Synthesis of N,N'-diallylmalonamide and its copolymer gels with acrylic acid and acrylamide

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SUMMARY: N,N'-diallylmalonamide (DAM) has been prepared via classical aminolysis of diethyl malonate with allylamine. Its structure was confirmed by elementary microanalysis as well as ¹H NMR and FT-IR spectroscopy. The new diallyl monomer is water-soluble and able to copolymerize radically with water-soluble monomers, such as acrylamide and acrylic acid, to give transparent hydrogels by using $K_2S_2O_8$ as initiator. Homopolymerization of DAM yields clear hydrogels with high swelling ability.

ZUSAMMENFASSUNG: N,N'-Diallylmalonamid (DAM) wurde durch klassische Aminolyse von Diethylmalonat mit Allylamin hergestellt. Seine Molekülstruktur wurde durch Elementaranalyse sowie ¹H-NMR und FT-IR-Spektroskopie bestätigt. Das neue Diallymonomere ist wasserlöslich und mit wasserlöslichen Monomeren wie Acrylamid und Acrylsäure radikalisch copolymerisierbar, wobei mit $K_2S_2O_8$ als Initiator transparente Hydrogele erhalten werden. Die Homopolymerisation von DAM liefert klare Hydrogele mit hoher Quellbarkeit.

Introduction

The radically initiated addition polymerization of allylic monomers is known to give only low molecular weight polymers with degrees of polymerization (DP) between 4 and 14, because of extensive chain transfer reactions¹). Easy of hydrogen abstraction from allylic carbon atom of unreacted allyl monomer and resonance stabilization of the resulting radical contribute to an inhibition effect on chain growing. This fact has been referred to as degradative chain transfer. For this reason, with the exception of special applications, radical initiation of monoallyl monomers has found little attention for commercial applications.

In contrast, diallyl monomers, especially diallyl esters and ethers, have found a wide variety of applications. For instance, homopolymers of diethylene glycol bis(allyl carbonate) are produced commercially (CR-39, Pittsburg Plate Glass Co., U.S.A.), for optical applications, because of its excellent clarity and abrasion-resistance. Diallyl esters of phthalic acids are commercially important diallyl monomers which, with radical initiators, give crosslinked polymers. Homo- and copolymers of diallyl phthalates are good insulators and they have mainly found industrial interest in coatings for electronic devices and computer systems. Moreover, triallylcyanurate and its isomer, triallylisocyanurate, are used as crosslinking agents with common comonomers².

Probably, allyl methacrylate is the most important compound having both allyl and vinyl-type double bonds. The lower reactivity of the allyl group in the monomer permits post crosslinking when used as comonomer in low concentrations. This has been reported to be very useful in dental prostheses³⁾.

One of the most important types of diallyl monomers are the monomers with two allyl groups attached to the same carbon or nitrogen atom. These diallyl monomers undergo cyclopolymerization yielding non-crosslinked polymers with average molecular weights around 1000. One of the first diallyl monomers of this type is diallyldimethylammonium chloride, yielding water-soluble polymers consisting of five-membered cyclic repeating units⁴). Similarly, diallyl diethylmalonate⁵ and N,N'-diallylcyanamide⁶ also undergo cyclopolymerization to give soluble, linear polymers.

Recently, N,N,N',N'-tetraallylpiperazinium dichloride, which is prepared from piperazine and allyl chloride, has been demonstrated to be an efficient water-soluble crosslinker for polymers of acrylic acid and acrylamide⁷⁾.

Although many papers dealing with polymers of allyl esters or ethers have been published, as far as we know no reports have appeared about allylamide polymers, so far.

In this paper we have described synthesis and polymerization of N,N'-diallylmalonamide (DAM). This monomer is water-soluble and a useful crosslinker for preparing hydrogels of poly(acrylic acid) and polyacrylamide. As a crosslinking agent, this monomer is expected to have advantages over the common crosslinker, i.e. N,N'methylenediacrylamide in preparation of hydrogels because N,N'-methylenediacrylamide incorporated in a polymer structure, even in presence of trace amounts of acid, releases formaldehyde, which is toxic⁸⁾.

Experimental

Synthesis of N,N'-diallylmalonamide (DAM)

15 g (0.31 mol) of diethyl malonate and 7 mL dioxane were placed in a 250 mL two-necked round-bottom flask which was equipped with a reflux condenser. While stirring, 6 mL (0.63 mol) allylamine was added to the solution. The mixture was stirred for 24 h at 55-60 °C. After cooling, the mixture was poured into 30 mL ether. The precipitated product was filtered and recrystallized from 30 mL toluene. The colourless, crystalline product was dried at 40 °C for 24 h, yield 4.15 g (78.0%), m.p. 145-146 °C. It is soluble in water, dioxane, DMSO, hot toluene, ethanol and methanol, partly soluble in acetone, and insoluble in ether, n-hexane and light petroleum ether.

 $\begin{array}{c} C_9H_{14}N_2O_2\,(182.22) & calcd. & C~59.32 & H~7.74 & N~15.37 \\ found & C~59.13 & H~7.60 & N~15.49 \end{array}$

¹H NMR (DMSO-d₆, internal standard TMS, δ in ppm): 8.15 (broad s, 2H, NH), 5.9 (m, 2H, CH₂=C<u>H</u>-), 5.15 (m, 4H, C<u>H</u>₂=CH-), 3.7 (t, 4H, -NH-C<u>H</u>₂), 3.3 (s, 2H, -CO-CH₂-CO-) (Fig. 1).

FT-IR (KBr, cm⁻¹): 3350 (N–H str.), 3083 (olefinic C–H str.), 2980 (aliphatic asym. C–H str.), 2800 (aliphatic sym. C–H str.), 1650 (C=O str.), 1630 (C=C str.), 1550 (N–H plane bending) (Fig. 2).



Fig. 1. ¹H NMR spectrum of N,N'-diallylmalonamide.

Homopolymerization of DAM

To a 100 mL round-bottom flask equipped with a reflux condenser, a nitrogen inlet and a magnetic stirrer was added a solution of 1 g (5.5 mmol) DAM in 10 mL of distilled dioxane and 38.72 mg (0.16 mmol) dibenzoyl peroxide in 5 mL dioxane. The system was purged with nitrogen to remove dissolved air. Then the flask was immersed in an oil bath thermostated at 65 °C. After stirring for about 47 h, a transparent, clear gel was obtained. The gel was washed several times with water and decanted, then soaked in 30 mL of acetone and left in contact over night to remove dioxane residues. The acetone was decanted and another 30 mL of acetone was added to the flask and boiled for 1 h. After decantation of the acetone, the crosslinked homopolymer gel was dried at 50 °C for 72 h under vacuum, yield 0.88 g.



4000 300 2000 1000 400 Wavenumber in cm⁻¹

Fig. 2. FT-IR spectra of (a) N,N'-diallylmalonamide (DAM), (b) homopolymer of N,N'-diallylmalonamide.

Copolymerization of DAM with acrylamide and acrylic acid

Copolymerizations were carried out in aqueous solutions, under identical conditions, using different DAM/comonomer ratios and initiator concentrations. A typical procedure is as follows:

In a 100 mL flask placed in an oil bath, 1 g (13.9 mmol) acrylamide monomer and 0.26 g (1.43 mmol) DAM were dissolved in 15 mL water. 0.12 g (0.45 mmol) $K_2S_2O_8$ in 15 mL water was added to the solution and the system was flushed with nitrogen. The temperature was kept at 65 °C and the mixture was stirred by a magnetic stirrer until gelation occurred.

This procedure was repeated with different monomer and initiator concentrations. The corresponding gelation times are listed in Tab. 1.

The resulting hydrated gels were dried in a similar manner as described above.

Swelling experiments

Swelling of the gel samples was followed by weightincrease, in contacting with water as in the following: Dry samples were weighed (approximately 0.3g) and placed in a sintered glass funnel which is in a 100 mL volume beaker containing 50 mL water. The samples were allowed to stand in contact with water several hours at room temperature. From time to time, the glass funnel was taken out, filtered by suction and weighed. The swelling ratios $(w-w_0/w_0)$ found were recorded as a function of time (Fig. 3 and Fig. 4).

Determination of the unreacted allyl groups

The unreacted allyl groups in the crosslinked polymer were estimated by measuring areas of olefinic C—H stretching vibration peaks at 3080 cm⁻¹. For this purpose, mixtures of

Tab. 1. Gelation times of DAM with different comonomer and initiator concentrations.

Run	Water (mL)	DAM (mmol)	Comonomer ^a	[C]/[DAM] ^b	Gelation time (min)	$[K_2S_2O_4]/TMC^c$	Unreacted allyl groups (%)
1	30	1.430	AAm	9.850	9	1/35	4.90
2	30	1.430	AAm	9.850	7	1/17.5	_
3	30	1.430	AAm	9.850	25	1/70	_
4	30	0.714	AAm	19.73	12	1/33.3	3.46
5	30	0.357	AAm	39.40	15	1/32.5	2.50
6	40	1.430	AAm	9.850	25	1/35	_
7	12	1.430	AAm	9.850	5	1/35	_
8	12	1.430	AA	9.710	3	1/35	_
9	30	1.430	AA	9.710	3	1/35	—

^a Aam: acrylamide, AA: acrylic acid.

^b [C]: comonomer concentration.

^c TMC: total monomer concentration.



Fig. 3. Swelling ratio vs. time plots of the homopolymer of N,N'-diallylmalonamide.



Fig. 4. Swelling ratio vs. time plots of DAM/AAm copolymers; [DAM]/[AAm]: (a) 1:40, (b) 1:20, (c) 1:10.

DAM monomer and linear polyacrylamide were mixed in different compositions and IR spectra of their KBr pellets (1/300) were taken. A calibration curve, plotted from peak areas and molar compositions, was linear. By using this calibration curve, corresponding molar compositions of gel samples were obtained and listed in Tab. 1.

Results and discussion

A classical ester aminolysis of diethyl malonate with equimolar amounts of allyl amine in dioxane gives rise to N,N'-diallylmalonamide with 78% of yield (Scheme 1).

Scheme 1:
O O

$$2 \text{ CH}_2 = \text{CH} - \text{CH}_2 - \text{NH}_2 + \text{EtO} - \text{C} - \text{CH}_2 - \text{C} - \text{OEt}$$

 \downarrow
CH₂=CH-CH₂-NH-C-CH₂-C-NH-CH₂-CH=CH₂+2 EtOH

The structure of diallylmalonamide was confirmed with elementary analysis, ¹H NMR (Fig. 1) and FT-IR spectra (Fig. 2). According to ¹H NMR, it is reasonably pure and does not contain impurities such as base-catalysed isomerization products. Water solubility of this compound has led us to use it as a crosslinker for water soluble polymers of acrylamide and acrylic acid.

Homopolymer gels of DAM

Compared with allyl ester monomers, DAM exhibits a similar polymerization behaviour. In dioxane solution it can be homopolymerized with high yields in presence of dibenzoyl peroxide initiator to give a transparent gel, whereas in aqueous solutions with $K_2S_2O_8$ initiator at 65 °C the gelation takes longer times, i.e. 75 h. FT-IR spectra of both products have the same patterns, which means that these products have the same structure.

Copolymer gels

Copolymerization experiments (run 6) reveal that with acrylamide comonomer, when the total monomer concentration is 0.38 M, gelation time is 25 min for $11.1 \cdot 10^{-3}$ M K₂S₂O₈. For monomer/comonomer ratios of about 1:10 (total monomer concentration 0.52 M) the gelation time varies between 7 and 25 min, depending on initiator concentration (runs 1, 2, 3). Apparently, increasing initiator concentration decreases the gelation period as expected. When the total concentrations are lower than

Scheme 2:



0.3 M (with $11.1 \cdot 10^{-3}$ M K₂S₂O₈) no gel is obtained. Under the same conditions, decreased DAM concentrations (runs 4, 5) decrease the gelation times. This clearly reveals that DAM acts as crosslinker during the course of copolymerization (Scheme 2).

In the FT-IR spectra of all the crosslinked gels, weak olefinic C—H stretching vibration peaks are observed as very weak bands, which indicates the existence of unreacted allyl groups. We have searched a suitable method for determining remaining carbon-carbon double bonds. But as far as we know, the use of current procedures is limited and not reasonable due to slow diffusion of any reagent into crosslinked polymers. Furthermore, there are additional difficulties in our case that neither the bromine nor the mercuric acetate method is suitable for this purpose. The bromine addition method is expected to produce N-bromamide as a by-product. The mercuric acetate method yields mercuric amide compounds as by-products⁹.

For this reason, for the determination of allyl groups in gel polymers we have preferred to follow the IR band intensities of the C—H stretching vibrations at 3080 cm^{-1} . This approach has been used frequently in the literature¹⁰). This inspection reveals that 2-5% of allyl groups remain unreacted in the gelled polymers, depending on the molar ratio of DAM. Swelling ratios of the crosslinked polymers in water are in accordance with their DAM contents. Increasing DAM content decreases the swelling ratios and of course the swelling rates, which is usual for cross-

linked polymers. But, on the other hand swelling rate of the homopolymer of DAM is higher than that of the copolymers. This can be ascribed to the lower reactivity of allyl groups in homopolymerization, which results in low crosslink density. Indeed a rough estimation of allylic unsaturation obtained by the ratio of the peak areas of the homopolymer and DAM indicates presence of 13% allyl groups in the homopolymer gel.

In conclusion, N,N'-diallylmalonamide is a useful water-soluble crosslinker for water-soluble monomers. Being obtained from readily accessible materials, it is a good candidate to replace N,N'-methylenediacrylamide to circumvent the toxicity of the latter.

- ¹ R. C. Laible, Chem. Rev. **58** (1958) 807
- ² B. H. Clampitt, D. E. German, J. R. Galli, J. Polym. Sci. 29 (1958) 515
- ³ U.S. Pat. 4,213,417 (1981), Pennwalt Corp., Inv.: C. J. Dyball, Chem. Abstr. **95** (1981) 442175s
- ⁴ G. B. Butler, A. Crawshaw, W. L. Miller, J. Am. Chem. Soc. **80** (1957) 3615
- ⁵ R. Y. Levina, N. N. Godovikov, Zh. Obshch. Khim. 24 (1954) 1572
- ⁶ K. Uno, K. Tsurub, Y. Iwakura, J. Polym. Sci., Part B 6 (1967) 85
- ⁷ N. Biçak, G. Koza, Macromol. Rep. A33 (1996) 375
- ⁸ Y. L Yin, R. K Prud'homme, F. Stanley, ACS Symp. Ser. 480 (1992) 99
- ⁹ N. Biçak, D. C. Sherrington, React. Funct. Polym. 27 (1995) 155
- ¹⁰ R. A. Spurr, B. M. Hanking, J. W. Rowen, J. Polym. Sci. **37** (1959) 431