

Poly(amide thioether)s by addition of ethanedithiol to diallylamides

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SUMMARY: The preparation of poly(amide thioether)s by addition of ethanedithiol to diallylamides in the presence or absence of peroxide catalysts is reported for the first time. Diallylamide monomers N,N'-diallyloxalamide, N,N'-diallylmalonamide and N,N'-diallylterephthalamide have been prepared by aminolysis of the corresponding esters with allylamine. The structures of the resulting polymers have been elucidated by elemental microanalysis and ¹H NMR and IR spectroscopy. The polymers obtained both as Markovnikov and anti-Markovnikov types of addition are highly crystalline compounds.

ZUSAMMENFASSUNG: Poly(amid-thioether) wurden durch Addition von Ethandithiol an Diallylamide in Gegenwart oder Abwesenheit von Peroxidkatalysatoren erstmalig hergestellt. Die Diallylamid-Monomeren N,N'-Diallyloxalamid, N,N'-Diallylmalonamid und N,N'-Diallylterephthalamid wurden durch Aminolyse der entsprechenden Ester mit Allylamin synthetisiert. Die Strukturen der erhaltenen Polymere wurden mittels Mikroanalyse und ¹H NMR- sowie IR-Spektroskopie ermittelt. Die Polymeren, die sowohl als Markovnikov- als auch anti-Markovnikov-Additionsprodukte gebildet werden, sind hochkristallin.

Introduction

Addition of dithiols to diethylenic compounds gives rise to polythioethers. The first example of this type of polymerization, the self-polymerization of allylthiol, was reported in 1926¹. Since then, many polymers have been prepared based on this principle. The most prominent study in obtaining high molecular weights as high as 60000 was the radical-catalysed addition of hexane-1,6-dithiol to hexa-1,5-diene². In the presence of radical catalysts, addition of thiols to double bonds proceeds according to the anti-Markovnikov addition mechanism. This mechanism has been proved by the fact that the polymer obtained by addition of hexanedithiol to hexa-1,5-diene in the presence of a peroxide catalyst is identical to the one obtained by condensation of 1,6-dibromohexane with hexanedithiol³.

Aliphatic polythioethers are rubber-like materials with low melting temperatures. These polymers have found special interest during the Second World War, in preparing artificial rubbers. Polythioethers are known as solvent- and oil-resistant materials. But these types of polymers have not found widespread commercial acceptance due to the disagreeable odor of these materials. The only known commercialized polythioether is the condensation product of bis(2-chloroethyl) ether with dithiols⁴.

On the other hand, activated double bonds are known to add thiols much faster than simple ethylenic compounds. Recently it has been reported that the condensation of 4,4-dimethylcyclohexa-2,5-diene-3-one with ben-

zene-1,3-dithiol proceeds rapidly to give high-molecular-weight polymers without using a radical catalyst. Interestingly, in the presence of chiral amines, polymerization gives optically active poly(γ -ketosulfide)s⁵. Another interesting example of this type of polyaddition of dithiols to bisoxazolines results in poly(amide thioether)s of relatively low molecular weights⁶.

In the present study, we have described the synthesis of new poly(amide thioether)s by addition of ethanedithiol to diallylamides in the presence or absence of peroxide catalysts. Up to now, only a limited number of reports in the literature has dealt with poly(amide thioether)s. Probably the first example of this type of polymers was obtained by addition of H₂S to N,N'-methylenediacrylamide⁷.

In a similar study, a poly(amide thioether) has been obtained by the reaction of hydrogen sulfide with N,N-dimethyl-N',N'-dimethacryloylhydrazine. Upon hydrolysis the resulting polymer releases hydrazine⁸. In one of the oldest references, a simple way to poly(amide thioether)s has been reported by interfacial condensation of thio-2,2-diacetyl dichloride with diamines⁹.

Also, in one of our previous papers, we have reported that the condensation of formaldehyde with cyanoethylated ethanedithiol in H₂SO₄ gives poly(amide thioether)s in high yields¹⁰.

In this study, three diallylamides, viz. N,N'-diallyloxalamide (DAO), N,N'-diallylmalonamide (DAM) and N,N'-diallylterephthalamide (DAT), have been polymerized by addition of ethane-1,2-dithiol. The structures of the

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resulting polymers have been elucidated by elementary microanalysis and ^1H NMR and IR spectroscopy.

Poly(amide thioether)s are considered to comprise both elastic properties of polythioethers and crystalline properties of polyamides. For this reason, thermal characteristics and crystallinity of the novel poly(amide thioether)s have also been investigated.

Experimental

All the reagents and solvents were analytical grade chemical products (Fluka) and were used without any further purification.

^1H NMR spectra were recorded on a Varian Gemini 200 spectrometer at 200 MHz with TMS as internal reference. The FT-IR spectra were recorded on a Mattson 1000 FT-IR spectrometer.

Synthesis of diallyloxalamide (DAO)

In a 250 mL flask, diethyl oxalate (5 g, 3.42 mmol) and dioxane (7 mL) was placed. Allylamine (5.13 mL, 68.4 mmol) was added dropwise to the mixture under stirring. The mixture was refluxed for 24 h. After cooling, the reaction content was poured into 200 mL of cold water. The white precipitate was filtered off and recrystallized from ethanol (15 mL). The product is soluble in cold DMSO, ethanol, acetone and dioxane, insoluble in water and CCl_4 ; yield 3.8 g (33%), m.p. 157 °C.

FT-IR (KBr pellet, cm^{-1}): 3300 (N—H stretch.), 3080 (olefinic C—H stretch.), 2950 (aliphatic C—H stretch.), 1660 (broad, amide C=O and C=C stretch.), 1540 (N—H plane bending).

The ^1H NMR spectrum of DAO is given in Fig. 3.

$\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2$ (168.20) found C 58.47 H 7.67 N 17.48
calcd. C 57.13 H 7.19 N 16.66

Synthesis of diallylmalonamide (DAM)

DAM was prepared according to the procedure described elsewhere¹¹; yield 77.5%, m.p. 145.5 °C. The product is soluble in DMSO, acetone, ethanol, water and dioxane, slightly soluble in methanol and insoluble in ether and toluene.

FT-IR (KBr pellet, cm^{-1}): 3350 (N—H stretch.), 3083 (olefinic C—H stretch.), 2980 (aliphatic, asym. C—H stretch.), 2800 (aliphatic sym. C—H stretch.), 1650 (broad, amide C=O stretch.), 1630 (C=C stretch.), 1550 (N—H plane bending).

The ^1H NMR spectrum of DAM is given in Fig. 2.

$\text{C}_9\text{H}_{14}\text{N}_2\text{O}_2$ (182.22) found C 59.13 H 7.60 N 15.49
calcd. C 59.32 H 7.74 N 15.37

Synthesis of *N,N'*-diallylterephthalamide (DAT)

DAT was prepared from commercial poly(ethylene terephthalate) (PET). For this purpose, a PET bottle was cut with scissors into pieces (2 mm size). The pieces (10 g) were

placed in a 250 mL flask. Ethanol (50 mL) and two drops of concentrated H_2SO_4 were added to the flask. Allyl amine (9 mL, 0.12 mol) was added slowly under stirring. Stirring was continued at room temperature for 1 h and the mixture was refluxed for 48 h. After cooling, the mixture was poured into 500 mL of cold water. The white precipitate was filtered off and recrystallized from ethanol (50 mL); yield 7.8 g (56.3%), m.p. 227 °C. The product is soluble in DMSO, slightly soluble in ethanol, acetone and dioxane, insoluble in water and CCl_4 .

FT-IR (KBr pellet, cm^{-1}): 3300 (N—H stretch.), 3080 (aromatic C—H stretch.), 3050 (shoulder, olefinic C—H stretch.), 1693 (combination of C=C stretch. and amide C=O stretch.), 1550 (N—H plane bending).

The ^1H NMR spectrum of DAT is given in Fig. 1.

$\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$ (244.29) found C 67.83 H 6.55 N 11.26
calcd. C 68.83 H 6.60 N 11.47

Polymerization of diallyl monomers with ethane-1,2-dithiol

Polymerizations were carried out at room temperature by interaction of ethane-1,2-dithiol with one of the diallyl monomers (DAO, DAM, DAT) in dioxane. Due to the unpleasant odor of ethane-1,2-dithiol, the reactions were performed in an efficient fume hood.

A representative procedure for the polymerizations is as follows: *N,N'*-diallyloxalamide (1 g, 5.95 mmol) is dissolved in 20 mL of dioxane in a 250 mL three-necked flask equipped with a reflux condenser, a thermometer and a dropping funnel. The solution is flushed with nitrogen to remove the dissolved oxygen. Under stirring with a stirring bar, ethane-1,2-dithiol (0.56 mL, 6.66 mmol) in 5 mL of dioxane is added through the dropping funnel. The mixture is stirred for 8 h at room temperature and added to 30 mL of ethanol. The precipitate is filtered off, washed with 10 mL of ethanol and dried at 40 °C under vacuum for 24 h; yield 0.142 g (91.6%). To investigate the peroxide effect, the same experiment was repeated in the presence of 0.1 mL of aqueous H_2O_2 solution (10%).

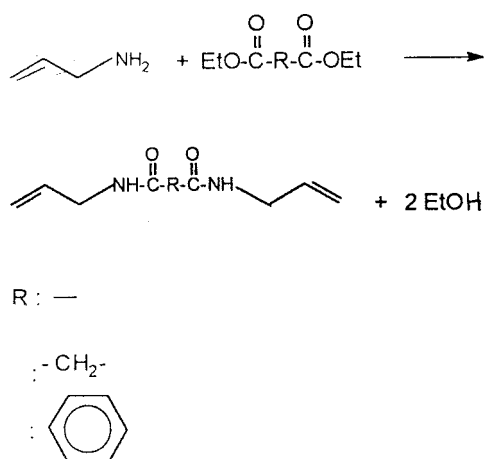
Kinetic experiments

The kinetic experiments were performed under the same conditions except that the reaction flask was kept in an oil bath at 25 °C. To observe reasonable mass differences, the reactions were carried out in dilute conditions using 0.5 g of diallylamide monomer in 50 mL dioxane. During the reactions, 10 mL aliquots were taken out, precipitated in 10 mL of ethanol, and dried under the same conditions as above. From the conversion-time plots obtained, the order of the reaction kinetics and the rate constants (Tab. 1) were determined.

Results and discussion

The diallyl monomers were obtained by classical ester aminolysis of diethyl oxalate, diethyl malonate and poly-

Scheme 1:



(ethylene terephthalate) in reasonable yields (Scheme 1). These monomers are white crystalline compounds. Elemental microanalysis and ¹H NMR spectra of the monomers clearly establish their structures.

In the ¹H NMR spectra of the monomers (Fig. 1–3) the N—H proton signals are observed in the range 7.6–8.2 ppm as broad singlets. The signals of the vinyl group protons adjacent to allylic carbon are observed in the

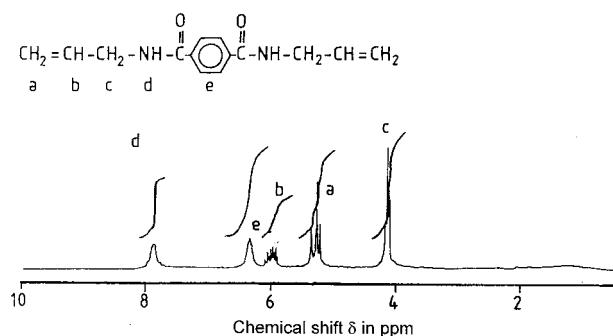


Fig. 1. ¹H NMR spectrum of N,N'-diallylterephthalamide monomer in CDCl₃.

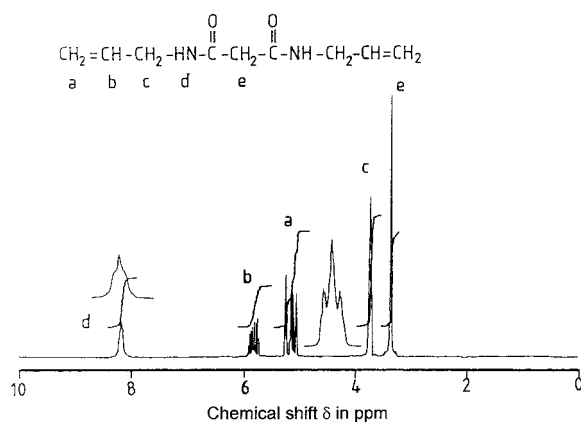


Fig. 2. ¹H NMR spectrum of N,N'-diallylmalonamide monomer in DMSO-d₆.

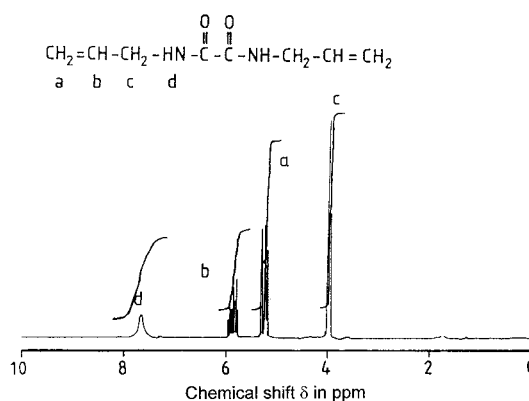


Fig. 3. ¹H NMR spectrum of N,N'-diallyloxalamide monomer in CDCl₃.

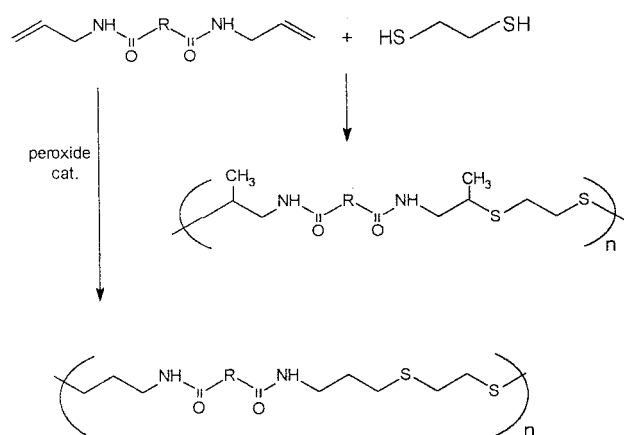
range of 5.85–5.97 ppm as multiplet peaks. The hydrogen atoms on allylic carbon represent a triplet in the 3.7–4.1 ppm range.

Terminal protons of the vinyl groups give multiple signals between 5.15 and 5.30 ppm. The NMR spectral patterns are consistent with those obtained by semiempirical calculations based on the Shoolery constant. The ¹H NMR spectra reveal that the diallylamides are obtained as pure compounds.

Polymerizations

Addition of ethanedithiol to the diallylamide monomers gives white polymers which are insoluble in common organic solvents. However, they can be dissolved in a *m*-cresol/DMSO (1:1, v/v) mixture. Without peroxide catalyst, the addition of ethanedithiol is believed to occur according to the anti-Markovnikov-type addition mechanism, which yields poly(amide thioether)s with pendent methyl groups (Scheme 2), whereas in the presence of a peroxide catalyst the thiol addition takes place at the β-carbon of the ethylenic group.

Scheme 2:



Tab. 1. Polymerization characteristics of the diallyl monomers with ethane-1,2-dithiol.

Monomer	Without peroxide catalyst		With peroxide catalyst	
	Yield ^a (%)	Rate constant (L mol ⁻¹ s ⁻¹)	Yield ^a (%)	Rate constant (L mol ⁻¹ s ⁻¹)
DAO	93.8	$2.1 \cdot 10^{-3}$	96.7	$3.6 \cdot 10^{-3}$
DAM	96.2	$6.1 \cdot 10^{-3}$	98.0 (99.1) ^b	$22.0 \cdot 10^{-3}$
DAT	92.5	$1.9 \cdot 10^{-3}$	97.4	$4.64 \cdot 10^{-3}$

^a Polymerization time 8 h.

^b Precipitated in water.

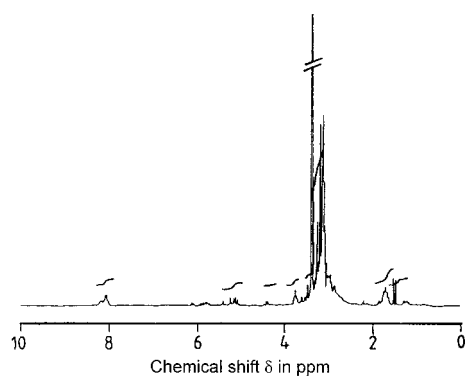


Fig. 4. ¹H NMR spectrum (in DMSO-d₆) of the oligomer obtained by reaction of N,N'-diallylmalonamide with 100% excess of ethane-1,2-dithiol.

The polymerization yields vary between 92 and 99%. The yields given in Tab. 1 are practical yields and do not include methanol-soluble oligomers, since the polymers were washed with methanol to remove the unreacted allylamides.

But the yield, when precipitated in water, for the polymer obtained from water-soluble DAM is 99.1%. Based on the simple Carothers equation, the number-average molecular weight of this polymer must be about 20000.

Owing to the insolubility of the polymers in deuterated solvents, the NMR spectra of the polymers could not be taken. In order to see the disappearance of vinyl groups during polymerization, the addition of ethanedithiol to DAM was carried out in the presence of 100% excess of dithiol. By this way an oligomer which is soluble in DMSO was obtained and its ¹H NMR spectrum was recorded (Fig. 4). In the spectrum it is clearly seen that the signals of the vinyl protons of DAM monomer in the 5–6 ppm range disappear almost completely after oligomerization. However, it is difficult to assign methyl protons formed by Markovnikov-type addition due to the other aliphatic proton signals observed at the same range, 2.9–3.7 ppm.

Thiol addition can also be followed by IR spectroscopy. C–H stretching vibrations of the vinylic groups of the monomers are observed at about 3040 cm⁻¹ (Fig. 5).

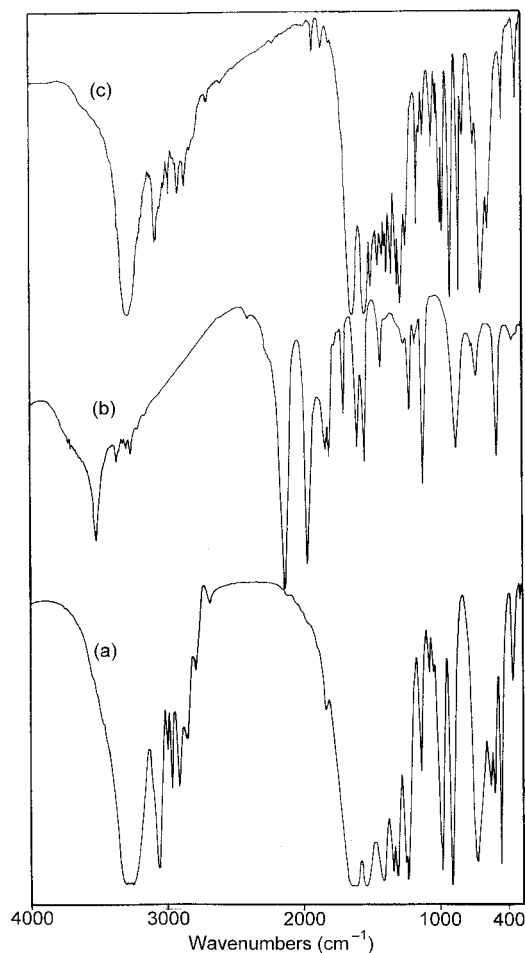


Fig. 5. FT-IR spectra of (a) N,N'-diallylmalonamide, (b) N,N'-diallyloxalamide, (c) N,N'-diallylterephthalamide.

In the FT-IR spectra of the polymers (Fig. 6) the disappearance of these bands implies that the thiol addition took place. C=C stretching and N–H plane bending vibrations of the monomers are shown as a combined band at 1640 cm⁻¹. After polymerization, the intensities of these bands become smaller due to the consumption of the double bonds. These evidences establish the formation of the polymer.

In order to investigate the kinetics of the additions, polymerizations have been performed in dioxane, which is a solvent for all the monomers studied. From the conversion-time plots, the kinetics of thiol addition were found to be second order. The rate constants of the ethanedithiol addition are in the $1.92 \cdot 10^{-3}$ – $22 \cdot 10^{-3}$ L mol⁻¹ s⁻¹ range (Tab. 1). Apparently, the addition of a peroxide catalyst effects higher rates of polymerization.

Thermal and crystalline properties of the polymers

No glass transitions are observed in the DSC thermograms of the polymers. The melting temperatures of the

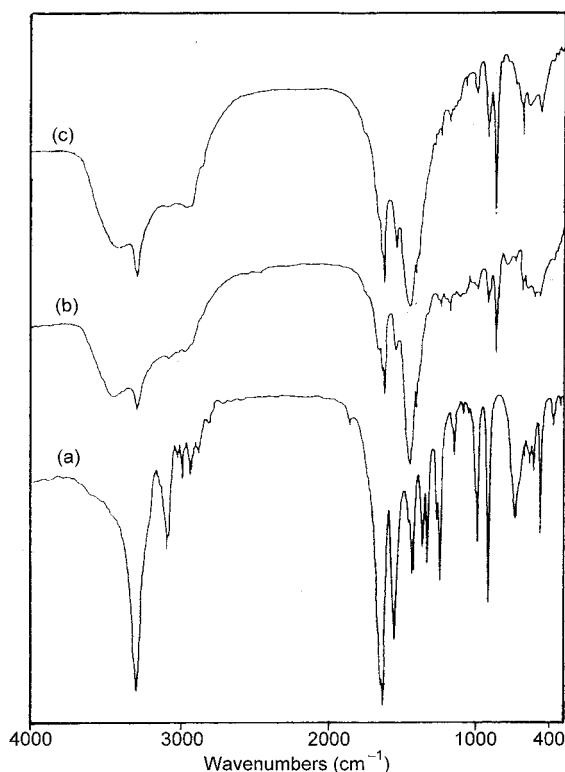


Fig. 6. FT-IR spectra of (a) *N,N'*-diallylmalonamide (DAM) monomer, (b) polymer of DAM and ethane-1,2-dithiol without peroxide catalyst, (c) polymer of DAM and ethane-1,2-dithiol with peroxide catalyst.

polymers obtained in the presence of a peroxide catalyst are markedly higher than those of the polymers prepared without peroxide. With the exception of the polymer obtained from DAT in the presence of peroxide catalyst, all the polymers melt without decomposition. These melting temperatures are lower than those of the ordinary polyamides with the same number of atoms in the repeating units. According to the thermogravimetric analyses, the polymer degradation temperatures (PDT) of the polymers lie between 235 and 302 °C (Tab. 2). In comparison with their melting temperatures, the PDT's of the polymers are about 15–50 °C higher. Also, the polymers which are prepared in the presence of a peroxide catalyst show somewhat higher decomposition temperatures than those obtained in the absence of peroxide. Although there exist no reports on thermal degradation of poly(amide thioether)s, this result can be ascribed to the formation of tertiary carbon atoms in the polymers obtained without

Tab. 2. Physical characteristics of the polymers.

Starting monomer	Peroxide catalyst	Viscosity ^a (cm ³ g ⁻¹)	T _m (°C)	Crystallinity ^b (%)	PDT ^c (°C)
DAO	no	8	218	>95	235
DAO	yes	11	240	>95	255
DAM	no	9	226	>90	261
DAM	yes	13	234	>85	295
DAT	no	11	254	>95	274
DAT	yes	18	>300 ^d	>95	302

^a In *m*-cresol/DMSO (1:1, v/v) at 30±2 °C.

^b Assigned from X-ray diffraction.

^c Polymer degradation temperature observed from thermogravimetric analysis (under 10 mL min⁻¹ N₂ flow, heating rate 10 K min⁻¹).

^d With decomposition.

peroxide catalyst, because thermal splitting from tertiary carbons is expected to occur more readily in comparison to unbranched carbon-carbon bonds.

A rough estimation based on the peak ratios of the X-ray diffraction patterns implies that all the polymers are highly crystalline compounds (Tab. 2). The crystallinities are as high as 95% (by neglecting the Lorentzian effects).

Like polyamides, polysulfides are also crystalline polymers¹². So, in our case, the addition of ethanedithiol to the diallylamides gives highly crystalline poly(amide thioether)s with relatively low molecular weights.

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