# New water-soluble polymer with allyl pendant groups

### NIYAZI BICAK\*, MUSTAFA GAZI and BUNYAMIN KARAGOZ

Department of Chemistry, Istanbul Technical University, Maslak, 34469 Istanbul, Turkey

**Abstract**—Polymerization of N-allyl maleamic acid (AMA) is described. The monomer, AMA, was prepared by reaction of maleic anhydride with allyl amine. It was demonstrated for the first time that only maleate double bonds are involved in the radical polymerization and the allyl groups remain unreacted. Water-soluble oligomers (1800–2100 Da) with allyl pendant groups were obtained in reasonably high yields (up to 78% within 45 h) by using 2,2'-azobis(2-methylpropionamidine) di-hydrochloride as a radical source. Notably no cyclo-polymers are formed in this polymerization. Experiments also showed that polymerization of this process is rather slow and proceeds with first-order kinetics ( $k = 1.03 \times 10^{-6} \text{ s}^{-1}$ ) in ethanol, at 75°C. Interestingly, in the co-polymerization with some other vinyl monomers, such as acrylamide, acrylic acid and vinyl acetate, AMA behaves as a bi-functional monomer and gives cross-linked polymers.

*Keywords*: N-Allyl maleamic acid; co-polymerization; cross-linking; polyelectrolyte; water-soluble polymers.

### 1. INTRODUCTION

Maleate double bonds in ester or amide form do not give homo-polymers by radical initiation. On the other hand, they mostly form alternating co-polymers with many vinyl monomers [1]. Co-polymerizability of maleate double bonds has found extensive use in hardening of unsaturated polyesters by cross-linking co-polymerization with vinyl monomers [2].

Mono- or di-allyl esters of maleic acid have been demonstrated to form cyclopolymers with five-membered butyrolactone units [3]. These cyclo-polymerizations involving allylic bonds can be considered as intramolecular co-polymerization with the maleate double bonds. The vicinity of those non-homo-polymerizable double bonds makes it possible to form cyclo-polymers. One important problem in their polymerization is maleate–fumarate isomerization [4], favored particularly at elevated temperatures. The percentage of the fumarate isomer strongly depends

<sup>\*</sup>To whom correspondence should be addressed. E-mail: bicak@itu.edu.tr

on the temperature and has been reported to exceed 60% at temperatures over  $150^{\circ}C$  [5].

Although N-allyl maleamic acid (AMA) has been known for a long time, its polymerization has been scarcely reported. The early reports concern its polymerization by gamma irradiation yielding a dark-brown solid [6, 7].

In this study, initially cyclo-polymers constituting pyrrolidinone rings were expected to form in the radical polymerization of AMA. In contrast, we have observed that only maleate double bonds are involved in the polymerization and allyl groups remain as pendant groups. Moreover, the kinetics of the polymerization have also been investigated.

### 2. EXPERIMENTAL

### 2.1. Materials

Allyl amine (Fluka) and dimethoxy ethane (Aldrich) were distilled before use. Maleic acid anhydride (Acros), initiator (2,2'-azobis(2-methyl propionamidine) dihydrochloride (Aldrich)) and other chemicals were analytical grade products. They were used as supplied.

<sup>1</sup>H-NMR spectra were recorded on a Bruker model 250 MHz NMR spectrometer. The light scattering (LS) method was employed for the determination of the molecular masses of the polymer samples, using a BI-MwA Molecular Weight Analyser equipped with two Agilent 1100 series isocratic pumps (Brookhaven Instrument) in 0.1 M NaCl solution.

### 2.2. Preparation of N-allyl maleamic acid (AMA)

Maleic anhydride (49 g, 0.5 mol) was dissolved in 50 ml dimethoxy ethane in a 250ml round-bottom flask. The flask was mounted in an ice-bath. While stirring 75 ml (0.5 mol) allyl amine was added to the solution drop-wise by means of a pressure equalizing dropping funnel, in about 45 min. The mixture was stirred for another 45 min and left to stand for 1 h at room temperature. The white crystalline mass formed was filtered and recrystallized from 150 ml water. The product was dried at 40°C under vacuum overnight. The yield was 86.4 g (81.3%), m.p. 98°C (97°C [6, 7]). The white product, N-allyl maleamic acid (AMA), is soluble in acetone, ethanol, DMF and THF, and insoluble in cold water, diethyl ether and benzene.

## 2.3. Polymerization of AMA

Polymerization of the monomer was performed in water and alcohol solutions under the same experimental conditions. A typical procedure is as follows: in a 100ml two-necked flask equipped with a nitrogen inlet and a reflux condenser was added 7.25 g (0.05 mol) monomer, 10 ml alcohol and 0.19 g ( $3.68 \times 10^{-4}$  mol) 2,2'azobis(2-methyl propione diamidine) dihydrochloride as initiator. The flask was mounted in a thermostated oil bath of which the temperature was adjusted to 75°C. Nitrogen was purged from the mixture for 3 min and the reaction was conducted under continuous stirring.

The kinetics of the polymerization were followed by determination of polymer contents of the aliquots (5 ml) taken at appropriate time intervals (30 min). The polymer samples were isolated by precipitation in 35 ml acetone. The precipitates were filtered, dried at 40°C under vacuum for 24 h and weighed. The data collected were used to build the conversion–time plot presented in Fig. 3. The resulting polymer is soluble in alcohol, THF and water, and insoluble in acetone, benzene and n-hexane.

#### 3. RESULTS AND DISCUSSION

The monomer (AMA) is obtained in high yields (81.3%) by the reaction of maleic anhydride with allyl amine in dimethoxyethane (Scheme 1).

In the <sup>1</sup>H-NMR spectrum of AMA (Fig. 1), =CH<sub>2</sub> and -CH= protons of the allyl group give sharp signals at 5.1 and 5.8 ppm, respectively. The doublet centered at 6.3 ppm is associated with protons of the maleate double bond. The singlet around 9 ppm indicates the amide protons. The allylic methylene protons give a sharp singlet at 3.8 ppm.

Interestingly, homo-polymerization of this monomer does not give cyclo-polymers. Instead, the polymerization proceeds *via* maleate double bonds and allyl groups remain unreacted. In another word, only maleate double bonds involve in the polymerization as evidenced by NMR measurements (*vide infra*). It was found that 2,2'-azobis(2-methyl propione diamidine) dihydrochloride is a better radical source for polymerization of this monomer.

Other radical initiators did not give satisfactory results in the conditions studied. For instance, no polymer was obtained within 4 h of reaction with dibenzoyl peroxide initiator. This is common behavior in the cyclo-polymerization of diallyl monomers as acid peroxides, such as dibenzoyl peroxide, because of oxidation, instead of addition to the double bond. Another conventional initiator, azo isobutyronitrile (AIBN), gave only 2% polymerization yield for the same reaction period. The overall polymerizations of AMA processes are presented in Scheme 2.

The monomer and polymer show distinct solubility behaviors. The monomer and polymer both are soluble in alcohol. Apparently, acetone is solvent for the monomer and non-solvent for the corresponding polymer. The polymer is water-soluble, while



Scheme 1. Synthesis of AMA.



Figure 1. <sup>1</sup>H-NMR spectrum of N-allyl maleamic acid in DMSO-d<sub>6</sub>.



Scheme 2. Homo- and co-polymerization of AMA.

the monomer has a limited solubility in water at room temperature. Such a solubility difference provides easy isolation of the polymer.



Figure 2. <sup>1</sup>H-NMR spectrum of N-allyl maleamic acid homo-polymer in DMSO-d<sub>6</sub>.

In the <sup>1</sup>H-NMR spectra of the polymer (Fig. 2), proton signals of the maleate double bond of the monomer disappear completely and new multiplets indicating saturated carbons emerge at 2.7 and 3.5 ppm. However, allylic proton signals remain unchanged and appear at 5.4 and 5.9 ppm. Slight downfield shifts are due to the change in electron densities after the polymerization. This is a direct evidence for the polymerization *via* maleate double bonds. Persisting amide protons at 8.4 ppm implies that, no cyclization takes place through the amide group. Moreover, carboxyl protons of the polymer give a broad band around 12 ppm, which can be observed by magnification ( $\times 10$ ).

These results clearly indicate that the allyl group of the monomer is not involved in the polymerization. The integral ratio of the allyl protons in Fig. 2 also implies that the polymer possesses allyl pendant groups in each repeating unit.

Unexpected polymerization behavior may be due to the change of  $\pi$ -electron densities on the carbon atoms of the maleate double bond. Since the allyl group does not take part in the polymerization, one can conclude that all maleamides with different substituents can also undergo homo-polymerization.

The possibility of homo-polymerization of maleamic acids with different substituents should also be considered. In order to check this possibility, we have prepared two additional monomers, namely N-propyl maleamic acid and N-phenyl maleamic acid, by applying the same procedure using propyl amine and aniline as the amine component. Unfortunately, all attempts at their polymerization failed. No polymers were obtained under the various time-temperature conditions studied.

Solvent	Monomer (mol/l)	Time (h)	Yield (%)	Rate constant $(s^{-1})$	$[\eta]^b$ (dl/g)	Mol. mass <sup>c</sup> (Da)
Ethanol	10.75	45	78.0	$1.03 \times 10^{-6}$	0.012	1800
Water	4.60	45	69.4	$1.0 \times 10^{-6}$	0.014	2100

 Table 1.

 Polymerization<sup>a</sup> of N-allyl maleamic acid (AMA)

<sup>a</sup> [I]/[M] (mol/mol): 0.011 at 75°C.

<sup>b</sup> Intrinsic viscosity in 0.1 M KCl.

<sup>c</sup> Determined by light scattering in 0.1 M NaCl solution.



Figure 3. Conversion–time plots of the polymerization in alcohol at 75°C, ([M] = 10.75 M, [I]/[M] (mol/mol) = 0.011).

The successful polymerization in the case of AMA may be due to amide–imide tautomerism facilitated by the allyl group involved. However, such an effect of the allyl substituent is yet unclear and needs further investigation.

The polymerization is rather slow in alcohol and aqueous solutions. Reasonable polymerization yields (78%) can be attained within 45 h, in alcohol. Light scattering experiments revealed that the molecular masses of the products are very low (1800–2100 Da), as shown in Table 1.

Conversion-time plots of the polymerization (Fig. 3) indicate first-order kinetics, as was deduced from  $\log(1/1-p)$  versus time plots (where p denotes the conversion ratio). Slopes of the linear semi-logarithmic plots yielded the rate constants  $k = 1.03 \times 10^{-6}$  and  $1.01 \times 10^{-6}$  s<sup>-1</sup> (correlation factors 0.998 and 0.995) for the polymerizations in alcohol and aqueous solutions, respectively.

Co-monomer	Solvent	Total monomer (mol/l)	[AMA]/[M]	Gelation time (min)
Acrylamide	Water	1.41	1/9	2.8
Acrylic acid	Water	1.35	1/9	4.0
Vinyl acetate	Butyl acetate	2.40	1/9	96

Gelation times in cross-linking<sup>a</sup> co-polymerization of AMA with some vinyl monomers

 $^{a}$  [I]/[M] (mol/mol) = 0.018 at 75°C.

### 3.1. Co-polymerizability of AMA

Table 2.

Although the allyl group of AMA does not take part in the polymerization, its copolymerization with some common vinyl monomers (Table 2), such as acrylamide, acrylic acid and vinyl acetate, results in cross-linking, as was described in our previous report [8].

This means that AMA behaves as bifunctional monomer in this case and the allyl group involves in the co-polymerizations.

Regarding the co-polymerization tendency of maleate double bond, it can be deduced that the kinetics of the cross-linking are mainly governed by reactivity of the allyl group of AMA.

### 4. CONCLUSIONS

Unlike allyl maleate, N-allyl maleamic acid does not form cyclo-polymers. Radical polymerization of the latter takes place *via* maleate double bonds and the allyl groups remain unreacted. The resulting low-molecular-mass polymers with allyl pendant groups are water soluble. On the other hand, maleamides derived from aniline and propylamine do not polymerize under the same conditions, whereas in co-polymerization with some vinyl monomers, this monomer behaves as cross-linker and yields cross-linked gels in reasonably short periods.

The oligomer presented might be useful precursor in preparing homo-polymer of maleic acid which is intractable by other means.

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