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The Polymerization Behaviour of 1-Benzyl-2,2-Dimethylaziridine

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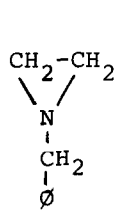
Summary

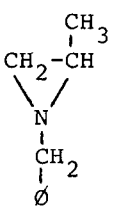
The polymerization of 1-benzyl-2,2-dimethylaziridine (BDMA) with triethyloxonium tetrafluoroborate (TEFB) under different reaction conditions was found to be impossible, although the initiation reaction (formation of 1-benzyl-1-ethyl-2,2-dimethylaziridinium tetrafluoroborate) was fast and quantitative. BDMA does copolymerize with 1-benzylaziridine (BA) but the amount of BDMA in the copolymer is always inferior to 50%. The reactivity parameters of the copolymerization (in dichloromethane at 20°C) are $r_{BA} = 3.1$ and $r_{BDMA} = 0.0$. These results demonstrate the importance of the presence of substituents on the polymerization behaviour of N-alkylaziridines.

Introduction

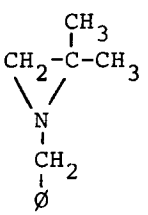
It has been reported earlier (GOETHALS et al., 1981) that the introduction of a methyl group in the 2-position of an N-substituted aziridine, has a marked effect on the polymerization behaviour: the rate constant of propagation decreases by several orders of magnitude but the rate constant of termination decreases even more drastically. Thus, under conditions where the polymerization of 1-benzylaziridine (BA) is very rapid but stops at low conversions, 1-benzyl-2-methylaziridine (BMA) polymerizes slowly with a quantitative yield.



BA



BMA



BDMA

In the present work it was investigated whether the introduction of a second methyl group in the 2-position of

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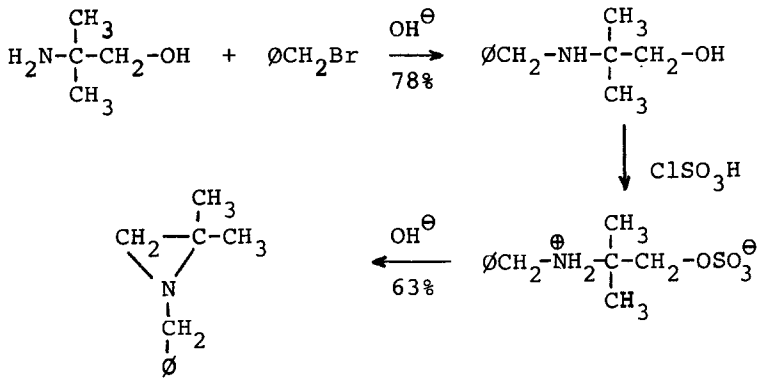
the aziridine ring would amplifie this difference in the hope that a polymerization with a very high living character would be obtained.

Results and Discussion.

1. Synthesis of BDMA.

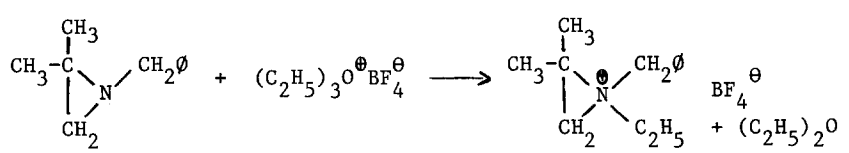
The monomer was obtained via the Wenker method (WENKER, 1935). The starting material 2-(benzylamino)-2-methyl-1-propanol, was obtained from 2-amino-2-methyl-1-propanol and benzylbromide.



BDMA is a colourless liquid with b.p. of 48-49° at 0,1 mm, density 0.93.
The structure of the monomer was confirmed by its ^{1}H-NMR spectrum, shown in Fig. 1, and by its mass spectrum.

2. Attempts to polymerize BDMA.

Polymerizations of N-alkylaziridines can be initiated by acids or alkylating agents (DERMER, HAM 1969). It was found earlier (GOETHALS, BOSSAER 1977) that triethyloxonium tetrafluoroborate (TEFB) is an excellent initiator because it reacts rapidly and quantitatively with the amino function to form the corresponding ammonium salt. Therefore this initiator was choosen for this study.
The polymerization of BDMA was tried in different solvents and in bulk at temperatures between 0 and 120°C. The result was invariably the same: there was no polymerization.
The initiation reaction between the monomer and TEFB to form the quaternary aziridinium salt did occur rapidly and quantitatively as expected. The 1-benzyl-1-ethyl-2,2-dimethylaziridinium tetrafluoroborate (BEDMAT) could be isolated by precipitation of the reaction mixture in ether. Fig. 2 shows the NMR spectrum of this salt.



BEDMAT

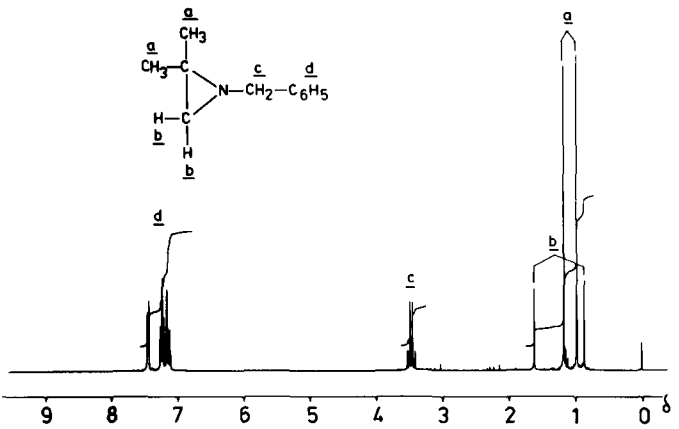


Fig. 1. 360 MHz ^{1}H-NMR spectrum of BDMA (in C_6D_6).

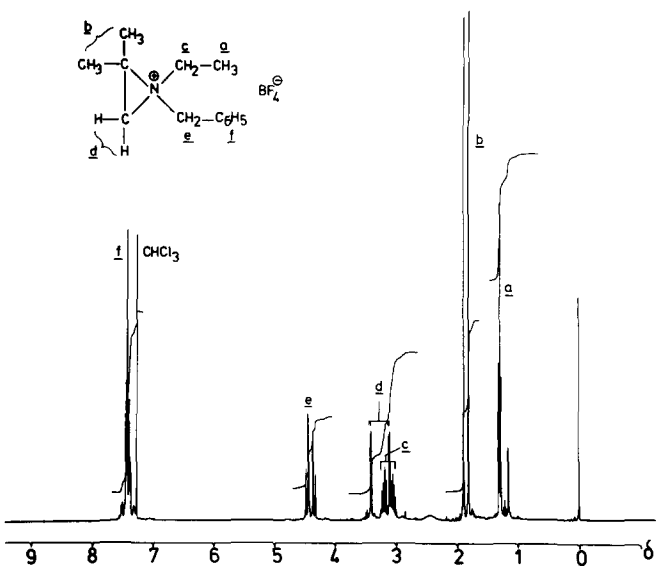
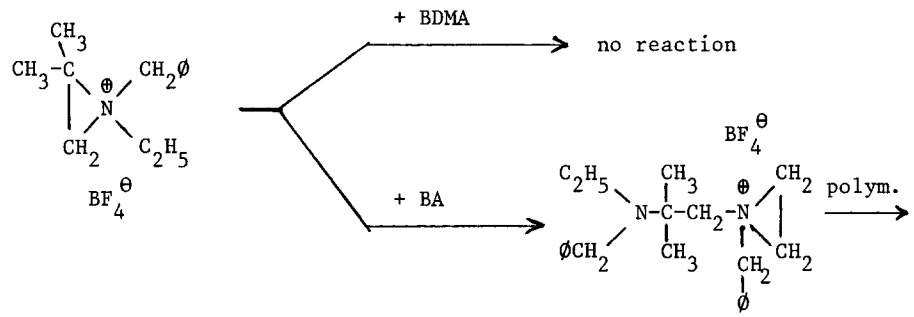


Fig. 2. 360 MHz ^{1}H-NMR spectrum of 1-benzyl-1-ethyl-2,2-dimethylaziridinium tetrafluoroborate (in $CDCl_3$).

This proves that the non-polymerizability of BDMA is not due to a bad initiation reaction but is really due to the fact that the ring opening of BEDMAT by monomer does not take place. This is a rather unexpected observation, taking into account that the aziridinium salt must have an important ring strain. As expected, BEDMAT is not able to initiate the polymerization of BDMA. However, if BEDMAT was added to a solution of BA, the polymerization started immediatly.



This proves that BEDMAT is indeed still reactive towards nucleophiles, such as BA. Clearly, the steric hindrance caused by the gem. dimethyl group in BDMA is the reason for the fact that this monomer does not react with the even more sterically hindered aziridinium salt.

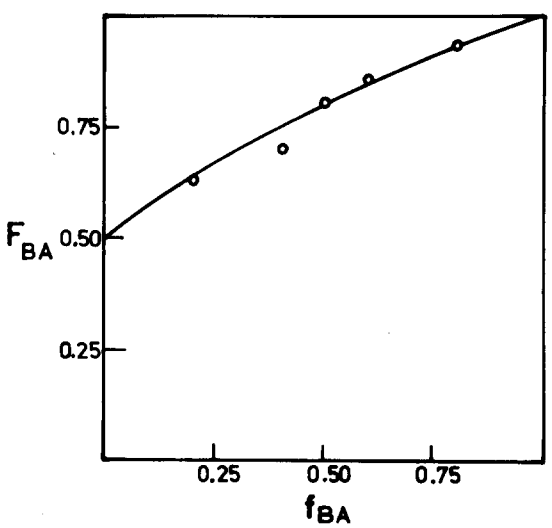


Fig. 3. Copolymerization curve for the monomer pair BA-BDMA (in CH_2Cl_2 at 20°C). The line represents the theoretical curve for r_{BA} = 3.1 and r_{BDMA} = 0.0.

3. Copolymerization of BDMA.

Although BDMA did not homopolymerize, it did copolymerize with BA. From the copolymerization curve, shown in Fig. 3, it is evident that the BDMA fraction in the copolymer is always markedly smaller than that of the monomer feed, the maximum amount incorporated being 50%. The copolymerization reactivity parameters derived by the Fineman-Ross method are :

$$r_{BA} = 3.1$$
$$r_{BDMA} = 0.0$$

The value of $r_{BA} = 3.1$ means that a polymer with a BA aziridinium ion end group reacts 3 times more rapidly with another BA than with a BDMA.
The value of $r_{BDMA} = 0$ was expected since the homopolymerization is impossible which implies that $k_p = 0$.
The fact that BDMA is incorporated in the copolymer thus means that a polymer with a BDMA end group only reacts with BA and consequently the highest content of this monomer can be 50% which corresponds to an alternating copolymer. Such a copolymer is obtained when a large excess of BDMA is employed.

Conclusion.

The results described above, demonstrate that the incorporation of methyl groups on a carbon atom of an N-alkyl aziridine has a dramatic effect on its polymerization behaviour. From the observation that BDMA does not homopolymerize but does copolymerize with BA, one can conclude that the steric hindrance of the active species as well as that of the incoming monomer are important. However, the most sterically hindered active species (the BDMA-ion) makes a much greater discrimination between the two monomers (a factor of infinity !) than the less sterically hindered active species (a factor of 3.1). These results confirm the theory (GOETHALS, 1976) that steric hindrance plays an important role in the cationic polymerization behaviour of heterocyclic monomers.

Experimental

Synthesis of BDMA.

68.4 g (0.4 mol) of benzylbromide are added dropwize to 106.8 g (1.2 mol) of 2-amino-2-methyl-1-propanol (Aldrich). The mixture is stirred for 8 hrs at 25°C. 32 g (0.6 mol) of potassium hydroxide are added and stirring is continued for another 3 hrs. Water is added to dissolve all salts and the mixture is extracted with benzene, the benzene solution is concentrated and the residue is fractionated in vacuum. After the excess of 2-amino-2-methyl-1-propanol, 57.5 g of 2-(benzylamino)-2-methyl-1-propanol distills over at 110-112°C at 0.2 mm (78.5%).
18.2 g of chlorosulfonic acid is added to a cooled and stirred solution of 27.9 g (0.052 mol) of 2-(benzylamino)-2-methyl-1-propanol in 600 mL of dichloromethane. After

stirring over night at room temperature, the solvent is evaporated on a rotavapor. The remaining salt is suspended in a 1/5 methanol-water mixture and is added slowly to a solution of 280 g of potassium hydroxide in 300 mL of water. The mixture is steam distilled, the distillate is made alkaline by addition of potassium hydroxide and is then extracted 3 times with ether. The ether solution is dried on sodium sulfate, the ether is evaporated and the residue is distilled in vacuum. 15.7 g of 1-benzyl-2,2-dimethylaziridine is collected at 48-49°C at 0.1 mm pressure (63%). Before polymerization the monomer is dried on calcium hydride and distilled under an atmosphere of dry nitrogen.

Triethyloxonium tetrafluoroborate was prepared according to MEERWEIN et al. (1949). The salt was stored at -20°C in sealed tubes as approx. 1 M solutions in dichloromethane.

1-Benzyl-1-ethyl-2,2-dimethyl aziridinium tetrafluoroborate (BEDMAT):

4.8 mL of 0.835 M solution (4 mmol) of triethyloxonium tetrafluoroborate is added dropwize to a stirred solution of 1.61 g (10 mmol) of BDMA in 10 mL dichloromethane, cooled at -5°C. The solution is poured into 50 mL of dry ether and the precipitate is filtered off under an atmosphere of dry nitrogen. The salt is purified by dissolving it in dichloromethane and pricipitation in dry ether. It has a m.p. of 86°C.

Polymerizations were carried out under an atmosphere of dry nitrogen.

The initiator solution was added to a stirred solution of the monomer(s) in dichloromethane. After the appropriate time, the mixture was poured into methanol. If no precipitate was formed, the methanol solution was concentrated and the residue analyzed by NMR spectroscopy.

Copolymers of BA and BDMA precipitate in the methanol. For the copolymerization curve, the yields were kept below 10% by using a low initiator concentration ($5 \cdot 10^{-3}$ $mol.l^{-1}$). The total monomer concentration was 1 $mol.l^{-1}$. The copolymer compositions were determined by 360 MHz ^1H NMR spectroscopy.

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