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Polymerization of Bicyclic Ethers. 3.[1] NMR Structure Study of Copolymers of 7-Oxabicyclo[2.2.1]heptane with Ethylene Oxide

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ABSTRACT: ^{1}H NMR spectra of 7-oxabicyclo[2.2.1]heptane/ethylene oxide copolymers obtained under cationic conditions clearly showed sequence effects due to the incorporation of both monomers into the polymer chain. The reactivity ratios calculated for one set of conditions (BF_3 initiator in methylene chloride at 0 °C) were $r_1 = 0.66$ and $r_2 = 0.11$ for 7-oxabicyclo[2.2.1]heptane and ethylene oxide, respectively. Spectral analysis led to the assignment of a trans configuration to the cyclohexane ring of the oxy-1,4-cyclohexylene unit. This result was explained by assuming an S_N2 ring-opening mechanism for 7-oxabicyclo[2.2.1]heptane. ^{13}C NMR spectra were interpreted in terms of compositional triad sequences and confirmed the presence of only one configuration for the above structural unit. Examination of the normalized intensity of the ^{13}C resonances of the different triads as a function of the monomer feed allowed the conclusion that the cationic polymerization of this binary system may be visualized as a process showing an alternating tendency, in agreement with the r_1r_2 value and the copolymerization diagram.

In recent years the cationic copolymerization of cyclic ethers has received much attention,[2,3] and now a great deal of information is available. The cationic copolymerization between 1,2-epoxides as well as the polymerization of 1,2-epoxides with other cyclic ethers has recently been reviewed.[4] In contrast, there is little information in the literature dealing with the copolymerization of bicyclic ethers.

The copolymerization of 7-oxabicyclo[2.2.1]heptane (1)

1

2

with other monocyclic ethers was first reported by Wittbecker et al. in 1960.[5] Since then, only a few patents[6,7] and reports[8-10] have appeared. The copolymerization of 1 with ethylene oxide (2) and some of its derivatives has been the subject of one of our previous investigations.[10]

However, this earlier report dealt only with the synthesis and determination of some characteristics of the polymers, and a detailed examination of the polymer structure was deferred.

With the aim of expanding our work on the polymerization of bicyclic ethers, we felt it desirable to employ NMR spectroscopy to study in greater detail the microstructure of the polymers obtained by copolymerizing monomer 1 with 2. It is well established that NMR spectral studies can provide much information about the chemical and configurational structure of macromolecules, including the determination of the monomer sequence distribution in copolymers. Here we report the results obtained from ^{1}H and ^{13}C NMR measurements on the structure of these polyethers.

Experimental Section

Monomers. 7-Oxabicyclo[2.2.1]heptane (1) (Aldrich Chemical Co.) was dried by refluxing over sodium and fractionated on a spinning-band column at a high reflux ratio. The product boiling at 119.4–119.5 °C was collected under dry nitrogen in a flask equipped with a break seal. The flask was sealed to the vacuum line and 1 was completely degassed by repeated freeze–thawing. Then 1 was distilled into a Pyrex bulb containing a sodium mirror attached to the line via a precision burette fitted with metal valves. The 270-MHz ^{1}H NMR spectrum of 1 did not show the presence of detectable impurities. Ethylene oxide (2) (Matheson Co.) having a stated minimum purity of 99.7% was purified further and dried according to Worsfold and Eastham.[11] Finally, 2 was stored at −20 °C over calcium hydride on a vacuum apparatus similar to that used for monomer 1.

Catalyst. Pure boron trifluoride (BF_3) was selected as initiator because it could be easily manipulated under dry conditions. BF_3 was prepared under vacuum by thermal decomposition at 140 °C of *p*-chlorobenzenediazonium tetrafluoroborate, obtained according to the method of Roe.[12] The crude tetrafluoroborate salt was purified by recrystallization from acetone (solvent)–ethyl acetate (precipitant) and dried in a vacuum oven at 35 °C. The nitrogen generated during the reaction was pumped off, while *p*-fluorochlorobenzene and BF_3 were collected separately in condensers at −80 °C and −190 °C, respectively. The first condenser was sealed off from the line and BF_3 purified further by several sublimations from a trap held at −90 °C. Finally, it was stored at liquid nitrogen temperature in a Pyrex bulb connected to the line via a metal valve. The dosing was carried out by measuring the pressure of gaseous BF_3 after expansion through a known volume of the vacuum system.

Solvent. 1,2-Dichloroethane (C. Erba product) was purified according to Weissberger[13] and dried by fractional distillation over P_2O_5. The solvent was degassed under high vacuum and stored over freshly sublimed P_2O_5 in a black-painted reservoir connected to the line by a 50-mL burette carrying at the end a metal valve.

Polymerization Procedure. The copolymerization reactions were carried out in glass ampules sealed under vacuum. Measured quantities of 1,2-dichloroethane and of monomers 1 and 2, according to different mole ratios, were distilled at liquid nitrogen temperature into the reaction ampule containing a magnetic stirrer. Before the BF_3 was condensed in, the solvent and the monomer were melted and mixed. The ampule was then sealed off from the vacuum line and allowed to stand, under vigorous stirring, at 0 °C. After an appropriate reaction time (1–3 and 60–70 min for low- and high-conversion experiments, respectively), the ampule was opened as quickly as possible, the polymerization quenched by adding a small volume of ammoniacal methanol, and the mixture filtered. The polymer was recovered by steam distillation of the solution and thereafter carefully dried to a constant weight under vacuum at 40 °C. The copolymers appear as sticky or powdery solids, depending on their composition, and are not contaminated by trace amounts of the insoluble homopolymer of 1 nor by the water-soluble homopolymer of 2. The conversions

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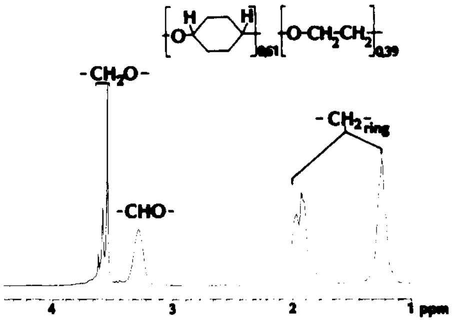


Figure 1. ^{1}H NMR spectrum at 270 MHz of 7-oxabicyclo[2.2.1]heptane/ethylene oxide copolymer. High-conversion (75%) sample observed as 3% (w/v) solution in $CDCl_3$; ppm are from Me_4Si as internal reference.

were calculated from the weight of the dried polymer. The presence of nonvolatile organic material was ascertained in the residual water extracted from the distillation apparatus, but the amount was negligible, so it was not further analyzed. In separate experiments it was also shown that BF_3 alone does not initiate the polymerization of 1. Therefore, the preparation of some poly-1 as a reference polymer was accomplished by PF_5, whose ability to initiate the polymerization of cyclic ethers without added cocatalyst is well-known.

Intrinsic Viscosities. Intrinsic viscosities were determined for all the examined polymers in an Ubbelohde viscometer in chloroform at 20 °C and fell in the range 11–25 cm^3 g^{-1}.

NMR Measurements. ^{1}H NMR spectra were measured with a Bruker WH270 pulsed FT spectrometer at 270 MHz on 3% (w/v) polymer solutions in $CDCl_3$ in 5-mm tubes. A total of 40 transients were accumulated and data were collected on 16K of memory at room temperature.

^{13}C NMR noise-decoupled spectra were obtained on a Bruker WH90 FT spectrometer at 22.63 MHz, accumulating from 800 to 3000 transients on 16K of memory. Samples were 15% (w/v) polymer solutions in 65:35 CH_2Cl_2–C_6D_6 in 10-mm tubes. Chemical shifts were measured in ppm from an internal Me_4Si standard. Addition of phenol was necessary for solutions of poly-1.

Results and Discussion

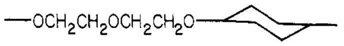
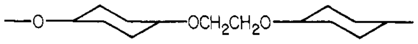
^{1}H NMR Spectra. The copolymers prepared by simultaneous cationic polymerization of the monomers 1 and 2 may be regarded as being composed of oxy-1,4-cyclohexylene and oxyethylene repeating units formed from the ring opening of 1 and 2, respectively. The copolymer compositions were calculated from the peak areas in their 270-MHz ^{1}H NMR spectra by the equation

$$x_{M_1} = 2A_1/(2A_1 + A_2)$$

where x_{M_1} is the mole fraction of monomer 1, A_1 is the peak area due to the methine protons of the repeating unit from this monomer, and A_2 is the methylene proton peak area of the repeating unit from monomer 2. Under the employed experimental conditions, it was possible to maintain the yield of the low-conversion experiments at approximately 5–10%. Therefore by using the Kelen–Tüdös equation,[14] one can calculate with confidence the reactivity ratios for this binary system. They were found to be $r_1 = 0.66$ for monomer 1 and $r_2 = 0.11$ for monomer 2. These values are comparable with those previously reported[10] for the same pair of monomers, the difference being probably due to slightly different experimental conditions.

Figure 1 shows the complete proton spectrum of a copolymer containing 61 mol % of 1. The main features of this spectrum can be reduced to four well-separated absorption bands. Those centered at approximately 1.2 and 1.9 ppm and that centered at about 3.3 ppm are assigned, according to their intensity ratios, to the methylene protons (8 H) and to the methine protons (2 H) of the disubstituted cyclohexane ring of the repeating oxy-1,4-cyclohexylene unit. In particular, the bands at 1.9 and 1.2 ppm are assigned to the axial (4 H) and equatorial (4 H) methylene protons of the ring. This assignment is based on the well-accepted fact that in the NMR spectra of cyclohexane derivatives the equatorial protons usually resonate downfield from their axial counterparts.[15] The separation of the ring proton signals of cyclohexane derivatives into two bands corresponding to the axial and equatorial protons is reported[16] as characteristic of those compounds having a highly favored conformation which does not undergo rapid ring inversion. This pattern is typical of *trans*-1,4-cyclohexane compounds, which are expected to exist mainly with both substituents in equatorial positions.[15] Conversely, in the cis configuration, where one substituent is axial and the other is equatorial, a single narrow band would be expected due to the fast interconversion.

Table I
270-MHz ^{1}H NMR Peak Assignments of Oxyethylene Protons for 7-Oxabicyclo[2.2.1]heptane (1)/Ethylene Oxide (2) Copolymer Containing 39 mol % of 2

chem shift,[a] ppm	triad sequence	structure[b]
3.62	EEE	$-OCH_2CH_2OCH_2CH_2OCH_2CH_2-$
3.58	EEH + HEE	
3.53	HEH	

[a] Chemical shifts are from internal Me_4Si. [b] The trans-1,4-disubstituted cyclohexane ring of the polymer unit is assumed to exist as a diequatorial conformer.

These observations and comparison with the spectra of 1,4-cyclohexanediol and other reference compounds[17] indicate a trans configuration for the oxy-1,4-cyclohexylene unit. The spectrum of the homopolymer of 1 is similarly consistent with the same stereochemical assignment. The assignment of a trans configuration to the structure of this homopolymer unit was previously suggested on the basis of its high melting point.[5] A trans structure has been previously reported also for the polymers of the 2-methyl derivatives of 1.[18,19]

Despite the dependence of the resonance pattern of the axial and equatorial protons on the copolymer composition, these bands have not been further analyzed, owing to insufficient signal resolution.

The fourth and last band in the spectrum, which occurs between 3.4 and 3.7 ppm, has been readily assigned to the protons of the oxyethylene repeating unit by observing that its overall intensity increases with increasing content of monomer 2 in the copolymer. The fine structure in this band has been interpreted as arising from copolymer sequence effects, where the peaks of the band have been assumed to represent three different types of triad sequences. The chemical shifts and the assignments of these peaks are reported in Table I, where the structural units of monomers 1 and 2 are labeled H and E, respectively.

The individual integration of these proton signals was not possible, owing to an appreciable overlap of the peaks. Thus the integrated areas could not be used for a precise quantitative analysis of sequence distributions.

For this reason the assignments reported in Table I were checked on the basis of rough quantitative observations as well as on simple statistical considerations based on the copolymerization diagram. The latter is reported in Figure 2 and shows the profile characteristic for the cases where r_1 and r_2 are less than one. It is clear from the curve that, for a concentration of ethylene oxide near the inflection

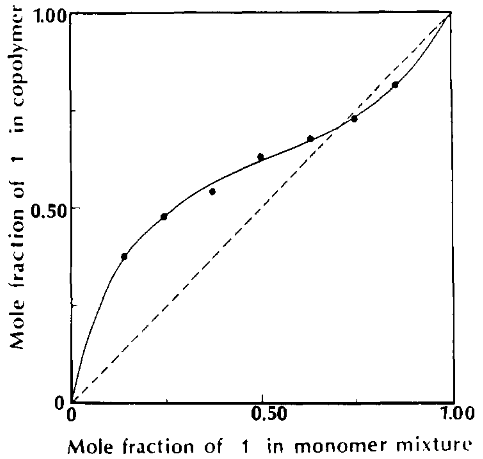


Figure 2. Copolymer composition curve in the cationic polymerization of 7-oxabicyclo[2.2.1]heptane and ethylene oxide. Experimental conditions: initial monomer concentration, 1 mol L^{-1}; catalyst, BF_3 (gas), 0.010 mol L^{-1}; solvent, 1,2-dichloroethane; temperature, 0 °C.

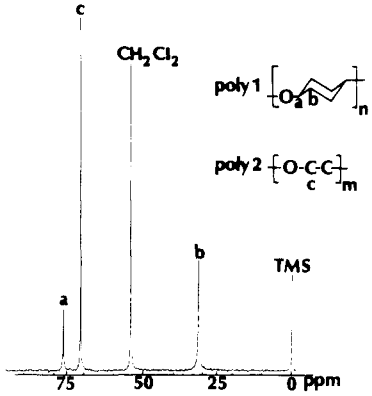


Figure 3. ^{13}C NMR spectrum at 22.63 MHz of a mixture of the homopolymer of 7-oxabicyclo[2.2.1]heptane and ethylene oxide, observed as a 15% (w/v) solution for each polymer in 50:30:20 CH_2Cl_2–C_6D_6–C_6H_5OH.

point or lower, the system approaches the ideal random behavior. At this composition the probability of occurrence of isolated units is high and increases as the concentration of ethylene oxide in the feed is decreased. This expectation is found to agree satisfactorily with the approximate estimate of the distribution of intensities between the three peaks assigned to the triads EEE, EEH = HEE, and HEH.

The assignment of the homopolymer-type sequence EEE has been confirmed by comparison with the proton spectrum of low-molecular-weight poly(ethylene oxide) made under the same conditions.

With regard to the asymmetric triad sequence EEH = HEE, one would expect to observe some fine splitting of the proton signal of the central unit. Indeed, replacement of one E unit by one H unit should give rise to two sets of methylene protons, intrinsically nonequivalent, which in turn should couple to each other. The failure to note any splitting for this signal is probably due to a difference in the proton chemical shifts too small to be detected under the analysis conditions used.

^{13}C NMR Spectra and Sequence Assignments. In order to get additional information about the copolymer microstructure, ^{13}C NMR spectra were also effectively utilized. The ^{13}C NMR spectrum of a solution of the homopolymers from 1 and 2 is reported in Figure 3. The spectrum is simple and the line assignments were made from known chemical shift literature data for methylene carbons of poly-2 and by the off-resonance decoupling

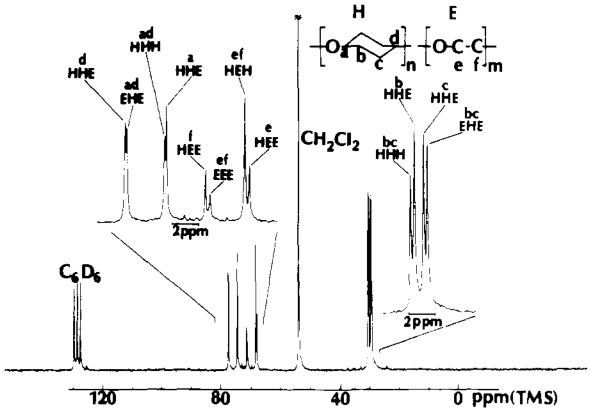


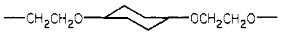
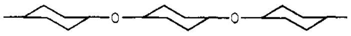
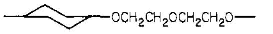
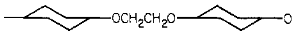
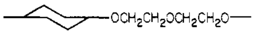
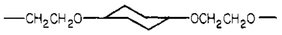
Figure 4. ^{13}C NMR spectrum at 22.63 MHz of the copolymer of Figure 1, observed as a 15% (w/v) solution in 65:35 CH_2Cl_2–C_6D_6.

technique for methine and methylene carbons of poly-1.

Figure 4 shows the ^{13}C NMR spectrum of the same copolymer as that in Figure 1. The spectrum appears more complicated than that of the homopolymer mixture. It shows a chemical shift multiplicity which reflects sequencing clearly due to the incorporation of both monomer units into the polymer chain. This fact suggests that the spectrum is rich in the amount of structural information it can provide. The spectrum can be divided into three main groups of peaks containing four lines. The resonances at ca. 30 and 78 ppm, as shown in the expanded regions of Figure 4, have been unambiguously assigned to the methylene and methine carbons of the structural H unit, while the resonance at ca. 70 ppm is due to the methylene carbons of the E unit. This assignment is consistent with the intensity changes observed for each group of resonances according to the copolymer composition. As we have seen, a total of 12 resonance lines is recognizable in the spectrum. This means that we are dealing with different types of compositional triads rather than dyad sequences. Indeed, an analysis of the copolymer structure in terms of dyad sequences cannot be applied since it does not explain the number of observed signals. Furthermore, the existence of conformational dyads, i.e., dyad sequences consisting of 1,4-axial–axial and 1,4-equatorial–equatorial conformers of the H unit, seems unlikely. Indeed for the H unit, to which a trans configuration has been assigned from the spectrum in Figure 1, one can expect the more stable diequatorial conformer to be the prevailing one. This conclusion is consistent with the lack of any multiplicity in the spectrum of the homopolymer of 1. Moreover, the spectra of both homopolymers are not affected by changing the temperature up to 90 °C.

Considering the copolymer microstructure on the basis of the triad sequences, one can predict a maximum of 12 resonance lines. The structure of all the possible compositional triads of H and E units and the assignment of all the observed lines are given in Table II. The assignment of the resonances of the spectrum of Figure 4 to each particular triad is based on the relative intensities as functions of the copolymer composition. In order to obtain meaningful results, only the ^{13}C NMR spectra of the low-conversion copolymers have been examined. Figure 5 gives a typical set of three spectra, A, B, and C, of copolymers with different molar ratios of 1 and 2. As this ratio increases on going from A to C, the HHH sequences become more prominent than the other H-centered triads, while the sequences EHE in the methine and methylene region decrease significantly as a result of the change of the

Table II
22.63-MHz ^{13}C NMR Chemical Shifts and Peak Assignments of 7-Oxabicyclo[2.2.1]heptane (1)/Ethylene Oxide (2) Copolymer Containing 39 mol % of 1

carbon atom	chem shift, ppm	triad	structure
d	77.60	HHE	
ad	77.40	EHE	
ad	74.60	HHH	
a	74.47	HHE	
f	71.45	HEE	
ef	71.10	EEE	—$CH_2CH_2OCH_2CH_2OCH_2CH_2O$—
ef	68.50	HEH	
e	68.10	HEE	
bc	30.90	HHH	
b	30.60	HHE	
c	29.85	HHE	
bc	29.60	EHE	

system from an alternating tendency to a random one. Such a tendency is clearly indicated by the profile of the copolymerization curve in Figure 2. Again the assignment of the triad HHH, as well as of EEE, has ben confirmed by adding a small amount of the homopolymer of 1 and 2 to a suitable copolymer solution. The assignments of the two pairs of asymmetric triads HHE are aided by recalling that the resonances of the methine and methylene carbons of the central unit are expected to split into two lines of the same intensity as a consequence of the replacement of one H unit for one E unit. The same holds for the sequences HEE, in which the coincidence of the intensities of the split carbon resonances is more evident, owing to a better signal separation. The discrimination between the same type carbon in different structural environments for each of the symmetric H- and E-centered triads has been made by assuming that the "near" effect on the carbon chemical shift is greater than the "far" one.

The "near" effect involves two-bond and three-bond distances for methine and methylene carbons, respectively; the "far" effect involves five bonds for methine and four bonds for methylene carbons for the H central unit.

For the E-centered triads, "near" and "far" effects involve two and three bonds, respectively.

The presence of the E unit in the EHH (HHE) triads produces a shift of the "near" methine and methylene carbons of the central unit of +3.0 and −1.05 ppm, respectively (a positive sign indicates a low-field shift), and a shift of −0.13 and −0.3 ppm for the "far" ones from the HHH triads. In the symmetric EHE triad, methine and methylene show a chemical shift that is just the sum of all these effects.

In the EEH (HEE) triads the presence of one H unit produces a "near" shift of −3.0 ppm and a "far" one of +0.35 ppm of the methylene carbons of E as compared with the EEE triad. Such a large shift with respect to the number of bonds involved can be explained by considering the effect on the ^{13}C chemical shift of the steric interaction between the axial protons of adjacent H units.[20] The presence of the oxyethylene unit in the copolymer chain removes such a steric interaction, thus giving rise to the chemical shift difference observed.

Conversely, the presence of the H unit in the HEE (EEH) triads produces on the central unit a steric interaction effect of the same magnitude. In the symmetric HEH triad the chemical shift is just the sum of the two effects.

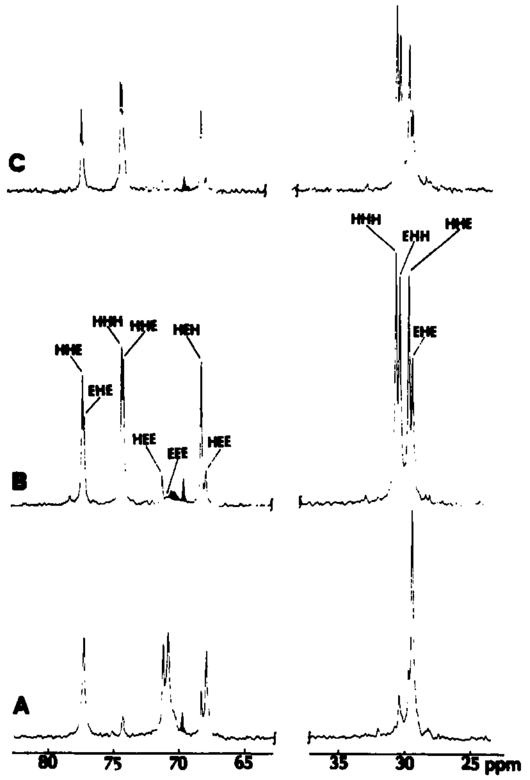


Figure 5. ^{13}C NMR spectra at 22.63 MHz of copolymers of 7-oxabicyclo[2.2.1]heptane and ethylene oxide with different H:E monomer unit ratios, observed as 15% (w/v) solution in 65:35 CH_2Cl_2–C_6D_6: (A) 0.381:0.619; (B) 0.631:0.369; (C) 0.827:0.173. Shaded peaks are attributed to unknown impurities.

It is well-known that differences among nuclear Overhauser effects give rise to difficulties in quantitative measurements of proton-noise-decoupled ^{13}C NMR spectra. In such cases no direct correlation between the integrated peak areas and the number of the involved carbon nuclei exists, and this remains true also for polymers. In the present case the measurements of NOE factors for the carbons of the different triads gives a NOEF close to the maximum (η = 1.98) for the methylene carbons of the E-centered triads and NOEF values considerably lower than the maximum for the methylenes of the H-centered triads.

Thus the quantitative analysis of the triad sequence distribution was not feasible. However, we considered it worthwhile in this respect to make a qualitative estimate based on the normalized peak intensities of all the assigned centered triads as a function of the monomer feed. The curves of Figures 6 and 7 show the change in the relative intensity of the ^{13}C NMR signals of the triad sequences for copolymers of 1 and 2 obtained at low conversion from varying feed compositions. It must be emphasized that these curves do not represent the true distribution, in mole fractions, of the corresponding sequences but only the distribution of the relative intensity of the triad resonance. The comparison in each group of centered triads is limited to carbon atoms of the same type. Specifically, for the central unit H, the methylene resonances have been selected, owing to their better signal resolution.

The curves of Figure 6 indicate that at lower feeds of 1 the resonance intensities associated with the triads EHE predominate over those of HHE (EHH) and HHH. This fact suggests that the lower the concentration of 1 in the initial monomer mixture, the higher the tendency of the

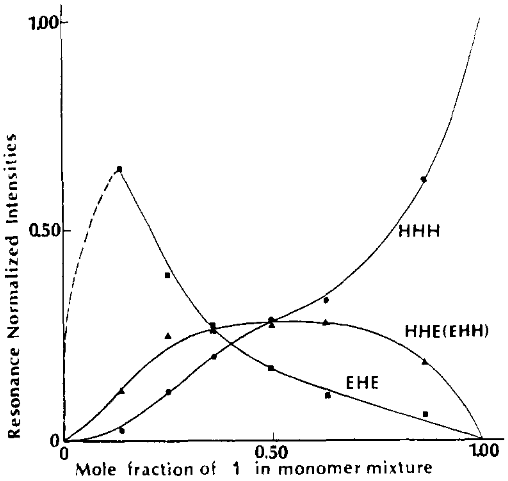


Figure 6. Distribution of the ^{13}C NMR normalized intensities for the H-centered triad resonance of low-conversion copolymer of 7-oxabicyclo[2.2.1]heptane (H unit) and ethylene oxide (E unit) as a function of monomer feed.

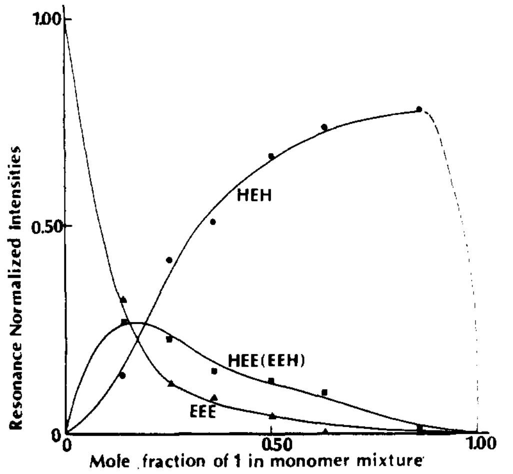


Figure 7. Distribution of the ^{13}C NMR normalized intensities for the E-centered triad resonance of low-conversion copolymer of 7-oxabicyclo[2.2.1]heptane (H unit) and ethylene oxide (E unit) as a function of monomer feed.

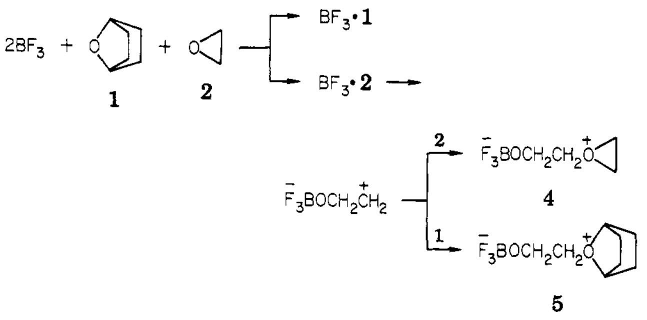
corresponding H units to be incorporated into the copolymer chain as separate units. An opposite trend is noted for the curve associated with the triads HEH (Figure 7), whose formation appears to prevail significantly over the sequences HEE (EEH) and EEE on decreasing the concentration of 2. In addition, this trend gives further support to the assignment of HEH sequences previously deduced from the proton NMR spectra.

The position of the maximum intensity of HEH and EHE is the most uncertain because of the difficulty in obtaining more experimental points. It is noteworthy that the curve of the intensity of EHH (HHE) is almost symmetrical and displays a very broad maximum. A satisfactory explanation may be given on kinetic grounds by observing from the copolymerization diagram of Figure 2 the higher rate of incorporation of the H units into the copolymer over a wide range of mixtures. The same observation probably holds also to explain the inflection point evident in the curve of HHH sequences. The trend of this curve, in spite of the inflection point, must be considered fairly regular. Indeed, the occurrence probability of the triads HHH is expected to approach to unity when monomer 2 disappears completely. Obviously, the sequences EEE must follow an opposite trend.

From the above considerations, it is concluded that the cationic copolymerization of 1 and 2 may be viewed as a process with some degree of alternating character. In particular, the analysis of the curves of Figures 6 and 7 can be regarded as a useful test for obtaining qualitative information about changes in copolymer microstructure when the monomers are polymerized starting from different feed compositions.

As far as the polymerization mechanism is concerned, it is difficult actually to formulate a precise reaction scheme to give a complete description of the entire copolymerization process. Furthermore, it must be kept in mind that the copolymerization reactions in epoxide systems, in the presence of cationic catalyst, are in many cases very complex and hard to understand mechanistically.[2a] On the other hand, a detailed study in this context was beyond the scope of the present investigation. However, it is possible to discuss some implications of the results in terms of a polymerization mechanism.

As pointed out in the Experimental Section, gaseous BF_3 does not initiate the polymerization of 7-oxabicyclo[2.2.1]heptane alone under the conditions used in the copolymerization experiments. This fact suggests that at least a trace amount of ethylene oxide is required to initiate chain growth. The use of ethylene oxide derivatives as cocatalysts in the polymerization of 1 initiated by BF_3 has been reported.[5] Therefore, monomer 2 seems to play the role of a real promoter. According to Entelis and Korovina,[4] a number of factors give support to the hypothesis that in the BF_3-catalyzed copolymerization of 1,2-epoxides with other oxyheterocycles, the active species appears in the form of a carbenium-type or oxonium-type zwitterion. To extend such a hypothesis to the copolymerization of 1 and 2 by BF_3, we may suppose a reaction scheme under anhydrous conditions that can be written as follows:



The one to one adduct BF_3·2 is assumed to be very reactive owing to the high ring strain existing in 1,2-epoxides, and it has been reported to be stable only below -80 °C.[21] The interaction of the complex BF_3·1 with the species 4 and 5 to produce other oxonium structures has been disregarded on the basis of previous indications concerning the copolymerization of 1,2-epoxides with tetrahydrofuran.[4] Considering now the propagation reaction, it is worthwhile pointing out that when the active species 5 adds a molecule of 1 or 2 to give polymer, the stereochemistry of formation of the base unit may be different according to the type of ring-opening mechanism of the cyclic oxonium ion. A direct-displacement mechanism (S_N2 type) through attack by the oxygen of the incoming monomer at the endocyclic carbon lying α to the positive oxygen of the propagating oxonium ion would give a trans configuration of the disubstituted cyclohexane ring. Indeed, according to the S_N2 mechanism, the configuration of the carbon at the oxonium center is inverted in the conversion of boat form of the cyclohexane ring in the monomer to the chair form in the polymer. On the contrary, a process involving carbenium ions from an S_N1 opening of the cyclic oxonium ion would give mixed cis–trans polymer units. The results from the NMR analysis of the copolymer structure indicate that all the 1,4-cyclohexane units in the polymer chain are linked in a trans configuration. Therefore, it is concluded that in the copolymerization of 1 with 2 initiated by BF_3, the ring opening of 1 proceeds entirely with inversion of configuration, thus suggesting that in the propagation rate-determining step, the active species of 1 is in the form of a cyclic oxonium ion.

No search was made for cyclic oligomers or for structural irregularities (e.g., methyl branches) in the polymers in connection with a possible formation of carbenium ions from monomer 2. Recently, the presence of methyl groups in cyclization products obtained in the homo- and copolymerization of 1,2-epoxides has been reported as a convincing argument in favor of the carbenium nature of the growing species involved in these systems.[4]

Exhaustive discussion of the reactivity ratios r_1 and r_2 in terms of a copolymerization equation without a detailed knowledge of the formation of oligomers and other possible side reactions would be difficult.

Considering the process to consist essentially of four propagation steps, one can observe that when an active species of 2 is at the chain end, it apparently prefers to react with monomer 1 about 9 times faster than with another 2 monomer, as indicated by the value $r_2 = 0.11$.

Monomer 2 is a Lewis base weaker than other saturated and less strained cyclic ethers, according to the order[22] four- > five- > six- > three-membered ring while the basic strength of 1 is intermediate between that of oxetane (four-membered) and tetrahydrofuran[22] (five-membered).

Let us assume the basicity to be parallel to the monomer reactivity as nucleophile and suppose the nucleophilicity to be in this case a dominant factor. The lower basicity of 2 would therefore result in a lower reactivity than expected from its ring strain in the competitive reaction with 1. The value 0.66 for r_1 indicates that when the propagation reaction involves the oxonium ion 5, monomer 1, in spite of its higher basicity, appears to react with 5 about 1.5 times more slowly than monomer 2. This reverse trend of reactivity might be mainly due to steric effects. An increase of steric hindrance (in comparison with the addition of 2) would be expected by the hydrogens of the hydrocarbon cage partially surrounding the oxygen atom in 1 when this monomer and its own oxonium species 5 are approaching each other to form the corresponding transition state.

Steric hindrance, in addition to the reactivity of the monomer and the propagating species, plays an important role in governing the rate constant of S_N2 propagation reactions.[21,23] Unfortunately, the lack of the relevant activation parameters does not allow us to proceed further in considering the formulated hypothesis.

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References and Notes

(1) Previous papers in this series are: Ceccarelli, G.; Andruzzi, F. *Makromol. Chem.* **1979,** *180,* 1371, and ref 17.

(2) (a) Ishii, Y.; Sakai, S. In "Kinetics and Mechanism of Polymerization"; Frisch, K. C., Reegen, S. L., Eds.; Marcel Dekker: New York, 1969; Vol. 1, Chapter 1, p 87. (b) Dreyfuss, P. *Ibid.*, Chapter 2, p 151.

(3) Tsukamoto, A.; Vogl, O. *Prog. Polym. Sci.* **1971,** *3,* 261.

(4) Entelis, S. G.; Korovina, G. W. *Makromol. Chem.* **1973,** *175,* 1253.

(5) Wittbecker, E. L.; Hall, H. K.; Campbell, T. W. *J. Am. Chem. Soc.* **1960,** *82,* 1218.

(6) "Montecatini" Società Generale per l'Industria Mineraria e Chimica Ital., 757820 (Cl. 6 08g), Apr 15, 1967, Appl. Mar 30, 1965; *Chem. Abstr.* **1970,** *73,* 36145.

(7) Pichler, J.; Kucera, M. Czech Patent 114256 (Cl. C 08f), Apr 15, 1965, Appl. Nov 19, 1962; *Chem. Abstr.* **1966,** *64,* 17801*e*.

(8) Weissermel, K.; Noelken, E. *Makromol. Chem.* **1963,** *68,* 140.

(9) Geller, N. M.; Kropachev, V. A.; Dolgoplosk, B. A. *Vysokomol. Soedin., Ser. A* **1967,** *9,* 575. *Polym. Sci. USSR (Engl. Transl.)* **1967,** *9,* 645.

(10) Baccaredda, M.; Giusti, P.; Andruzzi, F.; Cerrai, P.; Masetti, G. *Chim. Ind. (Milan)* **1968,** *50,* 81.

(11) Worsfold, D. J.; Eastham, A. M. *J. Am. Chem. Soc.* **1957,** *79,* 897.

(12) Roe, E. "Organic Reactions"; Adams, R., Ed.; Wiley: New York, 1949; Vol. 5, Chapter 4, method 1B.

(13) Weissberger, A. *Tech. Chem. (N.Y.)* **1955,** *7,* 115.

(14) Kelen, T.; Tüdös, F. *J. Macromol. Sci., Chem.* **1967,** *A9,* 575.

(15) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: Oxford, 1965; pp 696–709 and references cited therein.

(16) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1967,** *89,* 6612.

(17) Andruzzi, F.; Ceccarelli, G.; Paci, M. *Polymer* **1980,** *21,* 1180.

(18) Kops, J.; Spangaard, H. *Makromol. Chem.* **1972,** *151,* 21.

(19) Saegusa, T.; Matsumoto, S.; Fujii, J. *Macromolecules* **1972,** *5,* 233.

(20) Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967,** *89,* 5315.

(21) Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980,** *37,* 1.

(22) Tamres, M.; Searles, S.; Goodenow, J. M. *J. Am. Chem. Soc.* **1964,** *86,* 3934.

(23) Saegusa, T. *J. Macromol. Sci., Chem.* **1972,** *A6* (6), 997.

Cationic Copolymers of Isobutylene. 6. NMR Investigation of the Structure and Sequence Distribution of Isobutylene–2,3-Dimethylbutadiene Copolymers

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ABSTRACT: The cationic copolymerization of isobutylene (I) with 1,3-dimethylbutadiene (DB), performed homogeneously at −70 °C, was investigated by studying the structure of the resulting copolymer (I–DB). Spectroscopic investigations, carried out mainly by ^{1}H and ^{13}C NMR, on the copolymer as well as on the cationic and anionic DB homopolymers, showed that the enchainment of DB in I–DB is trans-1,4. The complete interpretation of the ^{13}C NMR spectra of I–DB permitted us to calculate the distribution of the monomeric units, which indicated that I–DB shows a tendency toward a block-type structure.

Introduction

In previous papers we have investigated the structure of cationic copolymers of isobutylene (I) with butadiene[1] and its methyl derivatives, i.e., isoprene[2] and *cis*- and *trans*-1,3-pentadiene.[3,4] Pursuing our work, we have examined the I copolymers with some dimethyl derivatives