2. In Table 2 the ^{13}C chemical shifts are listed for the repeat units in the four polymers of 1 to 4 including the corresponding trans and some cis diethyl ether model compounds. The model ethers were obtained from the appropriate cycloalkanediols. The polymer spectra were recorded at 67.89 MHz on sufficiently high molecular weight polymers ($\bar{M}_n$>10,000) to ensure absence of any signals from end groups. Accordingly, each polymer spectrum consisted of the indicated number of single lines or finely split signals corresponding to the number of non-symmetrical carbons in the repeat unit. The spectra of the model compounds recorded at 22.63 MHz, on the other hand, consisted in each

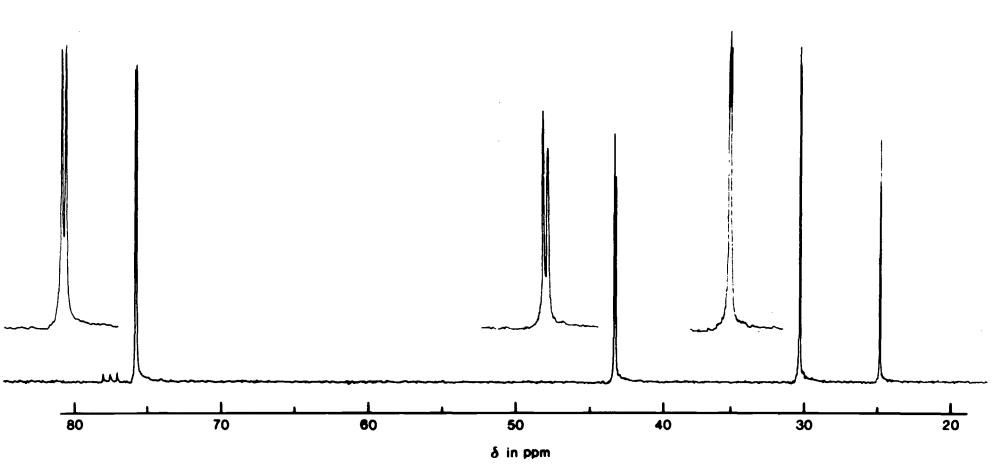


Fig. 1. ^{13}C NMR spectrum of poly(trans-3-oxabicyclo[3.3.0]octane). 10% solution in deuterochloroform, 1064 scans at 67.89 MHz, expansions 4× horizontally.

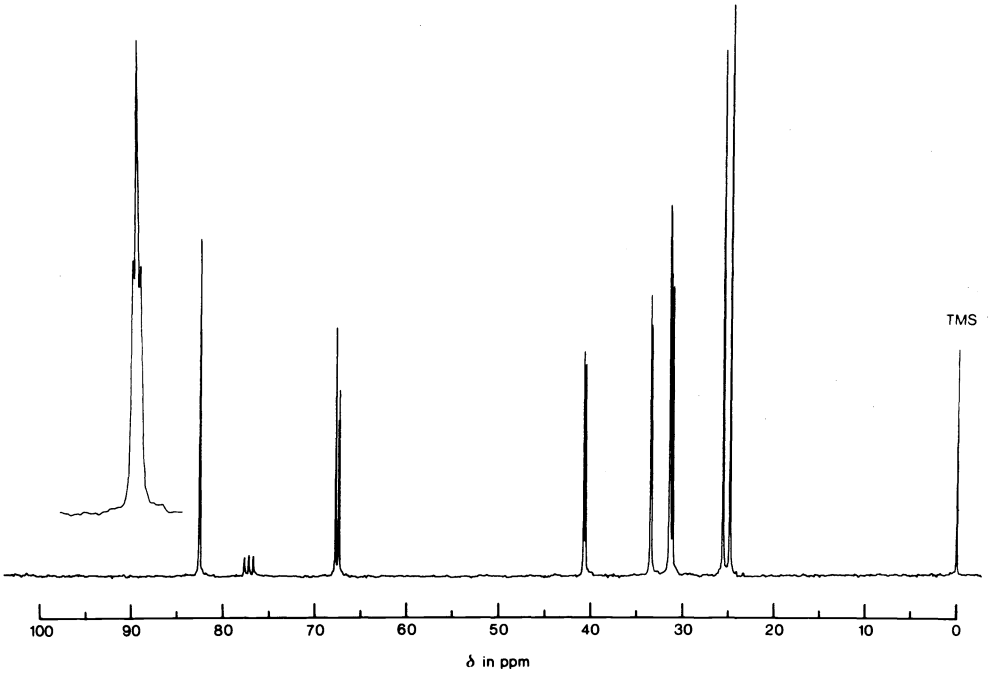
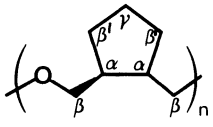
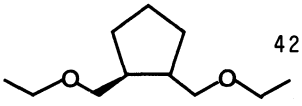
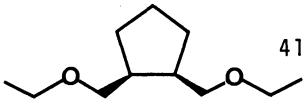
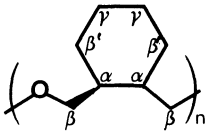
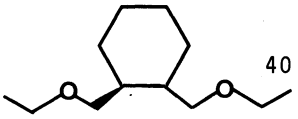
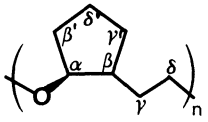
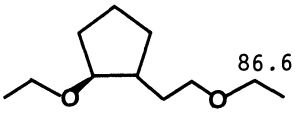
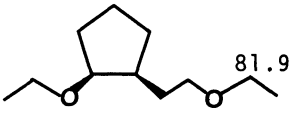
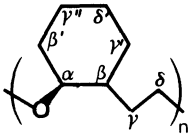
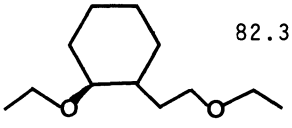


Fig. 2. ^{13}C NMR spectrum of poly(trans-7-oxabicyclo[4.3.0]nonane). 10% solution in deuterochloroform, 2400 scans at 67.89 MHz, expansion 9× horizontally.

case of a number of single lines corresponding to the number of non-symmetrical carbons of which only the relevant shifts are shown.

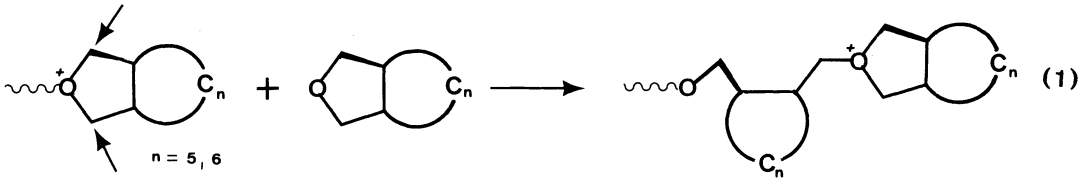
The comparison of the polymer spectral data with those of the appropriate models clearly reveals that the fine splittings do not originate from different configurational single units in the respective polymer chains. Isomeric cis units, if these were present, would generally be expected from the data on the models, to give rise to shieldings of the order of 1-5 ppm in the polymer chains, i.e. much larger than any of the detected splittings. On this basis we conclude that the trans configuration present in the monomers is unequivocally preserved after the insertion into the polymers. In the case of trans-3-OBCO and trans-8-OBCN the implication is that polymerization proceeds by

TABLE 2. ^{13}C Chemical shifts of poly(trans-3-OBCO), poly(trans-8-OBCN), poly(trans-2-OBCO), and poly(trans-7-OBCN) in comparison with model compounds[a].

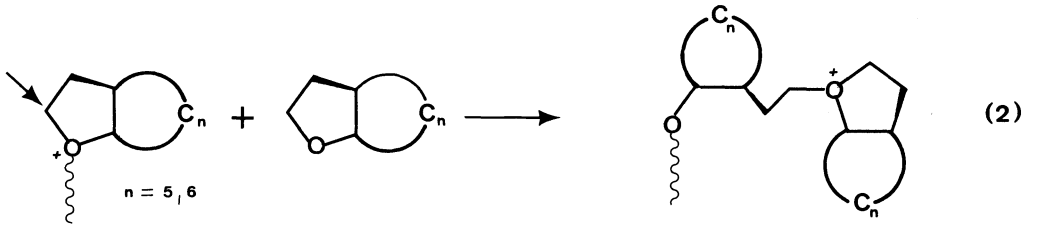
	α	β	γ	δ	β'	γ'	δ'	γ''
	42.85 42.76	75.30 75.22	24.77		30.25 30.23			
	42.8	74.9	24.6		30.2			
	41.4	71.3	23.4		29.0			
	40.32	74.62	26.10		30.29			
	40.3	74.2	26.0		30.2			
	86.85 86.82	42.79 42.65	34.72 34.69	68.41 68.29	31.32 31.26	30.32 30.25	22.54	
	86.6	42.7	34.4	69.7	31.4	30.4	22.6	
	81.9	41.7	29.1	70.0	30.8	29.3	21.9	
	82.44 82.38 82.33	40.73 40.54	33.45 33.35	67.67 67.37 67.29	31.33	31.22 30.98	25.50	24.71
	82.3	40.7	32.8	69.4	31.5	31.2	25.5	24.8

a δ_C, ppm downfield from internal tetramethylsilane.

nucleophilic attack on either of the two equivalent methylene carbons adjacent to the oxonium ion in the propagating species, succeeded by cleavage of the oxygen-methylene carbon bond:



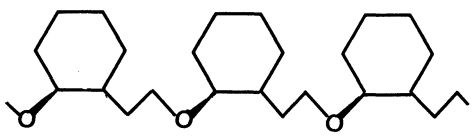
The polymerization of trans-2-OBCO and trans-7-OBCN is likewise in accordance with nucleophilic attack of the incoming monomer on the methylene carbon adjacent to the oxonium ion:



Attack instead on the other possible position, the tertiary methine carbon, would result in inversion of the configuration and require the presence of cis enchainments of the cycloaliphatic rings in the polymer. A mixture of both types of ring-opening would also require the presence of irregular units corresponding to head-to-head structures which as already indicated are not present. The preclusion of attack on the tertiary carbon is believed to be due to severe steric hindrance.

The fine splittings (0.02-0.5 ppm) listed in Table 2 for the polymers consisted in each case of two closely spaced peaks of nearly equal intensity, with the exception of poly(trans-7-OBCN) for which some triplet signals were observed. The doublet splittings are due to the existence of equal amounts of diastereomeric dyads in the polymers. These dyads originate from the presence of chiral carbons in the monomers exemplified by poly(trans-3-OBCO):

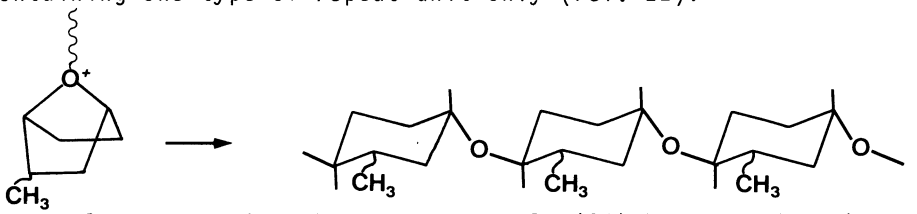
The carbons labelled β' in poly(trans-3-OBCO) and β' and γ' in poly(trans-2-OBCO) (see Table 2) are evidenced to be sensitive to the configuration of the closest chiral carbon in the next units. This configurational effect is thus ultimately experienced at a five bond distance corresponding to an ε substituent effect. In poly(trans-7-OBCN) a distinct triplet signal (see Fig. 2) with the intensity ratio 1:2:1 is observed for the methine carbon next to the oxygen. This is believed to originate from different triads in this chain exemplified with an isotactic triad:



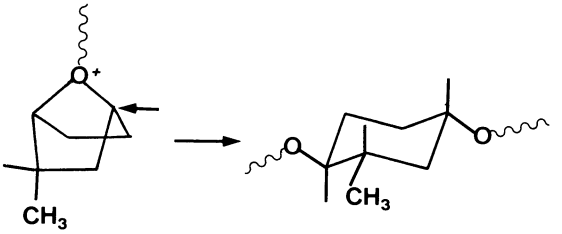
The observed intensity ratio also corresponds to the correct ratio between iso-, hetero-, and syndiotactic triads resulting from a random incorporation of the mixture of enantiomeric monomers. The information on the microstructure of the polymers consequently proves the expected homogeneous nature of the initiating systems responsible for the polymer growth without any indication of stereo selection in the propagation.

Ring-opening of atom-bridged monomers.

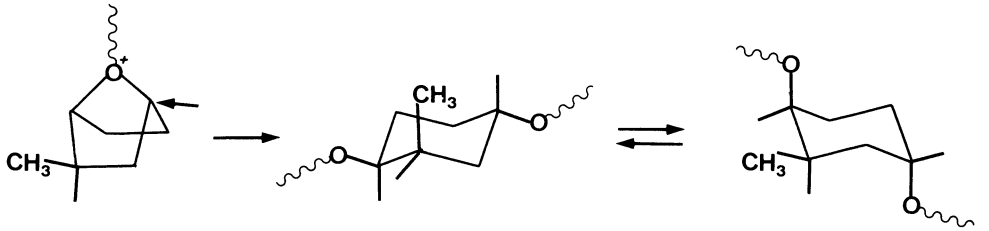
The polymerization of endo- and exo-2-methyl-7-OBCH has been studied extensively using phosphorous pentafluoride (ref. 22) or boron trifluoride•tetrahydrofuran in combination with epichlorohydrin (ref. 23). The question of the direction of the ring-opening in these polymerizations, involving a change in configuration of the C-1 or C-4 atom in connection with the nucleophilic attack, was elucidated by studies of the stereochemistry of the resultant polymers. IR was used to demonstrate that each monomer was converted to regular polymer structures containing one type of repeat unit only (ref. 22):



The same result was obtained by Saegusa et al. (23) by comparing the proton NMR spectra of the polymers with spectra of suitable model compounds. This study also revealed that both monomers attacked exclusively from the least hindered side at C-4 of the propagating oxonium ion. In case of the endo isomer this results in a polymer in which the two ether groups as well as the methyl group are equatorially positioned on the cyclohexane in a essentially fixed conformation:

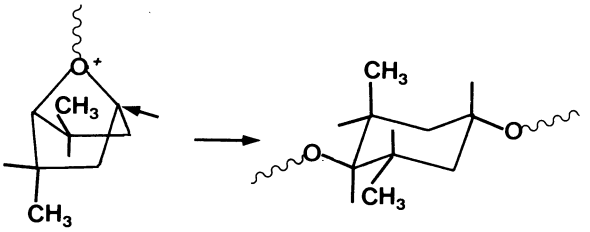


The exo isomer on the other hand, is converted to a polymer where the methyl group always is cis to the nearest oxygen bridge (axial-equatorial relationship) with an equilibrium mixture of conformers as a consequence:

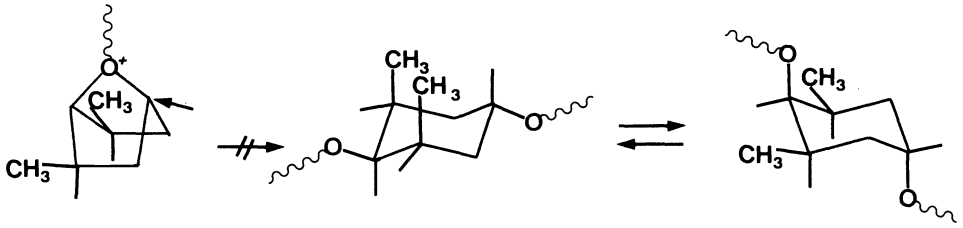


Almost identical conclusions were reached in a very similar study of the stereochemistry of the polymerization of endo- and exo-2-tert.-butyl-7-OBCH (ref. 24). However, in case of the exo polymer a predominance of the conformer having the tert.-butyl in an equatorial position and the other groups axially positioned, was indicated by proton NMR, which is not surprising in view of the size of the tert.-butyl substituent.

Polymerizability studies of the dimethyl derivatives of 7-OBCH with a systematic variation in the combination of substituents on the secondary carbons of the parent compound have revealed interesting stereochemical aspects of these systems. In a polymerization investigation of endo,exo- and exo,exo-2,6-dimethyl-7-OBCH with phosphorous pentafluoride (ref. 22) only the former polymerized, resulting in a highly crystalline and consequently insoluble polymer. The anticipated attack on the least sterically hindered methine, C-4, will result in repeat units with three equatorial substituents and one axial methyl on the chair cyclohexane:

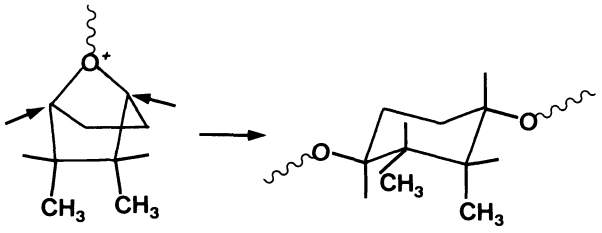


It should be noted, however, that attack on C-1, although not expected, would lead to the same structural unit. These units are not believed to exist in equilibrium with the other chair conformer containing the energetic very unfavourable three axial and one equatorial substituents. The failure of the exo,exo isomer to polymerize was explained on conformational grounds. Ring-opening at C-4 would result in the very unfavourable 1,3-diaxial interaction of two methyl groups:

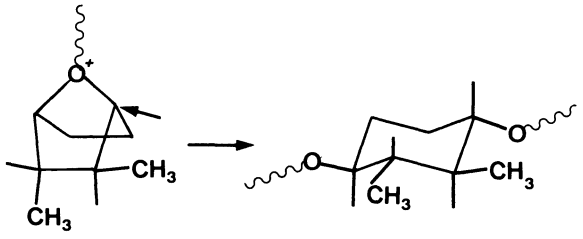


The indicated equilibrating conformer also contains two axial substituents, apparently still energetically unfavourable despite the resulting relief of strain in the monomer. As before attack on C-1 is precluded for steric reasons, although in this instance a very favourable conformer with four equatorial substituents would result.

The polymerization of endo,endo, endo,exo and exo,exo isomers of 2,3- and 2,5-dimethyl-7-OBCH by various cationic initiators has recently been investigated by Saegusa et al. (25). The direction of the ring-opening was again clarified by the stereochemistry of the resulting polymers as analysed by proton NMR. The symmetry of both endo,endo and exo,exo monomers and of the propagating species derived thereof makes the C-1 and C-4 indistinguishable, and the attack may occur with equal probability at both positions as exemplified for endo, endo-2,3-dimethyl-7-OBCH:



The same conformational structure is obtained with the exo,exo isomer. The polymers of the symmetrical monomers of the 2,5 series were also identical, different from the 2,3 isomers only by the positioning of one methyl. In case of the asymmetrical endo,exo-2,3-dimethyl-7-OBCH ring-opening at C-4 exclusively was demonstrated, leading to a conformationally very stable structure containing four equatorial substituents:



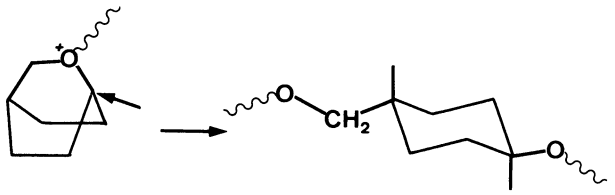
A similar situation was deduced to prevail in case of polymerization of the endo,exo-2,5-dimethyl-7-OBCH, although actually not demonstrated due to the insolubility of the polymer caused by high crystallinity.

Polymerization of bicyclic ethers containing larger oxacycloalkanes.

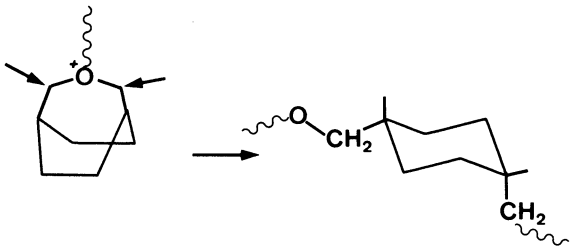
The inability of oxacyclohexane (tetrahydropyrane) to polymerize and the sluggish polymerization of oxacycloheptane (oxepane) (ref. 26) are understandable in view of the thermodynamic conditions existing in these systems (ref. 1). In line with the substitutional effects thoroughly discussed previously, it is, however, possible to introduce sufficient strain into bicyclic structure containing these parent compounds to promote polymerization. The polymerization of 2-oxabicyclo[2.2.2]octane formally regarded as a 2,5-disubstituted oxacyclo-

hexane has been demonstrated (ref. 27). Very recently 3-oxabicyclo[3.2.2]-nonane, which may be considered as a 3,6-disubstituted oxacycloheptane, has been polymerized (ref. 28).

The polymer prepared by ring-opening of 2-oxabicyclo[2.2.2]octane induced by various cationic initiators was demonstrated to contain one type of structural unit only (ref. 27). By comparing the proton NMR spectrum of the polymer with spectra of suitable model compounds it was concluded that this unit consists of a trans-1,4-disubstituted cyclohexane ring. This implies that the incoming monomer exclusively attacks C-1 and causes an inversion which leads to an all trans structure:



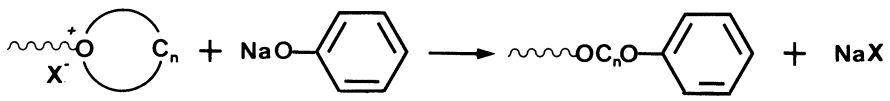
The initial attempt to polymerize 3-oxabicyclo[3.2.2]nonane with the powerful phosphorous pentafluoride initiator failed (ref. 29), although the necessary formation of an adduct between monomer and initiator was proved by ^{19}F NMR. The failure was not caused by unfavourable thermodynamics, but attributed to be due to the geometry of the adduct. The monomer was unable to approach closely the adduct to bring about the actual initiation. The cyclohexane boat form in this monomer deviates considerably from the rigid one in 7-OBCH due to the bridge consisting of three atoms which result in an almost globular form of this monomer. The conclusions were supported by addition of a small molecule promotor, epichlorohydrin, which ensured the polymerization (ref. 28). A ^{13}C NMR spectrum clearly revealed the polymer to consist of one type of structural unit only. It was found by proton NMR, in connection with studies on model compounds that the bridges of dimethylene ether in the 1,4 positions of cyclohexane are cis positioned. The monomer attack on either C-2 or C-4 of the propagating oxonium ion, being equally accessible due to the symmetry of the monomer, does not alter the configuration present at the two methine bridge carbons, and will result in the observed cis configuration:



KINETICS OF POLYMERIZATION

The main problem associated with kinetic studies of cyclic ethers is to obtain a reliable knowledge of the concentration of oxonium ions. Obviously this would be important if the rate of propagation is orders of magnitude higher than that of initiation. Other complications could turn up due to transfer or termination reactions in these cationic polymerizations, the latter often caused by the use of certain initiators of which the counteranions are ultimately derived. Unfortunately no spectroscopic technique allows direct detection of the oxonium ions, although high-resolution ^{1}H NMR and ^{13}C NMR indirectly will indicate the oxonium ions. Both methods have been used with some success in kinetic studies of simple monocyclic ethers, however, relatively high concentrations of oxonium ions are necessary. The use of the most suitable technique, ^{1}H NMR, would furthermore be complicated by many overlapping resonances in bicyclic monomers.

Another method, based on the conversion of oxonium ions to phenyl ethers by end-capping with sodium phenoxide (ref. 30):



nevertheless allows the original concentration of oxonium ions (including very small ones) to be estimated by UV spectroscopy. This method has only few limitations and has successfully been applied to many bicyclic monomers including the systems discussed in the following sections.

A recent very promising approach by Penczek et al. (31) is based on the instantaneous and quantitative trapping of the oxonium ions by reaction with triaryl- or trialkylphosphines to produce stable quarternary phosphonium ions. The general applicability possibly to all kinds of cations and the extreme sensitivity of the ^{31}P chemical shifts to the chemical environment in the generated ions make this method very advantageous. Very recent results indicate, however, that complications may arise if triphenylphosphine is used to detect oxonium ions in grafting polymerizations when the oxonium ions are generated by the alkyl halide/silver salt procedure due to multiple reactions between that phosphine and the silver salt (ref. 32).

Kinetics of polymerization of bond-bridged monomers.

A comprehensive study involving kinetics of initiation, propagation and termination was accomplished in case of trans-2-OBCO and trans-3-OBCO by polymerization with triethyloxonium hexafluorophosphate in methylene dichloride (ref. 14). This initiator produces a counteranion which is stable in the investigated temperature interval -30 to $0^{o}C$, and accordingly will not cause transfer or termination. Another main advantage is the inherent natur of the initiator already being an oxonium ion, which in addition allowed the kinetics of the initiation to be studied in connection with the end-capping, since it is possible to separate, for individual determination of the concentration, the two types of phenyl ether produced in the terminated polymerization mixture. Phenetole originates from the unreacted initiator and phenyl ether groups from the propagating oxonium ions.

The conversion of the monomers was demonstrated to be strongly temperature dependent, in case of trans-2-OBCO an actual equilibrium conversion was reached as previously stated. The apparent dependence was caused by a slow but continuous initiation throughout the entire conversion range investigated, the initiation itself being temperature dependent. Termination corresponding to a decrease in concentration of propagating species was never detected, not even after extended times. Initiation and propagation occur by S_N2 reactions where the monomer attacks the triethyloxonium ion or the strained propagating cyclic oxonium ion, respectively. The difference in the mode of propagation of trans-3-OBCO and trans-2-OBCO, as discussed previously, is evident from Eq. 1 and 2.

The rate data were obtained on the basis of the expressions for initiation and propation integrated with respect to time and are listed in Table 3. Based on Arrhenius plots of each set of rate constants the activation energy $\Delta E^{\ddagger}$ and A were obtained. The kinetics of polymerization of trans-8-OBCN was studied under the same conditions (ref. 11). This study was conducted at 0 and $-10^{o}C$ and again it was revealed that the active species retained their activity over very long periods of time (investigated up to 200 hours). The propagation reaction is depicted in Eq. 1 and the rate constants were calculated as above and the data are also listed in Table 3.

The most conspicuous feature of the kinetics of trans-2-OBCO and trans-3-OBCO is that the initiation of both monomers proceeds more than three orders of magnitude slower than the propagation, as summarized in Table 3. This very large difference in rate between initiation and propagation is seen to be related particularly to the lower activation enthalpy of the latter. The lower $\Delta H_p^{\ddagger}$ values are explained by a consideration of the stability of the two types

TABLE 3. Rate constants and activation parameters of the polymerization of bond-bridged bicyclic ethers[a].

Temperature	k_i		k_p		
	trans-2-OBCO[b]	trans-3-OBCO[b]	trans-2-OBCO[b]	trans-3-OBCO[b]	trans-8-OBCN[c]
°C	10^3 l.mol^{-1}s^{-1}				
0	0.27		530		3.6
-10	0.068	0.22	140	240	1.0
-20	0.019	0.047	56	75	
-30		0.014		27	
	x=initiation		x=propagation		
$\Delta E_x^{\ddagger}$, kJ·mol^{-1}	76	73	64	58	
A_x, l.mol^{-1}s^{-1}	10^{11}	7×10^{10}	10^{12}	8×10^{10}	
$\Delta G_x^{\ddagger}$, kJ·mol^{-1}(-20°C)	85	82	68	67	
$\Delta H_x^{\ddagger}$, kJ·mol^{-1}	74	71	62	56	
$\Delta S_x^{\ddagger}$, J·mol^{-1}·K^{-1}	-42	-45	-22	-44	

a Methylene dichloride solvent and triethyloxonium hexafluorophosphate initiator.
b Ref. 14
c Ref. 11

of oxonium ions involved. The structure of the triethyloxonium ion is expectative essentially strainless due to the free mobility of the substituents. In contradiction to this the propagating oxonium ion is influenced by the severe strain in the cyclic part of the ion which is impossible to relieve, owing to the trans configuration present at the bond-bridge. The high strain decreases the stability of the ion which is reflected as increased reactivity.

Due to the lack of comparable investigations with triethyloxonium hexafluorophosphate for related systems only, a kind of standard of comparison for the initiation may be obtained from a proton NMR study of the rates of reaction between triethyloxonium tetrafluoroborate and oxacyclopentane,-hexane, and -heptane from 2.5 to 35°C (ref. 33). These alkylations corresponding to initiations were characterized by activation enthalpies in the range 68-69 kJ·mol^{-1}, almost comparable to the values reported in Table 3. The activation entropies ($-\Delta S_i^{\ddagger}$) on the other hand were ranging from 67 to 71 J·mol^{-1}·K^{-1}, considerably higher than those of the bicyclic monomers. This difference is tentatively interpreted in terms of desolvation of the ground state due to the charge dispersion in the transition state when the monomer reacts with the initiator. The difference in counteranion is expected to play a minor role, negligible in this respect. The bicyclic monomer is a larger molecule than the monocyclic ones and will accordingly demand more space when it solvates the oxonium ion, thus permitting fewer solvent molecules in the solvation shell around the oxonium ion. The smaller change in orderedness when fewer molecules are arranged in the solvation shell may account for the more favourable entropies of the initiation for the bicyclic monomers. Preferential solvation of the oxonium ion by monomer has also been proposed in polymerization of oxacyclopentane (ref. 34).

The propagation rate constants for the two cyclopentane containing monomers, trans-2-OBCO and trans-3-OBCO, are more than two orders of magnitude higher than those of the cyclohexane containing analogue, trans-8-OBCN, as evident from Table 3, possibly reflecting the difference in strain energy as previous-

ly indicated. A confrontation of these constants with rates of propagation for oxacyclopentane obtained under similar conditions at 0°C computed to 4.19×10^{-3} as an overall constant (ref. 35) or 0.87×10^{-3} and 21×10^{-3} $l.mol^{-1}s^{-1}$ for propagation via ion pairs and free ions (ref. 36) disclose the rate of trans-8-OBCN to be in a comparable range and accordingly the rates of trans-2-OBCO and trans-3-OBCO are the two orders of magnitude higher.

Kinetics of polymerizations of atom-bridged monomers.

The propagation of the alkyl substituted 7-OBCH's (6-9) initiated by the boron trifluoride•tetrahydrofuran/epichlorohydrin system in methylene dichloride have been investigated by Saegusa et al. (19, 37, 38). The entire course of the instantaneous concentration of propagating oxonium ions could be established because the kinetic analyses were performed by the phenoxyl end-capping method. The conversions to polymer were generally low due to ineffective initiation, in as much as up to 10% of the nominal concentration of initiator was the maximum achievable concentration of active species, and the fact that polymerizations were accompagnied by terminations in the range -40 to 0°C. The tert. butyl monomers suffered from fairly rapid termination caused by generation of olefinic ends which was pronounced especially at higher temperatures. In the case of the methyl substituted monomers the reason for the termination, which was still appreciable, was never discussed. In all instances the propagations were considered as irreversible S_N2 reactions since depolymerization was never detected for any of these monomers, and the data could be treated according to the integrated rate expression for such a system. The further treatment and computation to obtain the activation parameters were performed according to the previously indicated route, and all the relevant information is summarized in Table 4.

TABLE 4. Propagation rate constants and activation parameters of the polymerization of atom-bridged bicyclic monomers[a].

	Temperature °C	exo-2-methyl 6[b]	endo-2-methyl 7[c]	exo-2-tert.-butyl 8[d]	endo-2-tert.-butyl 9[d]
	0			11.5	
	-10	9.4	26.7	5.7	
k_p,	-20	2.6	8.4	2.5	13
10^3 $l.mol^{-1}s^{-1}$	-25				9.9
	-30	0.87	4.0	1.0	2.9
	-40	0.18	0.85		0.82
$\Delta E_p^{\ddagger}$, $kJ \cdot mol^{-1}$		64.0	57.7	46.4	69.4
A_p, $l.mol^{-1}s^{-1}$		4×10^{10}	7×10^9	5×10^6	3×10^{12}
$\Delta H_p^{\ddagger}$, $kJ \cdot mol^{-1}$		63.5	55.2	42.6	64.8
$\Delta S_p^{\ddagger}$, $J \cdot mol^{-1} \cdot K^{-1}$		-63.5	-41.8	-125.4	-25.1

a Methylene dichloride solvent and borontrifluoride•tetrahydrofuran/epichlorohydrin initiator
b Original data of ref. 19 as corrected in ref. 38
c Original data of ref. 37 as corrected in ref. 38
d Ref. 38.

The propagation rate constants of the endo and exo isomers of the two series are similar to each other, but within one series the endo isomer is more reactive than the exo isomer. A tempting interpretation based on increased reactivity in the endo isomers due to less stability as a result of more strain arising from repulsions between the alkyl groups and hydrogens on C-3 and C-6 in the propagating oxonium ions, apparently is only valid for the methyl monomers. The activation parameters listed in Table 4 reveal that endo-2-tert.-butyl-7-OBCH has a considerably higher activation ethalpy than the exo isomer 8, however, this unfavourable contribution to the rate constants is obscured by the corresponding entropies of activation. The very unfavourable entropy of activation of 8 was tentatively explained by decreased solvation in the ground state (ref. 38). The very bulky tert.-butyl in the exo position is expected to shield the oxonium ion much more than in the endo position. The same explanation would account for the entropies of activation in the methyl series realizing that this difference is much smaller as expected when a substantially smaller group is involved.

These atom-bridged monomers are seen from Table 4 to propagate in a range from 1 to 2 orders of magnitude slower than the bond-bridged trans-2-OBCO and trans-3-OBCO (Table 3). The differences are much larger than those which could be expected to be due to the different initiators resulting in different counteranions.

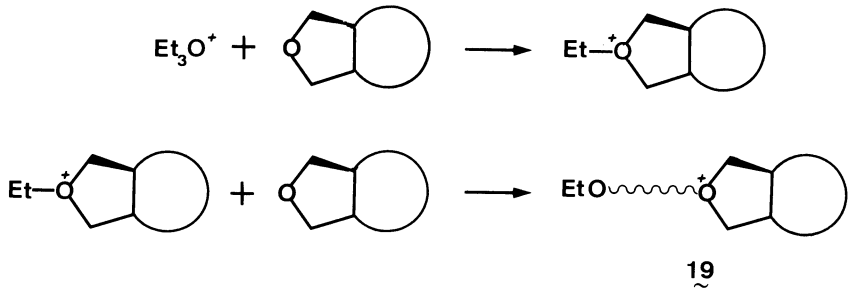
MECHANISMS AND OLIGOMERIZATION

The present available results on the polymerization of the bond-bridged monomers allow a rather detailed mechanistic interpretation which will be discussed below. On the other hand in case of the atom-bridged monomers the present information appear to be insufficient on many points and no attempt will be made to further discuss these systems.

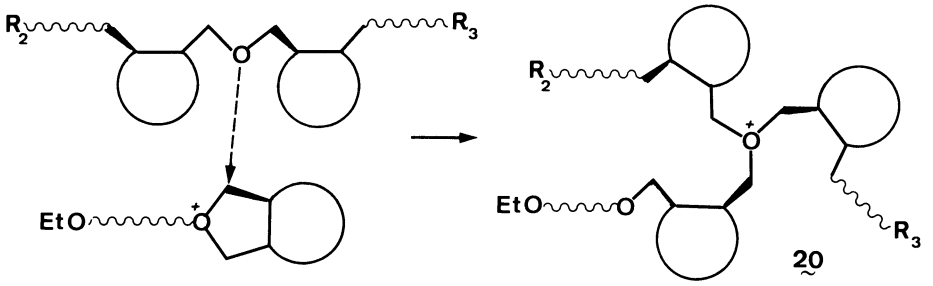
The kinetic analyses of the polymerization of the bond-bridged monomers have accounted for the fate of all initially charged oxonium ions. The lack of termination for these polymerizations indicates a "living" character. Normally the characterization of the system is also based on an inspection of the molecular weights and their ratios. Although the analysis is somewhat complicated in the case of trans-2-OBCO and trans-3-OBCO due to the initiation being much slower than the propagation, the investigation of the molecular weights, however, suggest the polymerizations to be influenced by two kinds of transfer. The first type results in polydispersity indices ($\bar{M}_w/\bar{M}_n$) in the range 2.0-2.4 and a very slow increase of the molecular weights of poly(trans-3-OBCO) and, in case of poly(trans-2-OBCO), even a decrease in the values are actually observed with reaction time, especially for $\bar{M}_w$ (ref. 14). The second kind of transfer is apparent from the fact that the expected molecular weight calculated on the basis of the ratio between the concentrations of converted monomer and propagating oxonium ions always was approximately twice that of $\bar{M}_n$ as determined by GPC. In other words, a process different from initiation creates new growing chains.

In contrast poly(trans-8-OBCN) showed a steady and parallel increase in molecular weights reflected in a polydispersity index of around 1.2 until approximately 30% conversion (ref. 11). This behaviour is apparently a result of the expected comparable rates of initiation and propagation for trans-8-OBCN. After this conversion is attained the transfer becomes noticeable resulting in a broadening of the distribution and finally a $\bar{M}_w/\bar{M}_n$ value close to 2 is obtained. However, also in this instance the expected molecular weights invariably were by a factor of two larger than the actually determined $\bar{M}_n$'s.

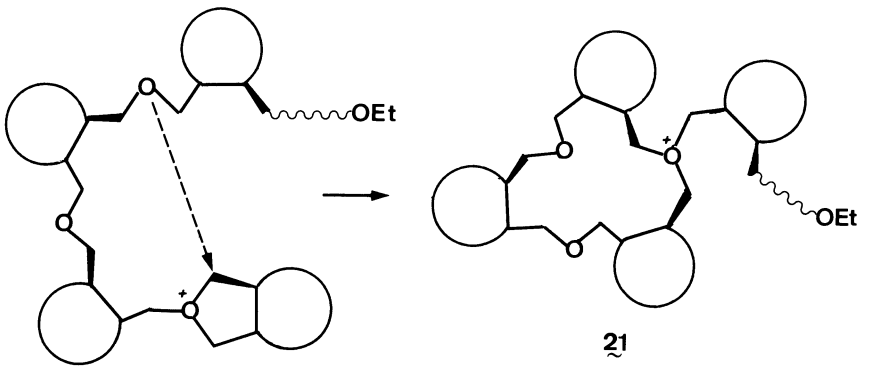
The entire course of polymerization of these bond-bridged monomers is then described by this simplified schematical outline where the counteranion is omitted (a scheme is shown describing the reaction of trans-2-OBCO and trans-8-OBCN):



19



20



21

The two transfer reactions are in accordance with inter- or intramolecular attack of oxygen in polymer chains on the propagating cyclic oxonium ion 19. The resulting new oxonium ions, the acyclic 20 and the macrocyclic less strained 21, are expected to have reactivities comparable to that of the triethyloxonium ion, which make them "dormant" in the case of trans-3-OBCO and trans-2-OBCO. Monomer reaction with the dormant acyclic species 20, by attack at one of the three equivalent α positions to the oxonium ion, will regenerate the original cyclic oxonium ion 19 and in two out of three instances result in the redistribution of the molecular weights. When monomer reacts with the macrocyclic oxonium ion 21, the regeneration of 19 may also be achieved by attack at two neighboring positions, however, attack at the exocyclic α position leads to formation of non-reactive cyclic oligomers. A reexamination of poly(trans-2-OBCO) and poly(trans-3-OBCO) by GPC optimized to resolution of the low molecular part clearly indicate the presence of small amounts (~1%) of cyclic trimer and tetramer in reasonable agreement with the number average weight considerations. Similar results from poly(trans-8-OBCN) substantiate the mechanism and an unequivocal proof was obtained from an investigation of this polymer by mass spectrometry using the chemical ionization technique. This analysis demonstrated the presence of species with molecular weights corresponding exactly to cyclic oligomers from trimer up to hexamer.

The mechanistic similarities of these polymerizations to that of oxacyclopentane should be stressed. The transfer to polymer oxygen of poly(oxytetramethylene) was first demonstrated by Dreyfuss and Dreyfuss (39) in a GPC investigation. Later Franta et al. (40-42) supplied an effective chemical proof by examination of multifunctional oxocarbenium initiators generating one, two, three or ten oxonium ions on each chain where the latter was obtained by grafting onto a polymer backbone. Mono- and difunctional initiators produced mobile polymers, whereas the use of the trifunctional initiator in the polymerization of oxacyclopentane resulted in formation of a gel which, however, could be dissolved by addition of methanol. If in contrast the multifunctional initiator was used the gel which was formed, was totally insoluble due to formation of permanent poly(oxytetramethylene) crosslinks between the original backbone polymers.

The first evidence of cyclic oligomer formation in the generic oxacyclopentane family was obtained when the presence of cyclic oligomers up to pentamer was demonstrated in the polymerization of the bicyclic monomer trans-7-OBCN (ref. 7). The generation and existence of cyclic oligomers in the polymerization of oxacyclopentane itself has recently been effectively demonstrated by Pruckmayr and Wu (43, 44). Dimer up to octamer was individually identified and characterized by gas chromatography coupled with mass spectrometry, the cyclic tetramer or 20-crown-4 the most abundant oligomer present was furthermore characterized by ^{13}C NMR (ref. 45). Moreover a decrease with increasing conversion in the original 2:1 ratio between the endo- and exocyclic protons β to the strained propagating oxonium ion was detected by high-resolution ^{1}H NMR (ref. 43). This is the first spectroscopic proof of the dormant species corresponding to 20 and 21 since all β protons in these species have the same chemical shifts and thus account for the decreasing ratio.

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