Improved synthesis and cationic polymerization of \textit{N-vinylmaleimide}

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Introduction

The cationic polymerization of olefins in the presence of strong protonic acids or Lewis acids has attracted considerable attention over a long period of time. As an example of significant industrial importance one can point to the production of butyl rubber obtained by the polymerization of isobutylene and isoprene in the presence of AlCl$_3$.\textsuperscript{1)}

In the early 1980s this area became even more promising, as it was discovered that vinyl ethers undergo a living cationic polymerization in the presence of HCl/I$_2$.\textsuperscript{2)} This process offers the possibility to prepare well-defined polymers with respect to structure, molecular weight and end-group functionality. In the last decadennium a number of research groups showed that also isobutylene (cumyl acetate/BCl$_3$), styrene derivatives (HCl/I$_2$) and \textit{N-vinylcarbazole} (HCl) can be polymerized in a living way.\textsuperscript{2)}

During our search for new monomers we became interested in \textit{N-vinylmaleimide} (1), which can be characterized as a dual monomer. It should be possible to polymerize the monomer by two different mechanisms, e.g., via cationic (vinyl group) and radical (maleimide group) species.

This paper describes an improved method for the preparation of 1 and preliminary results of the polymerization of 1 in the presence of BF$_3$·Et$_2$O and HCl/ZnCl$_2$.

Experimental part

Materials and methods

Vinyl acetate (2) (Janssen), maleimide (3) (Janssen), Na$_2$PdCl$_4$ (Janssen), BF$_3$·Et$_2$O (Aldrich), HCl (1,0 M solution in diethyl ether) (Aldrich), ZnCl$_2$ (1,0 M solution in diethyl ether) (Aldrich), dichloromethane (Merck), tetrahydrofuran (Baker) and chloroform-d$_1$ (CDCl$_3$) (Merck) were used as received. $^1$H NMR spectra were recorded on a Bruker ACF200 (200 MHz) under standard conditions. Gel-permeation chromatography (GPC) experiments were conducted with an equipment consisting of a Rheodyne injector, a Gilson 302 pump, a Waters 410 refractometer, a Severn Analytical SA 6503 detector and Styrargel columns 100, 500, 1000 and 10000 Å using tetrahydrofuran as the eluting agent. Calibration was carried out with polystyrene samples.

\textit{Synthesis of \textit{N-vinylmaleimide} (1)}

A mixture of 30 g (0,31 mol) of 3, 0,75 g (2,5 mmol) of Na$_2$PdCl$_4$ and 100 ml of 2 (1,2 mol) was stirred under reflux conditions for 17 h. The reaction product was isolated by filtration of the reaction mixture and subsequent evaporation of the excess of 2. Cooling of a solution of the reaction product in diethyl ether to $-17^\circ$C gave yellow crystals. Yield: 27,5 g (71 mol-%) of 1.
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$^1$H NMR (CDCl$_3$) (Fig. 1A): $\delta = 6.78$ (s; H$^a$), 6.68 (m; H$^b$), 5.87 (d; H$^c$), and 4.96 (d; H$^d$); $J_{b,c} = 17$ Hz, $J_{b,d} = 10$ Hz.


Polymerization of 1 in the presence of BF$_3$ · Et$_2$O

All polymerization experiments were performed in the same way. The following procedure serves as an example: A solution of 1.0 g (8.1 mmol) of 1 and 1.2 g (8.4 mmol) of BF$_3$ · Et$_2$O in 15 mL of dichloromethane was stirred at room temperature for 17 h. The reaction mixture was extracted with 20 mL of 1 N NaOH, subsequently dried on anhydrous Na$_2$SO$_4$ and finally evaporated to dryness to give a yellow solid material.

Polymerization of 1 in the presence of HCl/ZnCl$_2$

At $-30^\circ$C, 0.4 mmol of HCl was added to a solution of 0.89 g (7.2 mmol) of 1 in 15 mL of dichloromethane. After 90 min 0.4 mmol of ZnCl$_2$ was added. Stirring was continued for 17 h at $-20^\circ$C, after which the cooling equipment was removed. During the temperature rise, 0.4 mmol and 4.0 mmol of ZnCl$_2$ were added at 0°C (after 3 h) and 20°C (after 5 h), respectively. Samples were withdrawn for evaluation by means of GPC.

Results and discussion

Two routes were described for the synthesis of 1, namely the pyrolysis of N-hydroxyethylmaleamic acid at 600°C$^3$ and the reaction of N-vinyl-N-tert-butyl-carbamoyl chloride and maleic anhydride in N,N-dimethylformamide$^4)$. Both routes are inconvenient and result in low yields. It is known that succinimide reacts with 2 and catalytic amounts of Na$_2$PdCl$_4$ to give N-vinylsuccinimide$^5)$. So, we decided to test the same route for the synthesis of 1 starting from 3 (Scheme I).

Scheme I:

In the original paper, Bayer et al.$^5$) describe that the reaction of succinimide with 2 was carried out in two stages. After 20 h at reflux conditions the reaction product was isolated via filtration of the reaction mixture and evaporation of the excess of 2. The complete procedure was repeated with fresh 2 and the catalyst. However, reaction of 3 and 2 in the presence of Na$_2$PdCl$_4$ proceeded to completion within 17 h at reflux conditions. Additional experiments showed that the initial ratio of 2 to 3 can be reduced by a factor of ten without any detrimental effect on the yield of 1. Cooling of a diethyl ether solution of the reaction product gave bright yellow crystals in 71 mol-% yield.

The $^1$H NMR spectrum of this compound is depicted in Fig. 1A. The singlet (a) undoubtedly belongs to the vinylic protons of the maleimide group, while H(b) is split
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Fig. 1. \(^1\)H NMR spectra (\( * = \text{CDCl}_3 \)) of 1 (A) and the reaction mixture from 1 and 1.0 molequivalent of \( \text{BF}_3 \cdot \text{Et}_2\text{O} \) in dichloromethane after 17 h at room temperature (B).

![NMR spectra](image)

The delocalized \( \pi \)-system of the five-membered maleimide ring particularly affects the electron density of H(c) (cis position), the absorption of which is shifted to lower field; \( \delta \)H(c) - \( \delta \)H(d) (0.9 ppm) appears to be even larger than observed for \( \mu \)-methoxystyrene (0.5 ppm) and much larger than in the case of \( N \)-vinylpyrrolidone (0.2 ppm) or ethyl vinyl ether (0.1 ppm).6

We carried out the polymerization of 1 with \( \text{BF}_3 \cdot \text{Et}_2\text{O} \) and water, present in the solvent and the reaction vessel, to obtain a general picture of the reactivity of this monomer. The reaction of 1 and 0.1 molequivalent of the initiator in dichloromethane at room temperature was followed by means of GPC (Fig. 2).

After 1 h only a small amount of the monomer was consumed (Fig. 2A). Prolonging the reaction period to 17 h resulted in a further increase of the conversion to about 60% (Fig. 2B). Apparently, the polymerization proceeds very slowly compared to what is usually described for vinyl ethers (complete conversion in a few hours at temperatures of \(-40^\circ\text{C}\) to room temperature).21 Addition of 1.0 molequivalent of \( \text{BF}_3 \cdot \text{Et}_2\text{O} \) induced complete conversion of the monomer in 17 h. The reaction mixture contains dimer, trimer, tetramer, etc. (number-average molecular weight \( \bar{M}_n = 500 \)) according to the gel-permeation chromatography curve (Fig. 2C).
Two observations have to be clarified, viz. the very low reactivity of 1 in the presence of BF$_3$·Et$_2$O and the low molecular weight of the reaction products.

Chain-transfer to, e.g., monomer or collapse of the ion-pair can be responsible for the untimely termination of the growing chain (Scheme 2). Fig. 1B shows the $^1$H NMR spectrum of the reaction product from 1 and BF$_3$·Et$_2$O (GPC Fig. 2C, complete conversion of 1) after treatment with aqueous NaOH and evaporation of the volatiles.

Three groups of relatively sharp peaks can be discerned, viz., a doublet at 1.5 ppm, a multiplet at 4.8 ppm and two singlets around 6.7 ppm. Although definite proof is lacking, we propose that these signals belong to the dimer depicted in Fig. 1B. It is known that N-vinylpyrrolidone easily gives the dimer in high yield upon treatment with dry HCl$_7)$. The CH$_3$ group (b) absorbs at 1.5 ppm (doublet), the CH group (c) at 4.8 ppm (multiplet), while the two different maleimide CH groups (a) and (a’) give two singlets around 6.7 ppm. The peaks for the CH groups (d) and (e) are most probably situated in the same area around 6.7 ppm. In the case of ion collapse one would expect pronounced signals (two doublets) for the CH$_2$ group (Scheme 2) in the area of 3–5 ppm. The broad patterns around 2.5 ppm and 4 ppm probably belong to the CH$_2$ and CH groups of the higher molecular-weight homologues of the dimer. The presence of peak (a) and (a’) reveals that the maleimide groups are not attacked by the initiating system.

Initiation of 1 with the actual initiator H$^+$ is followed by addition of another monomer molecule (Scheme 2).

Chain-transfer to the monomer explains the preferential formation of low-molecular-weight compounds, but would not, in principle, prevent complete conversion of the monomer. We propose that the greater part of the initiating species is being deactivated.
via complexation of the maleimide groups, in particular to those belonging to the oligomers as a result of a cooperative effect exerted by two or more maleimide groups. Similar observations were described by Pernecker et al. in the case of methyl vinyl ether and TiCl₄ \(^{8}\). Polymerization of methyl vinyl ether proceeded successfully only in the presence of an excess of TiCl₄. The authors, however, postulated that the monomer complex adds to the growing chain instead of the free monomer.

Further evidence was obtained by treatment of 1 with HCl/ZnCl₂. Addition of 0.05 molequivalent of the initiating system to a solution of 1 in dichloromethane at -30°C resulted in the formation of oligomers according to the GPC analysis. After two hours at -30°C a conversion of about 20% was reached, which did not change during 17 h at -20°C. Subsequent addition of 0.05 molequivalent of ZnCl₂ slightly improved the yield of oligomers. No change was observed while going up to room temperature. Finally, complete conversion of 1 was forced by using an additional amount of 0,5 molequivalent of ZnCl₂. Furthermore, it was checked that HCl and ZnCl₂ themselves do not provoke the oligomerization of 1.

Throughout the experiments with HCl/ZnCl₂ only low-molecular-weight compounds were formed, in the beginning at low concentration of ZnCl₂ as well as at the end at high concentration of ZnCl₂. This phenomenon indicates that chain-transfer to the monomer dominates the course of the reaction, bearing in mind that the concentration of initiator HCl remains low. Large amounts of ZnCl₂ are needed to push the conversion of 1 towards 100%, from which we conclude that most of the ZnCl₂ tends to associate not with the Cl atom of the “initiated” monomer but with another part of the molecule, probably one of the carbonyl groups of the maleimide ring.

From the experimental results we conclude that the initiating systems BF₃·Et₂O and HCl/ZnCl₂ behave similar towards 1. The attempted cationic polymerization of 1 proceeds very slowly and affords oligomers, mainly the dimer.

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