Polymer Bulletin 2, 707-712 (1980)

Polymer Bulletin

Cyclic Oligomers in the Cationic Polymerization of 3,3-Diethyloxetane

M. R. Bucquoye and E. J. Goethals

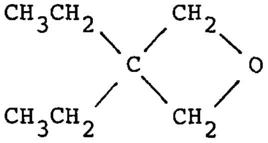
Institute of Organic Chemistry, Rijksuniversiteit Ghent, Ghent, Belgium

Summary

The cationic polymerization of 3,3-diethyloxetane leads to a mixture of polymer and cyclic oligomers. The cyclic tetramer is the most important oligomer and is formed in 20-35% yield. This behaviour is almost identical to that of the unsubstituted oxetane and 3,3-dimethyloxetane. The monomer consumption shows two distinct stages: a very fast stage is followed by a slow stage, leading to complete conversion. The cyclic oligomers are formed only during the second stage.

Introduction

In a study on the influence of alkylsubstituents on the polymerization behavior of four-membered heterocyclic monomers we have also investigated 3,3-diethyloxetane (DEO).



One of the characteristics of the polymerization of oxetane and of 3,3-dimethyloxetane is, that along with polymer, considerable amounts of cyclic oligomers are formed (ROSE 1956, DREYFUSS 1976, BUCQUOYE 1978). In the present paper we report on the formation of cyclic oligomers in the cationic polymerization of DEO.

Results and Discussion

Polymerizations were carried out in methylene chloride with triethyloxonium tetrafluoroborate as initiator. After complete monomer consumption the reaction mixtures were analyzed by gas-liquid chromatography (GLC).
Fig. 1 shows a typical chromatogram. Coupling of the GLC with a chemical ionization mass spectrograph (CI-MS) was used to determine the structure of the oligomers. It was found that the signals in the chromatogram correspond to trimer, tetramer (most intense peak) and pen-

0170-0839/80/0002/0707/$01.20

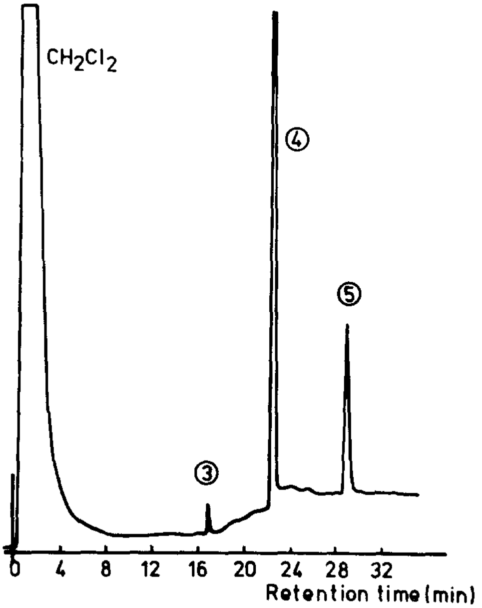


Fig. 1. GLC-analysis of the cyclic oligomers formed during the polymerization of DEO (50 m glass cappillary column with OV1 as stationary phase, temp. 50-240°, 4°/min). ③ : cyclic trimer, ④ : cyclic tetramer, 5 : cyclic pentamer.

tamer. In the case of oxetane and dimethyloxetane, cyclic oligomers up to nonamer have been detected. It is likely that also in the case of DEO, higher oligomers are formed. The fact that they are not detected by GLC is probably due to their low volatility.
The MS of the cyclic oligomers of DEO show fragmentation patterns which are similar to those described for the methyl- and unsubstituted homologues (VAN GAEVER 1978).
The tetramer could be isolated by selective crystallization from methylene chloride solution at 0°C. It is a needle-shaped crystalline material with a mp. of 138 °C.
The initial monomer concentration had a significant effect on the [oligomer]/[polymer] ratio, as is shown in Fig. 2. This observation is in agreement with the general dilution principle, according to which low concentrations of reactants favor the formation of cyclic reaction products. A remarkable but still unexplained relationship was found between the final [O]/[P] ratio and the initial monomer concentration $[M_o]$ (at 35 °C, [TEFB] = 10^{-2} mol/l and $[M_o]$ from 0,2 to 2 mol/l) :

$$[O]/[P] = -0{,}05 \ln[M_o] + 0{,}2$$

By means of ^1H NMR spectroscopy it is possible to observe the monomer, polymer and cyclic tetramer separately. The singlet at $\delta = 4{,}25$, corresponding to the methylene protons in the monomer is shifted to $\delta = 3{,}06$ for the polymer and to $\delta = 3{,}02$ for the cyclic tetramer. A similar but smaller upfield shift is observed for the ethyl methylene protons. The signals of the methyl protons of the ethyl substituent are not separated. As an

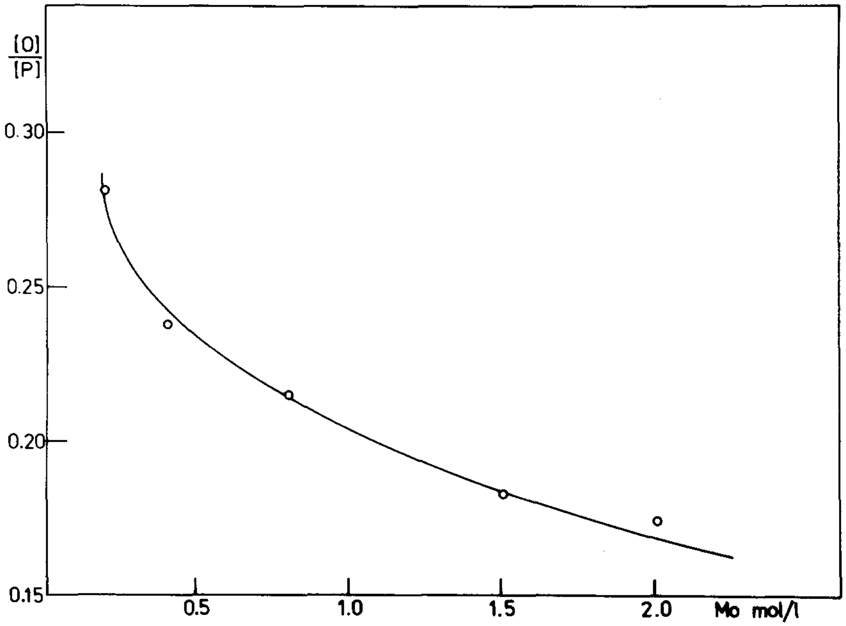


Fig. 2. Influence of initial monomer concentration (M_o) on [oligomer]/[polymer] ratio. (at 35 °C in CH_2Cl_2, $[Et_3OBF_4]$ = 0,01 mol/l).

example Fig. 3 shows the spectrum of a reaction mixture containing 19% of monomer, 57% of polymer, 20% of cyclic tetramer and 4% cyclic trimer. Using this technique it was possible to determine time-conversion curves for polymer and oligomer separately. Fig. 4 shows an example of such curves obtained at 35 °C in CD_2Cl_2. Experiments at lower temperatures were impossible because of the limited solubility of the reaction products.

From Fig. 4 it follows that during a first short period of the reaction there is a very rapid polymerization but no oligomer formation. In a second stage, polymer formation slows down markedly and cyclic oligomer is formed. Towards the end of the reaction, polymer concentration remains almost constant, the last part of the monomer apparently being converted exclusively into cyclic oligomer. This observation is in agreement with the mechanisms of cyclo-oligomer formation proposed for oxetane and 3,3-dimethyloxetane (BUCQUOYE 1978). It is also in partial agreement with the proposal of BLACK and WORSFOLD (1976) that only a minority of the oxonium ions, present during the polymerization of oxetane, are growing species. These authors have suggested that the four-membered ring oxonium ions are rapidly transformed into non-strained "dormant" oxonium ions by nucleophilic

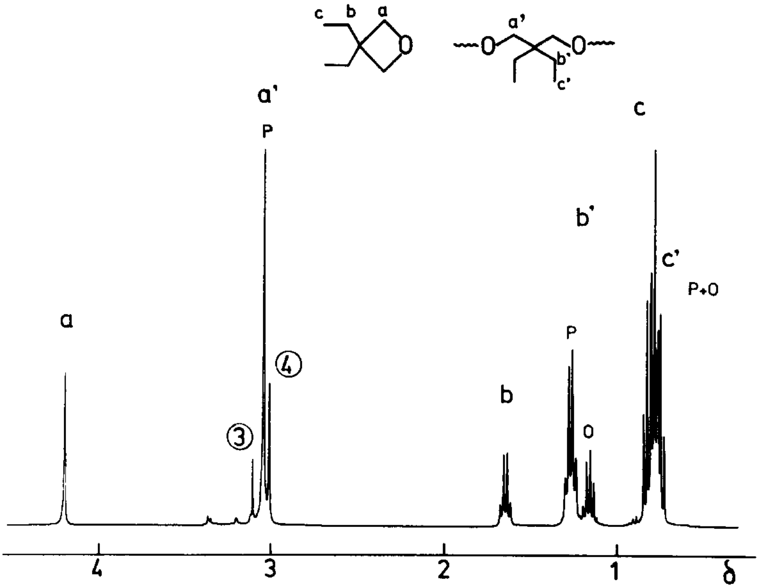


Fig. 3. 360 MHz ^{1}H NMR spectrum of a mixture of monomer, polymer (P) and cyclic oligomers (③ and ④).

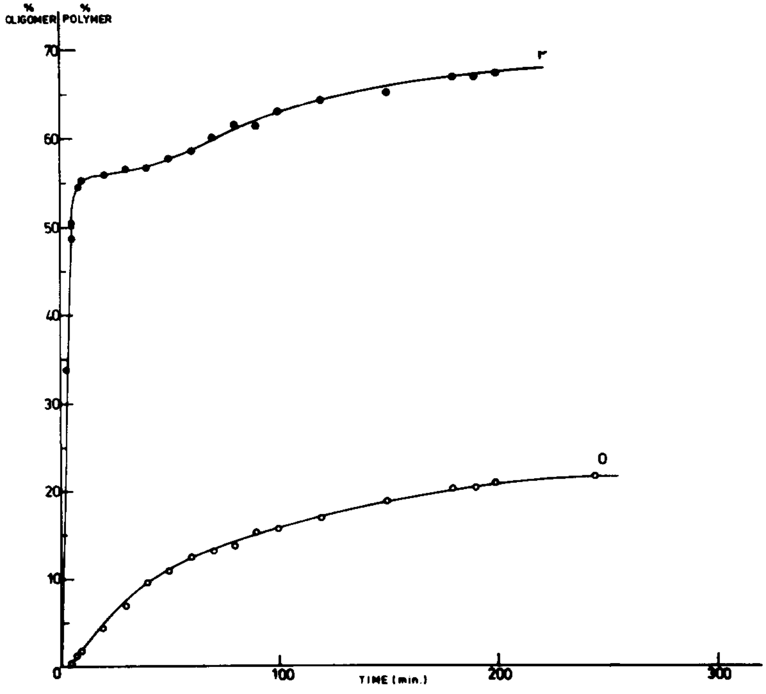
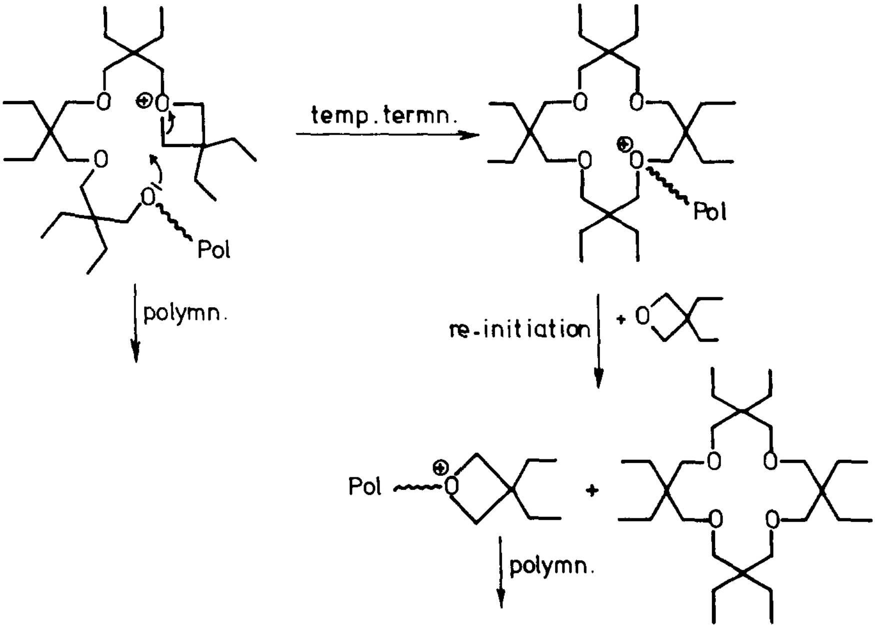


Fig. 4. Formation of polymer (P) and cyclic oligomers (O) as a function of time (at 35°C in CH_2Cl_2 $[M_o]$ = 0,3 mol/l, $[Et_3OBF_4]$ = 6,3 . 10^{-3} mol/l).

attack of an oxygen atom of the polymer molecules. Further polymerization in a slower phase, would occur via a re-initiation reaction with monomer. Our observation that the cyclic oligomers are formed only during the slow phase is a strong indication that the temporary termination reaction is an intramolecular one and consequently the dormant oxonium ions are macrocyclic. Thus the mechanism of cyclic oligomer formation is most probably as follows :



According to this mechanism, the ratio [oligomer]/[polymer] must increase with decreasing monomer concentration and although the oligomer is formed by a back-biting reaction from the polymer, its formation stops when the monomer is consumed.

ACKNOWLEDGEMENT
One of us (M.B.) thanks the Nationaal Fonds voor Wetenschappelijk Onderzoek for financial help.

REFERENCES

BLACK, P.E. and WORSFOLD, D.J.: Can. J. Chem. 54, 3325 (1976)
BUCQUOYE, M.R. and GOETHALS, E.J.: Makromolek. Chem. 179, 1681 (1978)
DREYFUSS, P. and DREYFUSS, M.P.: Polym. J. 8, 81 (1976)

ROSE, J.B.: J. Chem. Soc. 1956, 542; ibid. 1956, 546
VAN GAEVER, . et al.: Org. Mass. Spectr., 13, 8, 486 (1978)

Received May 1o/ Accepted May 12, 198o