Table II
Effect of Monomer Composition on k_D/k_S in the Copolymerization of *p*DVB and *p*MeSt by $AcClO_4$ in Benzene[a]

[*p*DVB]/[*p*MeSt]	(-C=C/-$C_6H_4CH_3$)	*r*	k_D/k_S
1/3	0.26	0.26	1/2.0
1/1	0.95	0.49	1/2.2
3/2	1.11	0.50	1/3.2
3/1	2.76	0.68	1/3.2
7/1	7.62	0.83	1/3.1

[a] $[p\text{DVB}]_0 + [p\text{MeSt}]_0 = 0.10$ M, $[\text{C}]_0 = 0.2$ mM, 70 °C.

Table III
Relative Reactivity (k_D/k_S) of DVB in the Copolymerization with Substituted Styrenes (Sts) by $AcClO_4$ in Benzene[a]

monomer (1/1)	-C=C/-C_6H_4X	*r*	k_D/k_S
[*m*DVB]/[*p*MeSt]	0.52	0.38	1/3.7
[*p*DVB]/[*p*MeSt]	0.95	0.49	1/2.2
[*p*DVB]/[*p*AcOSt]	1.93	0.62	1/1.3
[*p*DVB]/[ClMeSt]	7.44	0.83	1/0.4

[a] $[\text{DVB}]_0 = [\text{Sts}]_0 = 0.05$ M, $[\text{C}]_0 = 0.2$ mM, 70 °C, conversion ca. 50%.

Experimentally, *r* and hence k_D/k_S can be determined from the relative numbers (C=C/X) of terminal DVB and Sts units in a product on the basis of the equation

$$\frac{\text{C=C}}{\text{X}} = \frac{2[\text{DD}] + [\text{DS}]}{2[\text{SS}] + [\text{DS}]} = \frac{r^2 + r}{r^2 - 3r + 2} \qquad (2)$$

where the brackets mean the relative amount of the indicated polymer. Equation 2 requires that the end-group ratio C=C/X be independent of *n*, which was actually the case (Table I).

Table II lists end-group ratios (C=C/X) for polymer I-CH_3 at various monomer feed ratios together with *r* and k_D/k_S values calculated by eq 2 and 1. These data are for the products obtained at ca. 50% conversion of both *p*DVB and *p*MeSt, so that on calculation of k_D/k_S ratios, the monomer concentrations in eq 1 were taken as the means of the corresponding initial and final concentrations.

In spite of the large changes in the end-group ratio (or *r*), the k_D/k_S values remained practically constant over a wide range of the monomer feed ratio. This constancy strongly supports the reasonableness of our treatment and the k_D/k_S values. Table II indicates that each vinyl group of *p*DVB is 2–3 times less reactive than that of *p*MeSt.

Table III summarizes the reactivity ratios (k_D/k_S) for *p*DVB, *m*DVB, and various styrenes obtained by our method. The relative reactivities of the five monomers are in the order *p*MeSt > *p*AcOSt > *p*DVB > *m*DVB ≥ ClMeSt (*m*, *p*). *p*DVB is about 1.7 times as reactive as *m*DVB. The order found for *p*MeSt, *p*AcOSt, and ClMeSt agrees with that hitherto known in their conventional cationic polymerizations. For a given DVB/Sts pair, it may be possible to prepare polymer I of desired molecular weight by regulating the monomer feed ratio $[\text{DVB}]_0/[\text{Sts}]_0$ according to the k_D/k_S, because the molecular weight of polymer I is critically dependent upon the feed ratio and the DVB/Sts pair (k_D/k_S) (see Figure 4).

Acknowledgment. We thank Dr. M. Sawamoto of this laboratory for helpful discussion.

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Polymerization of 2,2-Dimethyloxacyclobutane

Jørgen Kops* and Hans Spanggaard

Instituttet for Kemiindustri, The Technical University of Denmark, DK-2800 Lyngby, Denmark. *Received October 30, 1981*

ABSTRACT: The polymerization of 2,2-dimethyloxacyclobutane has been studied in bulk as well as in CH_2Cl_2 solution in the temperature range −25 to −78 °C using the cationic initiators PF_5 and Et_3OPF_6. Extensive transfer reactions result in the formation of only low polymers and oligomers. The end-group structures have been identified as isopropenyl and primary hydroxyl, respectively. A mechanistic scheme is presented that accounts for the formation of these structures, and it is proposed that oxonium ion and carbenium ion species are present and active during the course of the polymerization. The ring-opening reaction is found to occur by bond breakage between carbon C-2 and oxygen.

Introduction

Initially, oxacyclobutane (oxetane) and various derivatives of this four-membered cyclic ether were found to undergo polymerization under the influence of cationic initiators.[1,2] Later, the kinetics of polymerization of the derivatives substituted at the 3-position were investigated[3,4] as well as the kinetics of the oligomerizations that often accompany the polymerizations.[5-7] These monomers also undergo polymerization when the coordination initiators developed by Vandenberg are used.[8] Less attention has been paid to derivatives substituted at the 2-position although recently, structural aspects of the cationic ring-

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Table I
Polymerization Experiments with 2,2-DMOCB

temp, °C	initiator, mmol PF_5	initiator, mmol Et_3OPF_6	monomer, mmol	solvent CH_2Cl_2, mL	time, h	yield, %	GPC $\bar{M}_n$	GPC $\bar{M}_w$	GPC top point count
−78/−25	0.05		9.6	none	5	50	820	1080	22.9
−25		0.11	9.5	1.4	93	92			25.5
−25	0.05		9.7	none	120	74			24.3
−50		0.01	5.9	3.0	46	32			28.6
−60	0.05		9.3	none	43	74	800	1020	23.6
−60	0.05		9.1	none	67	84			23.6
−60	0.05		10.8	none	50	82			23.4
−60	0.05		10.2	3.0	48	45			25.8
−60	0.008		10.2	none	72	80	1060	1490	23.1
−60	0.25		49.5	15.0	140	67			~26.0
−60	0.25		49.3	15.0	140	72			~26.0
−78		0.004	2.4	1.5	25	2.7			27.3

opening polymerization of 2-methyloxacyclobutane (2-MOCB) were investigated and high proportions of head-to-head and tail-to-tail irregularities were found in all the polymers.[9] In continuation of these studies very high molecular weight polymers were obtained and the kinetics of the polymerization investigated.[10] We have now investigated the polymerization of 2,2-dimethyloxacyclobutane (2,2-DMOCB) and report our findings here: the additional methyl substituent has a very marked influence on the polymerization behavior of the monomer.

Experimental Section

Preparation of Monomer. 2,2-DMOCB was prepared from isoprene that was first converted to 1,3-dichloro-3-methylbutane by reaction with concentrated hydrochloric acid according to a published procedure.[11] This compound was refluxed with 33% sodium carbonate solution under agitation for 12 h to yield 4-chloro-2-methyl-2-butanol, which was distilled: bp 82 °C (25 mm); n^{25}_D 1.4445; the IR spectrum was in accordance with that previously published.[12] The ring closure to 2,2-DMOCB was effected according to the method of Bennett and Philip[13] whereby the 4-chloro-2-methyl-2-butanol was reacted with solid potassium hydroxide. After redistillation on a spinning-band column, the 2,2-DMOCB was obtained in a purity better than 99.9% as determined by gas chromatography: bp 67.5–68 °C (760 mm) (uncorrected); ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 6 H, 2 CH_3), 2.40 (t, 2 H, CH_2, J = 8 Hz), 4.47 (t, 2 H, CH_2O, J = 8 Hz) (similar to previously published data[12]); ^{13}C NMR ($CDCl_3$) δ 29.4 (2 CH_3), 34.2 (CH_2), 63.7 (CH_2O), 84.6 (>C<).

Polymerization Procedure. The polymerizations were carried out under high vacuum in all-glass equipment with break seals essentially as previously described.[14] CH_2Cl_2 was prepurified according to a published procedure[15] and finally distilled from CaH_2. PF_5 initiator was generated by decomposition of *p*-chlorobenzenediazonium hexafluorophosphate, *p*-$ClC_6H_4N_2PF_6$ (recrystallized from water), under high vacuum at 156 °C. Et_3OPF_6 initiator was purified and used as previously described.[16] Polymerizations were stopped by addition of ethanol containing about 10% water. After the polymer was dissolved in CH_2Cl_2, the solvent was removed under vacuum on a rotary evaporator and the polymer finally dried to a constant weight at room temperature under vacuum (2 mmHg). Termination of some of the polymerizations with THF–sodium phenoxide yielded polymers with identical molecular weight distributions by bulk as well as by solution experiments. Heating to 70 °C together with drying did not cause any change in the molecular weight distributions.

Characterization of Products. Molecular weight distributions were determined by gel permeation chromatography on a Waters Model 200 instrument using THF as solvent and columns with porosities 2000, 500, 100, and 60 Å. The molecular weight values were calculated on the basis of a calibration curve obtained with narrow molecular weight samples of poly(propylene oxide) and polystyrene from Waters. The principle of extended chain lengths was used in calculating molecular weight average values, utilizing a Q value (weight per Å) of 18.4.

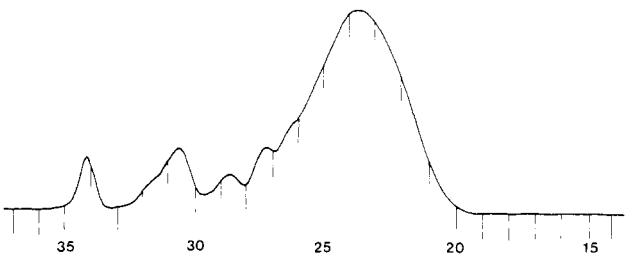

Figure 1. GPC curve for poly(2,2-DMOCB) prepared by bulk polymerization.

The oligomers were separated with a VL Watt 10-stage molecular still. A 5.4-g sample was fractionated by starting with a pressure of 0.2 torr and gradually decreasing the pressure to 0.01 torr while simultaneously gradually increasing the temperature from 34 to 102 °C.

The ^{1}H NMR spectra were recorded in $CDCl_3$ solutions on a Varian 60-MHz instrument. The ^{13}C NMR spectra were recorded on approximately 10% solutions in $CDCl_3$ with a Bruker WH 90 FT instrument operating at 22.63 MHz.

IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer.

Mass spectrometric analysis was performed on a VG 7070 instrument using chemical ionization with isobutane as the reactant gas. The ion source temperature was 220 °C.

Results and Discussion

Table I summarizes the data for the polymerization experiments carried out with 2,2-DMOCB in bulk and in CH_2Cl_2 solution using the initiators PF_5 and Et_3OPF_6. It is evident that in all cases the molecular weights are low. Molecular weights are only calculated for the samples with the lowest elution volumes. Actually, all the samples consist of blends of low polymers and oligomers as illustrated by the GPC curve in Figure 1 for the polymer with $\bar{M}_n$ = 800 and $\bar{M}_w$ = 1020. In most other samples oligomers constituted a larger fraction, and only the elution counts for the GPC peak positions are given for comparative purposes.

No significant difference between the two initiators was found with respect to the molecular weight of the resulting polymers. The molecular weights decreased when the polymerization was carried out in solution. It is seen that a large decrease in the added amount of PF_5 initiator results in only a modest increase in the molecular weight. A similar result was obtained with the oxonium salt initiator, and it is concluded that low molecular weights are inherent in these polymerization systems. In comparison, monomethyl-substituted 2-MOCB yielded at −50 °C under similar polymerization conditions a polymer with $\bar{M}_w$ > 200 000, i.e., about a 3 order of magnitude higher value.[10]

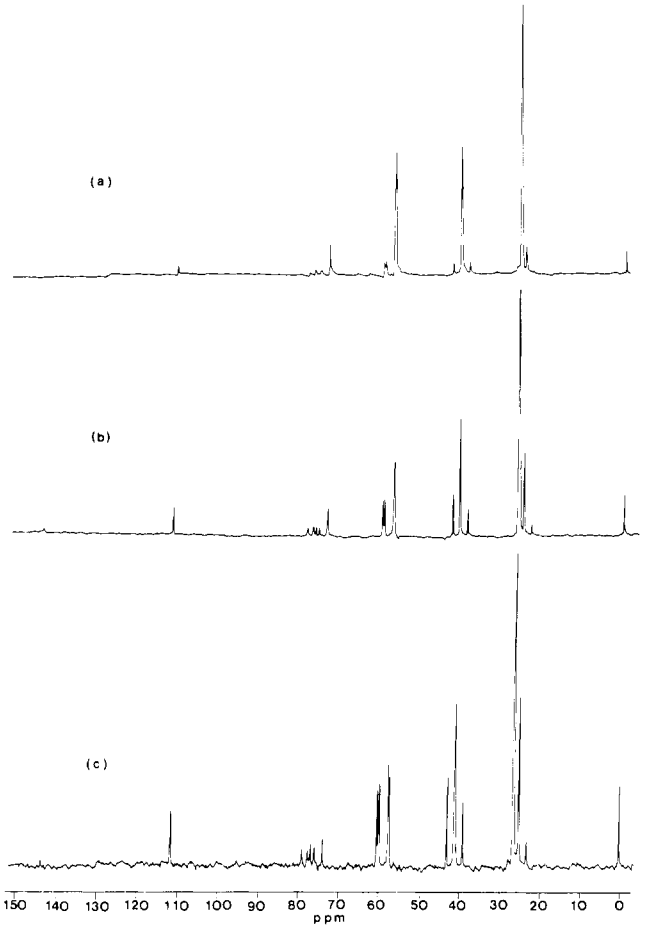

Figure 2. ^{13}C NMR spectra of poly(2,2-DMOCB) (a), pentamer of 2,2-DMOCB (b), and tetramer of 2,2-DMOCB (c).

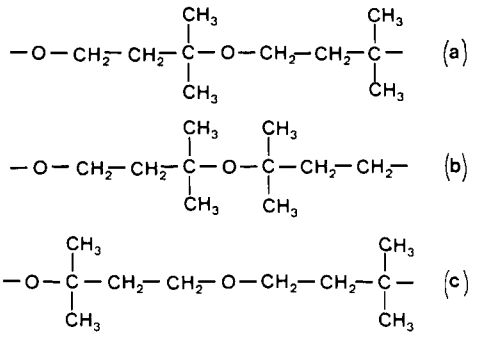

Figure 3. Head-to-tail (a), head-to-head (b), and tail-to-tail (c) structures in poly(2,2-DMOCB).

In Figure 2a a ^{13}C NMR spectrum is presented for a polymer of 2,2-DMOCB corresponding to that of Figure 1. The major peaks are easily identified and the values assigned relative to Me_4Si. The methyl groups appear at 26.0 ppm and the tertiary carbon, which gives a very weak signal due to the absence of hydrogens, appears at 73.7 ppm. The two methylene carbons are found at 57.4 and 40.8 ppm, where the signal at lower field arises from the carbon adjacent to oxygen. In addition, a number of minor peaks appear in the spectrum. The question arises whether any of these may be due to head-to-head or tail-to-tail irregularities as found in the polymerization of 2-MOCB.[9]

Each of the methyl carbons will experience the interaction of two additional δ carbons (see Figure 3), which is expected to cause a deshielding.[17] However, the additional signal is found upfield from 26.0 ppm, and it may therefore be concluded that the small peak does not originate from a head-to-head structure. Similarly, the absence of tail-to-tail structures is indicated by the position of the small peaks at 59.7 ppm, downfield from the methylene carbon at 57.4 ppm. In the tail-to-tail structure, the absence of the interaction of two methyl carbons in the γ position would be expected to cause a downfield shift of the order of 4–5 ppm, i.e., larger than the recorded shift of 2.3 ppm.

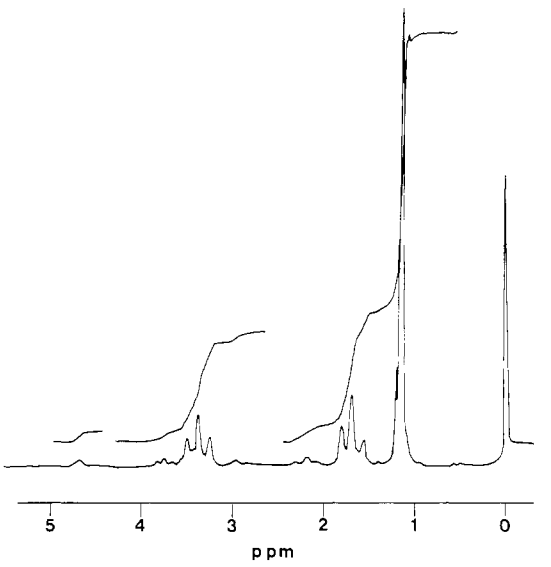

Figure 4. ^{1}H NMR spectrum of poly(2,2-DMOCB).

The additional small signals in the ^{13}C NMR spectrum (aside from those of Me_4Si and $CDCl_3$) are all attributed to the carbons present in the end groups. These may be detected by ^{13}C NMR since the molecular weights are, as already pointed out, quite low and the sample contains oligomers. A small signal at 111.1 ppm assigned to an olefinic carbon is seen in the ^{13}C spectrum. The chain end is indicated to consist of an isopropenyl group, in accordance with the signal from C-1 in 2-methyl-1-heptane (110.2 ppm)[18] or the corresponding carbon in an isoprene dimer (110 ppm).[19] The C-2 signal from this olefin structure should appear around 145 ppm[18,19] although it is expected to be very weak. In the ^{13}C spectrum of poly(2,2-DMOCB) no such signal is observed, probably due to the relatively low concentration of end groups. However, in the ^{13}C spectra for the oligomers (Figure 2b,c) a signal is clearly seen at 143.2 ppm. The signal from the methyl carbon in the isopropenyl group should appear around 22 ppm,[18,19] i.e., upfield from the methyl groups in the repeating units. This is in accordance with the spectrum shown in Figure 2a, although the recorded shift is smaller, probably due to some deshielding by the neighboring oxygen. The presence of a vinyl-type olefinic bond can be ruled out since such a C-1 signal should have appeared around 114.5 ppm, corresponding to that in 1-octene.[18]

The ^{1}H NMR spectrum shown in Figure 4 reveals the same structural features as the ^{13}C spectrum. The methyl protons appear at 1.14 ppm, with a smaller peak at slightly lower field. The methylene protons appear, as expected, as triplets in the vicinity of 1.68 and 3.37 ppm, respectively. In addition, a small peak appears at 4.69 ppm, in accordance with the presence of olefinic protons in the sample. Finally, the singlet signal at 3.0 ppm, the position of which was found to be somewhat labile, is assigned to a hydroxyl group. In the case of the isolated oligomers (to be discussed below) a proton signal was found to disappear when D_2O was added to the sample solution, in accordance with the presence of a hydroxyl group.

Infrared analysis confirmed the presence of double bonds and hydroxyl groups since absorptions were ob-

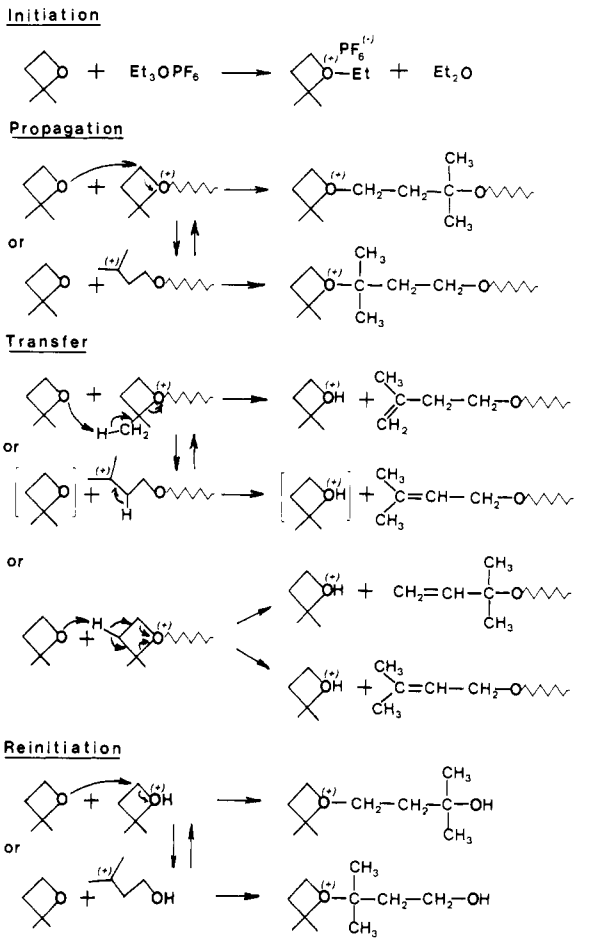

Figure 5. Mechanistic possibilities in the polymerization of 2,2-DMOCB.

served at 1650 and 3480 cm^{-1}.

The mechanistic possibilities are shown in Figure 5 and will be evaluated in light of the various experimental observations. The initiation is presented only for the case of the oxonium salt initiator, where the process simply is transfer of an ethyl cation to monomer for formation of the cyclic oxonium ion with the PF_6^- counterion. For PF_5 initiator the process is more complex although the same species eventually is formed, i.e., the cyclic oxonium ion with a PF_6^- counterion. It has been shown[20] that for the case of tetrahydrofuran, PF_6^- is generated along with the oxonium ion from an initially formed donor–acceptor complex of the cyclic ether and PF_5. POF_3 may be eliminated from the noncyclic end to yield a fluorine-terminated chain. Eventually, further reaction of this end with a donor–acceptor complex may yield a bifunctional oxonium ion.

Propagation may be visualized to occur by nucleophilic attack of monomer oxygen on an adjacent position to the oxonium ion. This possibility is illustrated in the scheme by an S_N2-type displacement reaction at the C-4 methylene carbon. A similar attack at the C-2 tertiary carbon is effectively prevented by steric hindrance at that carbon or will be an exceedingly slow reaction by such a mechanism in accordance with general knowledge about nucleophilic displacement reactions on organic molecules.[21] A preceding carbenium ion formation is considered necessary prior to the attack of monomer at C-2 and the propagation will in that case occur by a two-step S_N1-type mechanism as shown in the scheme. This propagation reaction results first in the formation of the rather stable tertiary carbenium ion, which is in equilibrium with the oxonium ion species, and second in the combination with monomer, which again leads to formation of the oxonium ion. The actual concentration of carbenium ions could be rather small since recombination with oxygen in the various species is prevalent. Interception with monomer leads to progression of the degree of polymerization. The direction of the ring opening that is taking place in connection with the propagation reaction cannot be deduced on the above basis, since the same structure of the repeat unit will be obtained whether the bond breakage occurs exclusively at C-2 or at C-4. However, inference from the conclusion regarding the reinitiation reaction (see below) points to ring opening at the tertiary carbon–oxygen bond.

Since the molecular weights are exceedingly low, transfer reactions are likely to be operating, which also results in the formation of olefinic and hydroxyl groups in the polymers. The transfer to monomer can, in principle, occur from either the oxonium ion or the carbenium ion species, as shown. The proton abstraction by monomer from one of the methyl groups in the oxonium ion results in the formation of the isopropenyl group, which, as already discussed, is indicated to be present by the spectral data. Proton abstraction from C-3 in the oxonium species, on the other hand, would result, as illustrated in Figure 5, in formation of either a vinyl group or an internal double bond. As already pointed out, the spectral data do not indicate the presence of the former nor is an internal double bond found to be present by the NMR data. According to published values for the model compound for the internal double bond, 2-methyl-2-heptene,[18] signals are found at 131 ppm for the C-2 carbon and at 125.5 ppm for the C-3 carbon. Even when corrections are made for the influence of a neighboring oxygen on these chemical shift values,[22] as is present in the actual possible chain end structure, the signals are still predicted to appear at positions different from those actually observed (110.2 and 143.2 ppm) and already assigned to the isopropenyl group.

In the case of elimination from the carbenium ion species, an end-group structure having either a terminal or an internal double bond could also, in principle, be formed. According to the Saytzeff rule for an E1-type elimination reaction,[23] however, the most highly substituted double-bond structure should be formed. Since this is not observed for our system, at least not to any significant extent, it appears that the elimination (and the transfer to the monomer) does not occur from the carbenium ion species. We, therefore, conclude that the elimination is taking place from the oxonium ion species, shown in Figure 5, yielding the least substituted structure, which is in accordance with the Hoffman rule for elimination from an onium ion.[23] A molecular model of the oxonium ion indicates that methyl protons in contrast to the methylene protons at C-3 may be in an antiperiplanar position to the oxonium ion bond, which will promote the elimination of the former protons.[24]

We suggest that transfer by elimination from the carbenium ion is not able to compete with the propagation reaction during the time span available before the carbenium ion reverts back to the oxonium ion structure. On the other hand, transfer reaction and elimination will easily take place with the oxonium ion.

The reinitiation step, where monomer reacts with the protonated monomer species, may again be visualized to occur either via the oxonium ion or via the carbenium ion route as illustrated in Figure 5. Here, the same considerations apply as already presented for the propagation step. The nucleophilic displacement on the oxonium ion may take place at C-4 but not at C-2, leading to a structure

Table II
22.63-MHz ^{13}C NMR Signals[a] for Poly(2,2-DMOCB) and Model Compounds

	CH_3–	–C–	–CH_2–	–CH_2O	CH_2=C
		Polymer			
repeat unit	26.0	73.7	40.8	57.4	
olefinic end unit	24.9		38.7	59.7	111.1
hydroxyl end unit			42.9	60.1	
		Model Compounds			
$HO-C(CH_3)_2-CH_2CH_2OH$	29.4	71.7	46.4	59.7	
$HO-C(CH_3)_2-CH_2CH_2OCH_2CH_3$	29.3	70.6	41.4	67.9	

[a] Ppm downfield from Me_4Si.

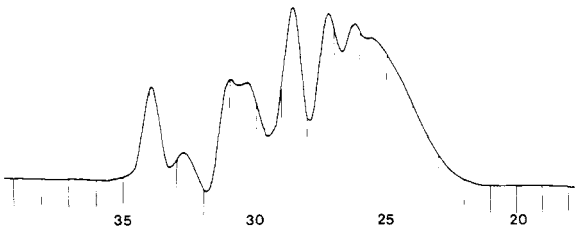

Figure 6. GPC curve for poly(2,2-DMOCB) prepared by solution polymerization and used for oligomer fractionation.

with a tertiary hydroxyl group. However, if dissociation occurs at C-2 to form the carbenium ion prior to the attack of monomer, the end-group structure will contain a primary hydroxyl group.

In order to determine which end-group structure actually is formed, we compared the ^{13}C NMR data for the polymer with those for two model compounds. From Table II it is seen that for the model 3-methyl-1,3-butanediol the signal from the methyl carbons at the tertiary hydroxyl appears at 29.4 ppm and the signal for the tertiary carbon itself at 71.7 ppm. The carbon at the primary hydroxyl group is found at 59.7 ppm. In the ether derivative little change is found for the methyl and the methine carbons; however, the primary carbon becomes more deshielded after the ether formation. The important point is that signals corresponding to the presence of the methyl groups of the tertiary hydroxyl group are not found in the polymer, while the observed signal at 60.1 ppm corresponds closely to the signal found for the primary hydroxyl carbon in the model compound, which is influenced by one less deshielding δ carbon ca. 0.4 ppm. We conclude therefore that the polymer has an end-group structure with a primary hydroxyl group and the direction of the ring opening must occur along the tertiary carbon–oxygen bond. The propagation reaction is considered to occur by an equivalent mechanism and it is inferred that the ring opening occurs with formation of a tertiary carbenium ion followed by attack of monomer.

Oligomers formed during the course of the polymerization could be isolated by molecular distillation. Two experiments were carried out at –60 °C with somewhat larger amounts of monomer (see Table I for conditions). The yield was around 70% and the GPC curve is shown in Figure 6. The sample clearly contained oligomers from dimer to pentamer. The molecular distillation was carried out by gradually raising the temperature while decreasing pressure on a 5.4-g sample, which was separated into 16 fractions. The molecular distillation is expected to yield

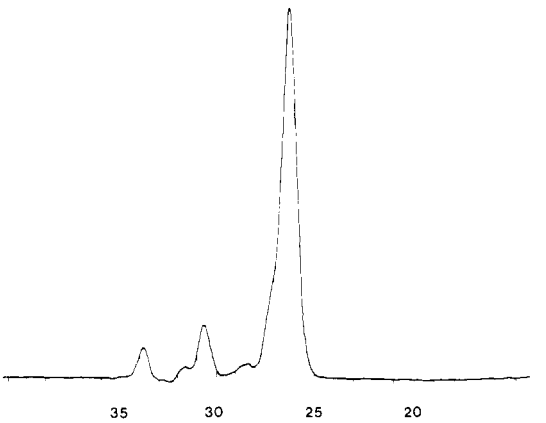

Figure 7. Tetramer fraction from poly(2,2-DMOCB).

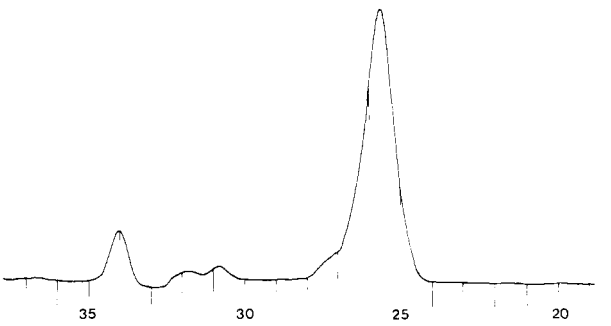

Figure 8. Pentamer fraction from poly(2,2-DMOCB).

the oligomers formed during the polymerization. As mentioned in the Experimental Section, neither the method of termination nor a moderate heating of the sample causes any change in molecular weight distribution. The fractions were analyzed by GPC, and the oligomer fractions were obtained better than 90% pure as determined by this analytical method. In Figures 7 and 8 the GPC curves are shown for the fractions isolated and identified as tetramer and pentamer. The elution volumes for the oligomers correspond to those observed for the components of the original sample before distillation. The elemental analysis for the tetramer (C, 69.25; H, 11.73) and the pentamer (C, 69.32; H, 11.43) is in good agreement with the overall theoretical values based on $(C_5H_{10}O)_n$ (C, 69.72; H, 11.71).

Analyses by mass spectrometry with chemical ionization showed in the case of the pentamer fraction the presence of predominantly protonated species with masses of 431, 345, 259, and 173 corresponding to pentamer, tetramer, trimer, and dimer but only very little hexamer (mass 517).

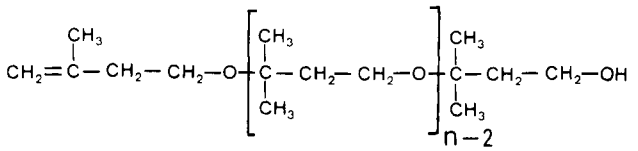

Figure 9. General formula for oligomer and polymer of 2,2-DMOCB.

Similarly, for the tetramer fraction, species from protonated tetramer and downward were found, but only very little pentamer was detected. Also the trimer and dimer fractions contained very little of the higher homologues. It appears that considerable breakdown to lower oligomers occurs during the analysis on the mass spectrometer along with the formation of many other species that were found to be present in relatively smaller quantities. The GPC analyses showed that lower species certainly were not present in such quantities from the start. Nevertheless, the mass spectrometric analysis identifies the original masses of the fractions and these are in accordance with the general formula for the oligo- and polymeric species shown in Figure 9.

Figure 2b,c presents the ^{13}C NMR spectra for the pentamer and tetramer fractions, respectively, and may be compared with that of the polymer in Figure 2a. The same signals are observed as for the polymer, and, as already pointed out, also a small signal is seen at 143.2 ppm corresponding to the C-2 carbon in the isopropenyl group. Obviously, the signals already assigned to the end groups of the polymer are accentuated in the oligomers. Noticeable are the olefinic carbon at 111.1 ppm, the methyl group at the olefinic bond at 24.9 ppm, and the methylene carbons (between carbons) at the olefinic end at 38.7 ppm and at the hydroxyl end at 42.9 ppm. The methylene carbons adjacent to oxygen in the end groups are found downfield from the corresponding carbon at 57.4 ppm in the repeat unit. Some additional small peaks are seen, particularly in the methyl region, which indicates that the elimination reaction occurring in connection with the transfer is not a completely specific reaction.

The ^{13}C spectrum for the dimer is in accordance with a structure consisting of a combination of the two end-group units, and signals arising from the repeat units, present in higher oligomers (the middle portion of Figure 9), were essentially absent in the spectrum.

The presence of hydroxyl groups in the oligomers was confirmed by exchange of the protons with D_2O. In all the oligomers the OH peak appearing in the range 3.07–3.55 ppm in the ^1H NMR spectra disappeared after exchange with D_2O. It was confirmed by area integration that for each oligomer one proton was removed by exchange. The proton signals, excluding the protons at geminal methyl groups, were divided into two groups A and B, which for each oligomer represent an equal number of protons before exchange with D_2O. Group A consisted of the methylene protons adjacent to oxygen of the repeat units (see Figure 9) around 3.37 ppm, the corresponding proton in the end-group position appearing at lower field (may be seen in Figure 4), the proton of the hydroxyl group, and finally the two protons at the double bond. Group B consisted of all other methylene protons and in addition the methyl protons at the double bond. After the initial area ratios were normalized to $A/B = 1$, the same ratios for the oligomers after exchange with D_2O were determined to be 0.84, 0.87, 0.88, and 0.89 for the dimer, trimer, tetramer, and pentamer fractions, respectively. This compares with theoretical values of 0.86, 0.89, 0.91, and 0.92 based on the disappearance of the hydroxyl proton in each of the pure oligomers after exchange. The reasonable agreement between the normalized and theoretical values, in spite of some systematic deviation, indicates, as already found by the ^{13}C NMR analyses, that all the oligomeric species contain a hydroxyl end group. The ^1H NMR data, on the other hand, are not in the present case suitable for accurately calculating the size of the various oligomers.

The presence of appreciable amounts of cyclic oligomers without hydroxyl end groups in the fractions would have had the effect of increasing the above experimental area ratios relative to the theoretical values. Also, the GPC curves for the original unfractionated sample and the various fractions do not indicate the additional presence of sizeable amounts of cyclic oligomers since the elution volumes would be expected to be slightly longer for these species and additional peaks should have been observed. The presence of a few percent of cyclic oligomers, however, cannot be completely ruled out.

We note that the same structural features arising from end-group structures are found in all fractions of poly(2,2-DMOCB) although the relative amounts decrease with molecular size. We propose that essentially all the molecular species, irrespective of size, arise from the transfer processes by our proposed mechanisms.

Conclusion

The polymerization of 2,2-DMOCB is found to be governed by the structure of the active species. Only low polymers and oligomers are formed with an isopropenyl group at one end and a primary hydroxyl group at the other end. The double substitution at one of the carbons adjacent to oxygen will partly cause steric hindrance toward nucleophilic attack by monomer on the oxonium ion species and partly cause a weakening of the tertiary carbon–oxygen bond, resulting in formation of tertiary carbenium ion species. The presence of both types of species is indicated. The transfer to monomer occurs with the oxonium ion at the tertiary position, yielding the least substituted olefinic end group. Reinitiation by attack of monomer on the protonated monomer resulting from the transfer reaction leads to formation of a primary and not a tertiary hydroxyl end group and must involve the carbenium ion species and likewise the following propagation step. The direction of the ring opening is along the tertiary carbon–oxygen bond in these reactions.

A dynamic equilibrium between oxonium and carbenium ion species is visualized where the latter will propagate rather than undergo transfer reaction with monomer. The oxonium ion species, on the other hand, may undergo transfer reaction to monomer but not propagation. The transfer reactions are responsible for the low molecular weights of the polymers and determine the predominant end-group structures in all the molecular species that are formed.

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High Molecular Weight Poly(2-methoxy-1,3,2-dioxaphospholane 2-oxide) by Ring-Opening Catalysis of Tertiary Amines. Initiation and Stepwise Propagation Mechanisms As Studied by the Stoichiometric Reaction with Triethylamine

Hajime Yasuda, Mitsuhiro Sumitani, Keonil Lee, Takeo Araki,† and Akira Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received December 3, 1981*

ABSTRACT: Ring-opening polymerization of an unsubstituted cyclic phosphate, 2-methoxy-1,3,2-dioxaphospholane 2-oxide, by catalysis of tertiary amines gave a linear high polymer of $\bar{M}_n = 5 \times 10^4$. The corresponding mono- and dimethyl-substituted cyclic phosphates are also polymerized but with less efficiency. Ionic mechanisms for the initiation and propagation steps were proposed based upon the ^1H, ^{13}C, and ^{31}P NMR data of solution species formed in 1:1, 1:2, and 1:5 reactions between triethylamine and 2-methoxy-1,3,2-dioxaphospholane 2-oxide.

Introduction

Much effort has been devoted to the preparation of high molecular weight polymers containing phosphorus atoms in the main chain.[1] Condensation of a glycol with $P(O)Cl_3$ or $ROP(O)Cl_2$[2] and anionic[3] or cationic[4] ring-opening polymerization of 1,3,2-dioxaphospholane, 1,3,2-dioxaphospholane 2-oxide, and 1,3,2-dioxaphosphorinane in many cases have given low molecular weight polymers. Recently, organometal-catalyzed ring-opening polymerizations of a series of cyclic esters of phosphoric acid to give high molecular weight polymers have been reported by Penczek,[5] and the analysis of microstructure, polymerization mechanisms and interconversion into an acidic polyester have been extensively studied. In a previous paper, we reported a unique method for preparation of acidic polyesters by thermal elimination of isobutylene from poly(2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide).[6]

In seeking excellent catalysts for linear polymerization of five- or six-membered cyclic phosphates, we have found that a simple tertiary amine such as triethylamine or pyridine catalyzes the ring-opening polymerization of 2-methoxy-1,3,2-dioxaphospholane 2-oxide to give a high molecular weight linear polymer in good yield. Other characteristics of this type of polymerization are (1) the polymerization procedure and the removal of catalysts are facile and do not require any special techniques and (2) water-insoluble high molecular weight polymers and water-soluble relatively low molecular weight polymers can be prepared at one's option by controlling the ratio between the monomer and catalyst.

High molecular weight polyesters of phosphoric acid thus prepared will be useful as novel functional polymer materials with specific physical properties such as hydrophilicity, nonflammability,[7] thermal stability, high adhesion to glass and metal, etc.[8] If it is possible to convert efficiently $O{=}P(OR)_3$ groups in the main chain into $O{=}P(OH)(OR)_2$ groups, a wide applicability may appear because its polymer backbone is analogous to that of polynucleotides. Preparation of synthetic polynucleotides bearing hydrogen phosphate groups in the main chain has been attempted by condensation of $ROP(O)Cl_2$ with a glycol involving nucleic acid bases.[9] However, the polymer prepared so far has a molecular weight too low for synthetic polynucleotides.

Results and Discussion

1. Polymerization by Tertiary Amine Catalysts. The results of the polymerization of 2-methoxy-1,3,2-dioxaphospholane 2-oxide (1) with tertiary amine catalysis at 90 °C are listed in Table I. The polymer was separated into three fractions according to the solubility or magnitude of the molecular weight by fractional precipitation in methanol and water. The methanol-soluble fraction contains polymers of molecular weight 1×10^3 to 8×10^3 and the water-soluble fraction (but insoluble in methanol) contains polymers of $\bar{M}_n = 8 \times 10^3$ to 5×10^4 as analyzed by VPO (vapor pressure osmometry) and GPC (gel permeation chromatography). The molecular weight of the water-insoluble fraction was estimated to be $>5 \times 10^4$. The degree of cross-linkage for the water-insoluble polymer will be very small because practically no difference was ob-

† Present address: Department of Chemistry, Faculty of Science, Shimane University, Nishikawazu 1060, Matsue 690, Japan.

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