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# Synthesis and polymerization of N,N-diallyl morpholinium bromide

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### Abstract

N,N-diallyl morpholinium bromide has been synthesized in high yields (96%) by stepwise condensation of morpholine with allyl chloride and allyl bromide. Polymerizability of the quaternary ammonium salt has been studied using various solvents and radical initiators such as  $K_2S_2O_8$  and *t*-butyl hydroperoxide. High yields of polymers have been obtained by precipitation polymerization in *n*-butanol with *t*-butyl hydroperoxide as radical initiator. This method gives low molecular weight polymers, whereas polymers with moderate molecular weights have been obtained in concentrated aqueous solutions. Copolymerization of the monomer with sulfur dioxide has also been studied. The structures of the monomer and polymers have been elucidated by elemental microanalysis, NMR and FT-IR spectroscopy. © 2000 Elsevier Science Ltd. All rights reserved.

### 1. Introduction

Since the pioneering study of Butler and Ingley [1] cyclopolymerization of diallyl dialkyl ammonium salts has been reported. It has been demonstrated that not only diallyl ammonium salts, but also some other diallyl monomers such as diallyl cyanamide [2], diallyl ptoluene sulfonamide [3] can give cyclopolymers consisting of five-membered repeating units in the main chain. In these monomers, two allyl groups are attached to the same atoms and the close proximity of the two allyl groups induces cyclization. It is interesting to note that hydrochloride salts of N-alkyl, N,Ndiallyl amines have been reported to form water-soluble polydiallylamine hydrochlorides by gamma irradiation or persulfate initiation. On the other hand, these monomers in their free base tend to form gel during polymerization under the same conditions [4].

Polymers of diallyl quaternary ammonium salts are water soluble linear cationic polyelectrolytes. These polymers have potential applications in various fields [5]. These types of polymers show interesting physical properties in solution. Recently, it has been reported that the homopolymer of 1,1-diallyl 4-formyl piperazinium dichloride and its copolymer with  $SO_2$  show unusual phase separation, when their aqueous solutions are mixed together [6].

The present work deals with the synthesis and polymerization of diallyl morpholinium bromide (DAM).



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Although synthesis of this monomer and its polym-

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erization was reported by Butler and Bunch [7] as early as 1949, no spectroscopic confirmation has been published so far concerning the structures of the monomer and its polymer. This monomer has not found much interest in polymer chemistry, compared with its analogue, diallyl dimethyl ammonium salt. As far as we are concerned, no other reports have appeared since then.

In this study, synthesis of DAM has been studied and its structure has been elucidated by spectroscopic methods such as <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and FT-IR. Its polymerizability in various solvents and copolymerization with sulfur dioxide have been investigated.

### 2. Experimental

All the chemicals used were analytical grade chemical products: morpholine (Fluka), allyl chloride (E. Merck), allyl bromide (Fluka),  $K_2S_2O_8$  (E. Merck), DMSO (E. Merck); other chemicals and solvents were used without further purification.

Distilled water (conductivity 2  $\mu$ S) was used for the polymerizations. *t*-butyl hydroperoxide was prepared

according to the published procedure [8]. <sup>1</sup>H-NMR spectra were recorded on Bruker Model spectrometer in  $D_2O$  solvent; FT-IR spectra were taken by using Mattson 1000 spectrometer, with KBr disc. Viscosities were measured using a standard Ubbelohde viscometer.

### 2.1. Preparation of N-allyl morpholine (AML)

This compound was prepared from morpholine and allyl chloride as described elsewhere [9]. The liquid product boils at  $147-151^{\circ}$ C.

## 2.2. Synthesis of N,N-diallyl morpholinium bromide (DAM)

This was prepared by quaternization of AML with allyl bromide as follows: 35 ml (0.41 mol) of allyl bromide was placed in a flask in an ice bath. While stirring 66 ml (0.4 mol) of AML was added dropwise to the flask over about 30 min. White precipitates were observed after 1 h of stirring. Stirring was continued for another 3 h. Then the flask was closed tightly and left to stand for 5 days at room temperature. The



Fig. 1. <sup>1</sup>H-NMR spectrum of N,N-diallyl morpholinium bromide (DAM) in DMSO d-6.



Fig. 2. <sup>13</sup>C-NMR spectrum of N,N-diallyl morpholinium bromide (DAM) in DMSO d-6.

white crystalline mass formed was dispersed in 50 ml of diethyl ether and filtered. It was washed with ether and dried under vacuum at  $45^{\circ}$ C for 24 h, yield 99.2 g (96%), mp: 210°C (lit<sup>7</sup> 213°C). The product is very hygroscopic and it is soluble in water, DMF, DMSO, methanol, ethanol and butanol and insoluble in ether, cyclohexane, benzene and toluene.

Elemental microanalysis, found (calculated for  $C_{10}H_{18}NOBr$ ), C: 47.75% (48.38%), H: 7.95% (7.26%), N: 5.44% (5.64%).

<sup>1</sup>H-NMR, <sup>13</sup>C-NMR and FT-IR spectra of the monomer are given in Figs. 1–3a, respectively.

### 2.3. Polymerization of the monomer (DAM)

Polymerization of DAM has been conducted in sol-

vents such as water, DMSO, methanol and *n*-butanol in the presence of  $K_2S_2O_8$  or *t*-butyl hydroperoxide (TBH) as radical initiators. In most cases, only small amounts of polymer were obtained (Table 1).

Best yields were obtained by using 60% (w/w) monomer concentrations. In a typical procedure, 4.5 g (18 mmol) DAM was dissolved in 3 ml distilled water and 0.05 ml of TBH was added. The mixture was stirred at 85°C for 24 h. After cooling, the polymer was precipitated by pouring the mixture into 40 ml methanol with stirring. The white precipitate was filtered washed with methanol and dried at 60°C for 72 h under vacumm, yield 3.84 g (85.3%). The inherent viscosity in 0.1 M KBr solution was found to be 0.32 dl  $g^{-1}$ .

The procedure was repeated using n-butanol and

Table 1 Polymerization characteristics of diallyl morpholinium bromide at various concentrations with TBH initiator

Monomer (concentration) % (w/w)	Solvent	Initiator <sup>a</sup>	Temperature (°C)	Time (h)	Yield (%)	Inherent viscosity <sup>b</sup> (dl g <sup>-1</sup> )
10	Water	TBH	85	24	2.2	> 0.04
30 40	Water Water	ТВН ТВН	85 85	24 24	11 47	0.11 0.18
60	Water	TBH	85	24	85.3	0.32

<sup>a</sup> TBH *t*-butyl hydroperoxide with  $2.75 \times 10^{-2}$  initiator/monomer ratio in mol/mol.

 $^{\rm b}$  In 0.1 M KBr solution (with 0.5 g polymer in 50 ml solution at 30  $\pm$  1°C).



Fig. 3. FT-IR spectrum of N,N-diallyl morpholinium bromide (DAM) (a), Homopolymer of DAM (b). The copolymer of DAM with sulfur dioxide (c).

methanol as solvents. In those cases in about 15 min, the polymer began to precipitate. At the end of reactions white polymers were obtained in good yields (Table 2).

Table 2 Polymerization yields of DAM in various solvents with TBH initiator

### Inherent viscosity<sup>b</sup> (dl $g^{-1}$ ) Monomer (concentration) % (w/w) Solvent Initiator<sup>a</sup> Temperature (°C) Time (h) Yield (%) 10 Water TBH 85 2.2 > 0.04 24 10 Methanol TBH 85 24 6 0.07 10 **B**utanol TBH 85 24 93 0.05 50 85 Methanol TBH 24 88 0.12

<sup>a</sup> TBH *t*-butyl hydroperoxide with  $2.75 \times 10^{-2}$  initiator/monomer ratio in mol/mol.

<sup>b</sup> In 0.1 M KBr solution (with 0.5 g polymer in 50 ml solution at  $30 \pm 1^{\circ}$ C).

### 2.4. Copolymerization with sulfur dioxide

The reaction was conducted in a two-necked flask equipped with a reflux condenser. In a fume cupboard, 2.5 g (10 mmol) DAM monomer was dissolved in 20 ml of butanol and 0.05 ml of TBH was added and the temperature of the mixture was raised to  $50^{\circ}$ C. Then sulfur dioxide gas (which was generated by dropping 2 M Na<sub>2</sub>SO<sub>3</sub> solution into 40% H<sub>2</sub>SO<sub>4</sub> solution) was bubbled through the solution. An immediate precipitation took place when the gas contacted the solution. The reaction was complete in about 30 min and no more precipitation occurred. The polymer was filtered, washed with ether and dried as described above, yield 1.45 g (88%). This procedure was repeated in water as solvent. The yield was 86%.

### 2.5. Sulfur analysis of the copolymer

This was performed by fusing a 0.3 g sample in solid  $Na_2O_2/Na_2CO_3$  (1 : 3) mixture (6 g) at 1000°C. After cooling it was dissolved in 100 ml of water and neutralized with concentrated HCl. The sulfate ions formed were precipitated by BaCl<sub>2</sub> solution. The precipitated, BaSO<sub>4</sub> was filtered, washed with water, dried at 100°C for 5 h and weighed.

The sulfur content was calculated based on the weight of the  $BaSO_4$  (0.202 g) and found to be 9.24%S. Taking into account a water content (6.4%, from elemental analysis), this corresponds to 9.83%S (theoretical value 10.25%).

Elemental microanalysis: found (calculated for  $C_{10}H_{18}NO_3SBr$ ) with 6.4% water by neglecting end groups): C: 36.6% (36.0), H: 6.1% (6.11), N: 4.0% (4.48).

<sup>1</sup>H-NMR and FT-IR spectra of the copolymer are given in Figs. 5 and 3c, respectively.

### 3. Results and discussion

The monomer DAM can be prepared by quaternization of *N*-allyl morpholine with allyl bromide.



Scheme 1.

However, when the reagents interact at room temperature as in the original procedure described by Butler, severe explosions occur within 30 min contact time. For safety considerations, we have observed that efficient cooling is essential at the beginning of the reaction. Then the reaction proceeds smoothly at room temperature and five days of standing gives almost quantitative yields (Scheme 1). With solvents such as methanol and ethanol, however, the yields are always low even at prolonged times.

Elemental microanalysis and NMR spectra of the monomer clearly establish its structure. Thus, in the <sup>1</sup>H-NMR spectrum (Fig. 1) the multiplet at 6.1 ppm represents –CH= protons of the allyl group. The second multiplet centered at 5.7 ppm shows =:CH<sub>2</sub> proton signals. Protons of the allylic carbon give a doublet at 4.1 ppm. Two triplets at 4 and 3.42 ppm indicate –N–CH<sub>2</sub>– and –OCH<sub>2</sub>– protons of the morpholine ring, respectively.

<sup>13</sup>C-NMR spectrum of this compound in Fig. 2 represents five types of carbon atoms as expected. The carbons of morpholine rings are observed at 57 ppm (-C-N-) and at 60 ppm (-C-O-) the allylic carbons give a signal at 60.5 ppm. CH<sub>2</sub>— and CH— carbon signals appear at 125 and 128 ppm, respectively.

In the FT-IR spectrum of the monomer (Fig. 4a), the intense peaks at 3070 and 1680 cm<sup>-1</sup> indicate =C-H and C=C stretching vibrations of the allyl groups. Out of plane bending vibrations of olefinic C-H groups are observed as sharp peaks at 830 and 950 cm<sup>-1</sup>, which indicates unsaturation.



Fig. 4. <sup>1</sup>H-NMR spectrum of the homopolymer of N,N-diallyl morpholinium bromide in D<sub>2</sub>O.



### 3.1. Polymerization of the monomer DAM

Polymerization of the monomer was first studied by using aqueous solutions with various monomer concentrations, 10%, 30%, 40% and 60% (w/w) (Scheme 2).

Only small amounts of polymers were obtained with monomer concentrations less than 40%. Best results were obtained by using 60% monomer concentrations in the presence of TBH as initiator at 85°C. Most probably lower polymer yields in dilute solutions are due to the electrostatic repulsion of the positive charges as described for polymerization of diallyl dimethyl ammonium chloride [10]. In the same literature, it was claimed that, as the polymerization proceeds, the electrostatic repulsion between growing cation radical and the monomer cation decreases due to increasing ionic strength by formation of ion pairs.

No polymer was obtained with  $K_2S_2O_8$  Initiator, as in the case of diallyl dimethyl ammonium salts, presumably due to radical decomposition of the monomer by persulfate radicals [11]. Also the polymerization in methanol solution (with 10% (w/w) monomer concentration) with TBH gave lower yields (3–6%). In *n*-

butanol solution, DAM underwent precipitation polymerization with high yields; however, the inherent viscosity of the polymer so obtained was only 0.05 dl  $g^{-1}$ (in 0.1 M KBr solution).

The polymerization can also be followed by comparison of the FT-IR spectra of the polymer and monomer in Figs. 3a and b. The bands at 3070, 950 and 830 cm<sup>-1</sup> disappear from the spectra of the polymer. Although the sharp intense band at 1680 cm<sup>-1</sup> disappear in the spectrum of the polymer, new broad bands of the pyrrolidinium ring arise at the same region. For this reason, this band alone does not give clear-cut evidence for the polymerization as has already been stated by Jacson [4].

In the <sup>1</sup>H-NMR spectra of the polymer (Fig. 4), only a very small amount of residual unsaturation is observed. The unsaturated proton signals of the monomer at 5.7 and 6.1 ppm disappear almost completely from the spectrum of the polymer and new saturated proton signals are observed at 2.9 and 1.5 ppm as broad bands. The doublet at 2.9 ppm can be ascribed to the protons  $\beta$  to the nitrogen atom of the pyrrolidine ring formed. The remaining broad bands in the 0.9-1.8 ppm range must be due to protons out of the pyrrolidine ring. The positions of the signals of the morpholine ring protons do not show any significant change. Thus, -CH<sub>2</sub>-N- and -O-CH<sub>2</sub>- proton signals are observed at 4.08 and 3.6-3.4 ppm, respectively. The first strong signal at 4.08 ppm may be expected to represent  $CH_2$  protons  $\alpha$  to nitrogen of the pyrolidine ring. The second and third signals centered at 3.6 and 3.4 ppm must be due to -CH2-N-and -CH2-O- protons, respectively.

However, theoretical analysis of the NMR spectrum of a hypothetical molecule based on the hydrogenated form of the repeating unit in the polymer reveals that the first two signals represent the protons on the carbon atoms attached to the quaternary nitrogen. Also the signal at 3.6 ppm is due to  $-CH_2-N-$  and

Table 3						
Copolymerization	of DAM	with	$SO_2$	under	various	conditions

Monomer (concentration) % (w/w)	Solvent	Initiator <sup>b</sup>	Temperature (°C)	Time	Yield (%)	Inherent viscosity <sup>c</sup> (dl g <sup>-1</sup> )
10	DMSO	TBH	40	Explosion!		
10	Butanol	TBH	85	30 min	88	0.08
60	Water	TBH	85	15 min	86	0.11
10	DMSO	$K_2S_2O_8$	40	Explosion!		

<sup>a</sup> Under continous flow of SO<sub>2</sub>.

<sup>b</sup> TBH *t*-butyl hydroperoxide with  $2.75 \times 10^{-2}$  initiator/monomer ratio in mol/mol.

 $^{\rm c}$  In 0.1 M KBr solution (with 0.5 g polymer in 50 ml solution at 30  $\pm$  1°C).

-CH<sub>2</sub>-O- protons of the morpholine ring. The third signal at 3.4 ppm arises from -CH<sub>2</sub>-O- protons.

Integral of the weak signals arising from residual unsaturation at 5.7–6.1 ppm provides a rough estimate of the number average molecular weight of the cyclopolymer. The ratio of the integrals of saturated proton peaks to those of the unsaturated protons is about 960/1. If one allyl group is assumed to be present at the end of each polymer chain, this will correspond to  $M_n = 39.300$  daltons. TGA experiments (10°C/min nitrogen flow) show that this polymer decomposes at about 350°C without melting.

### 3.2. Copolymerazition with $SO_2$

Copolymerization of DAM was first studied in DMSO as solvent, because DMSO is able to sorb a large amount of SO<sub>2</sub>. When DMSO was used after preabsorption with the requisite amounts of SO<sub>2</sub>, copolymerization of DAM with  $K_2S_2O_8$  or TBH gave only 4–6% of polymerization yields.

The copolymerization was also studied with continuous flow of  $SO_2$  in DMSO as solvent. Each attempt resulted in violent explosions, presumably due to formation of  $SO_3$  reacting with DMSO. With continuous flow of  $SO_2$  in *n*-butanol or in concentrated aqueous solutions, copolymerization was completed in about 30 min and resulted in high yields (Table 3).

In aqueous solutions with 60% (w) monomer concentrations, the SO<sub>2</sub> flow causes an immediate rise in the viscosity and a highly viscous gel is obtained. The resulting product is soluble in water and has a moderate viscosity,  $\eta_{inh} = 0.11$  dl g<sup>-1</sup>.

In the <sup>1</sup>H-NMR spectra (Fig. 5) of the copolymer, small amounts of residual unsaturation are observed (signals at 5.7 and 6.1 ppm). All the other aliphatic protons give a broad band in the 3.2–4.5 ppm range. By assuming the existence of one allyl group at each chain end, molecular weight of the copolymer can be estimated from the integral ratio of the residual unsaturated and saturated proton signals.

This inspection gives  $M_n = 4600$  daltons. Undoubtly, continuous SO<sub>2</sub> flow lead to a relatively rapid termination of growing chains and this is responsible for the low molecular weight of the copolymers. Under the same conditions TGA represents that the copolymer decomposes at 280°C with sulfur dioxide evolution.

Incorporation of  $SO_2$  into the polymer structure is



Fig. 5. <sup>1</sup>H-NMR spectrum of the copolymer with sulfur dioxide.

also established by its FT-IR spectra shown in Fig. 3c. Thus, a sharp band observed at 1310 cm<sup>-1</sup> represents asymmetric stretching S=O band. The second characteristic band associated with S–O symmetric stretching vibration which is expected at about 1100 cm<sup>-1</sup> is not discernible due to other bands in the same region. Based on the elemental analysis and the sulfur analysis, molar S/N ratio of the copolymer is found to be very close to unity (1 : 1, 106). Since this result is obtained with an excess of the SO<sub>2</sub> component, the polymer is an alternating copolymer of SO<sub>2</sub>, in accordance with previous reports based on diallyl ammonium copolymers with sulfur dioxide [12]. Also fast polymerization in the presence of SO<sub>2</sub> is further evidence for the copolymer formation.

In conclusion, DAM can be prepared from morpholine and allyl bromide in high yield and affords homopolymers with moderate molecular weight. Hence, the diallyl monomer is a promising monomer and a good alternative to its analogue, diallyl dimethyl ammonium chloride, to obtain polyelectrolytes with strong cationic groups.

It also forms copolymer with sulfur dioxide in high yield. As might be expected, both the homo- and copolymers serve as flocculating agents. Preliminary investigations indicate that these polymers are able to form complex salts with anionic chloro complexes of some metal ions, such as  $FeCl_4^-$  etc. These will be considered in subsequent publications.

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