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Investigations on the Stereochemistry and Polymerization of the 1,3-Dioxolane Derivatives. VIII.

Influence of the Cation and Anion Nature on the Polymerization of 1,3-Dioxolane Initiated by Trisubstituted 1,3-Dioxolan-2-ylium Salts

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Summary

The polymerization of 1,3-dioxolane initiated by a new type of initiator - trisubstituted 1,3-dioxolan-2-ylium salts was studied. It was found that the rate of monomer consumption depends on the kind of substituents and anions as well as on the geometrical structure of the isomeric salt used. The dioxolenium salts with an aliphatic substituent at C-2 and with stable anions are more active then salts with an aromatic substituent or those having unstable anions. In all these cases the cis isomers are more active than respective trans salt isomers.

Introduction

The use of the stable salts of organic cations as initiators in the cationic polymerization is recently an object of considerable interest. These compounds, particularly triphenylmethylium and trialkyloxonium salts with different anions, have been descri-

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bed in detail (LEDWITH, SHERRINGTON 1976).
To this group of initiators belong also the substituted 1,3-dioxolan-2-ylium salts.

Unsubstituted 1,3-dioxolan-2-ylium salts are formed as a result of a hydride ion transfer reaction in the first step of 1,3-dioxolane polymerization initiated by triphenylmethylium and trialkyloxonium salts (PENCZEK 1974). They are relatively unstable when compared with their substituted derivatives obtained in an analogous reaction of the respective substituted dioxolane with an organic cation, e.g. Ph_3C^+(JEDLIŃSKI et al. 1976). The stability of the salts of substituted dioxolane recommends compounds of this type as a new group of cationic initiators of particular use in investigations of polymerization initiation mechanism.

It was found previously (JEDLIŃSKI et al.1976; GIBAS,JEDLIŃSKI 1978), that 2,4,5-trisubstituted isomeric dioxolenium hexachloroantimonates initiate the polymerization of 1,3-dioxolane as well as that of some other cyclic monomers. These findings induced us to perform more detailed studies of the influence of the structure of trisubstituted dioxolenium salts on the course and mechanism of cationic polymerization.
This paper presents results of our investigations on the polymerization of 1,3-dioxolane using as catalysts salts having a general formula $RDMD^+A^-$ where $RDMD^+$ = = 2-alkyl /or aryl/ - 4,5-dimethyl-1,3-dioxolan-2-ylium cation, A^- = anion.

Experimental

<u>Solvent</u>: CH_2Cl_2 was purified by the procedure commonly used for ionic polymerization solvents.

<u>Monomer</u>: 1,3-Dioxolane /Fluka AG/ was purified by distillation over Na-K alloy and then dried in a closed distillation cycle with Na-K alloy under dry nitrogen.

Initiators: Isomeric trisubstituted 1,3-dioxolan-2-ylium salts were obtained in the reaction of tritylium salts with respective acetals, as previously described(JEDLIŃSKI et al. 1976). Commercial trityl salts were used: $Ph_3C^+SbCl_6^-$, $Ph_3C^+PF_6^-$ - Fluka AG, $Ph_3C^+AsF_6^-$ - Merck, $Ph_3C^+SbF_6^-$ - ICN Pharmaceuticals.

Dioxolane polymerization: The polymerization was carried out in methylene chloride solution at room temperature; monomer and initiator concentrations were $[M]_0 = 4.36$ and $[I]_0 = 1.18 \times 10^{-2}$ mol/l, respectively.

The appropriate amounts of catalyst, monomer and solvent were introduced into an NMR test tube, which was previously dried by heating under vacuum and dry nitrogen.

After mixing, the ^{1}H-NMR spectra were recorded using a JNM-C-60H /JEOL/ spectrometer. Actual monomer and polymer concentrations were determined by integrating the well-separated signals of both the methylene and ethylene protons of the monomer and polymer units /fig.1/.

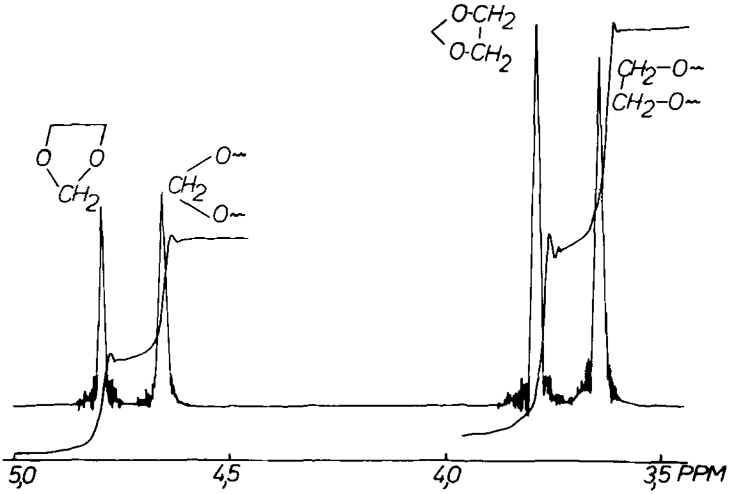
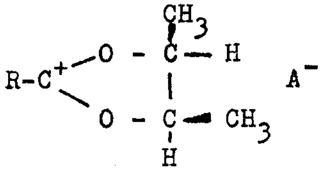


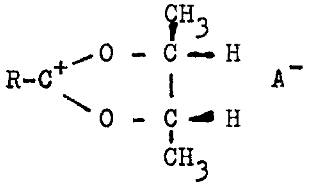
Fig.1. The ^{1}H-NMR spectrum of the polymerization system 1,3-dioxolane-c-PhDMD$^+$SbCl$_6^-$ in CH_2Cl_2

Results and discussion

Isomeric cis and trans trisubstituted 1,3-dioxolan-2-ylium salts with different substituents at C-2 and different anions were employed as catalysts:



cis



trans

where: R = CH_3 - /MDMD$^+$/, CH_3CH_2 - /EDMD$^+$/
$/CH_3/_2CH$ - /IPrDMD$^+$/, C_6H_5 - /PhDMD$^+$/,
C_6H_5-CH=CH - /SDMD$^+$/
$A^- = SbCl_6^-$, PF_6^-, SbF_6^-, AsF_6^-

When analysing the conversion-time curves shown in the fig.2,3 one can see that the structure of the cation influences distinctly the rate of dioxolane polymerization.
Both the type of the substituent at C-2 and the configuration of the methyl groups at C-4 and C-5 are responsible for different courses of polymerization.

The influence of the kind of the substituent at C-2 is shown in the fig.2. Conversion-time curves obtained when initiating with dioxolenium salts were compared with similar results obtained for well known initiators, i.e. $Ph_3C^+SbCl_6^-$ and $SbCl_5$.

The rate of polymerization initiated by salts with alkyl substituent at C-2 was found to be much faster when compared with that of a polymerization catalysed by a salt with an aromatic substituent.

The results obtained make it possible to arrange the catalysts having different substituents at C-2 and applied in 1,3-dioxolane polymerization, in the following order of decreasing activities:

$CH_3- > CH_3CH_2- > /CH_3/_2CH- > C_6H_5- > C_6H_5-CH{=}CH-$

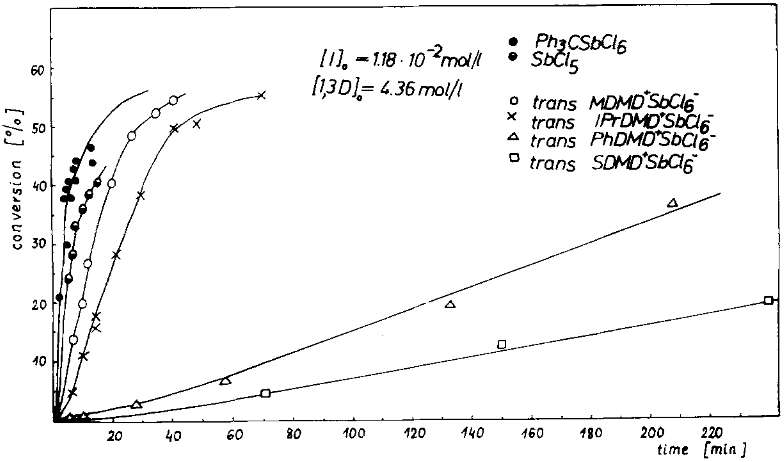


Fig.2. The influence of the kind of substituent at C-2 on the course of 1,3-dioxolane polymerization initiated by 2,4,5-trisubstituted 1,3-dioxolan-2-ylium hexachloroantimonate

This order is valid both for the series of salts with trans configuration and for the respective cis isomers of 1,3-dioxolan-2-ylium salts /fig.3/.

The results obtained when using salts with the same substituents at C-2 show that the geometrical configuration of the methyl groups at C-4 and C-5 appears to be a factor of considerable importance. The results shown in the fig.3 indicate that the salts with a cis configuration are more active than the respective trans isomers.

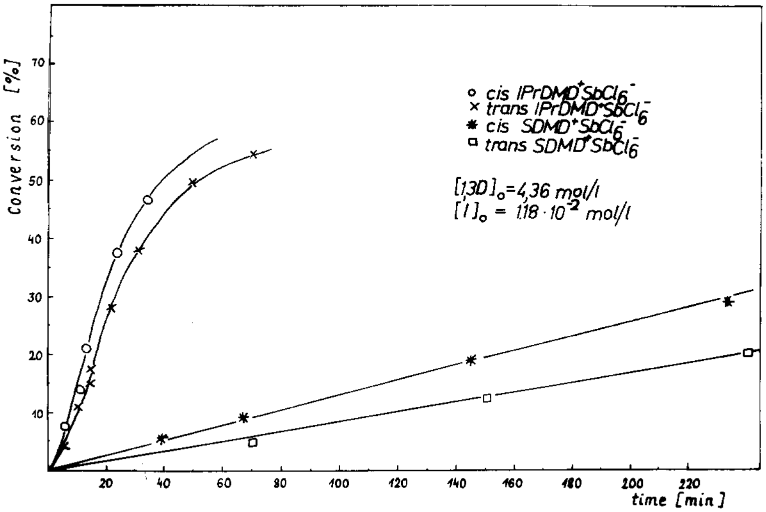


Fig.3. The relation between the rate of polymerization of 1,3-dioxolane and the configuration of substituted dioxolenium salts.

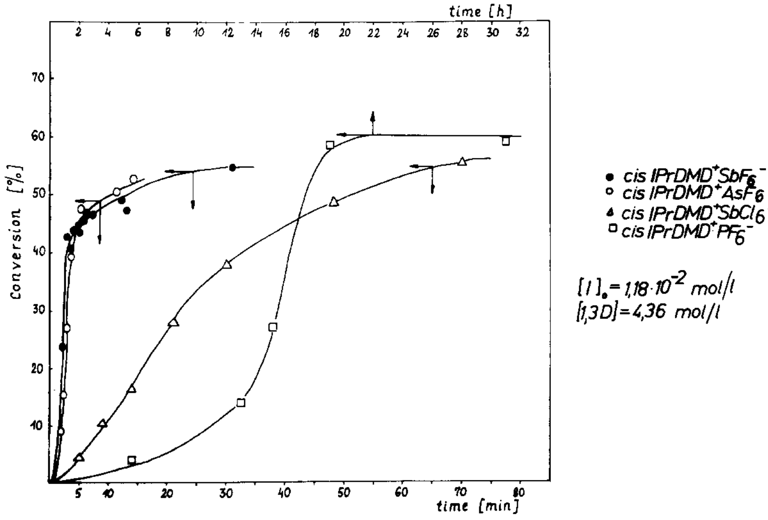


Fig.4. The influence of the kind of the anion on the rate of the polymerization of 1,3-dioxolane initiated by cis-IPrDMD$^+$A$^-$

The rate of 1,3-dioxolane polymerization initiated by 2,4,5-trisubstituted 1,3-dioxolan-2-ylium salts depends also on the type of the anion. Some results are shown in the fig.4 for the polymerization initiated by $IPrDMD^+A^-$.

The polymerization initiated by salts with anions known to be stable e.g. SbF_6^- (KUBISA 1976) is considerably faster than that found when using salts with PF_6^- or $SbCl_6^-$ anions.

The differences in the rate of 1,3-dioxolane polymerization initiated by stable dioxolenium salts depend both on the type of substituents and configuration of the 1,3-dioxolan-2-ylium cation, and may be due to steric effects as well as to differences in charge distribution.
Both these factors may influence the rate and the efficiency of initiation. Further investigations in this field are under way.

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