Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Godet, Monique(1987) 'Synthesis of Polyamides-11 with Sulfonamide End Groups', Journal of Macromolecular Science, Part A, 24: 5, 539 — 555
To link to this Article: DOI: 10.1080/00222338708068140
URL: http://dx.doi.org/10.1080/00222338708068140

J. MACROMOL. SCI.—CHEM., A24(5), pp. 539-555 (1987)

SYNTHESIS OF POLYAMIDES-11 WITH SULFONAMIDE END GROUPS

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ABSTRACT

α,ω-Diaminooligoamides-11 were prepared and their structure was controlled by endgroup titration, elemental analysis, and infrared and ^{1}H NMR spectroscopy. A fundamental study of the reaction between α,ω-diaminooligoamides and *p*-toluenesulfonyl chloride in DMF showed that a side reaction takes place. This was carefully characterized. When the reaction was carried out in chlorobenzene (on models and on polymers), well-defined compounds were obtained which were characterized by different techniques.

INTRODUCTION

Due to its high stiffness, polyamide-11 must be plasticized. Unfortunately the most commonly used plasticizers (sulfonamides such as *N*-butylbenzenesulfonamide) exude or are extracted from the polymer. It should be possible to overcome this difficulty by using plasticizers of molecular weight sufficiently high to decrease their mobility and with structures close to that of the polyamide.

Oligoamides-11 with sulfonamide end groups should satisfy these requirements. This first article describes their synthesis, and another article [1] will deal with mechanical properties of blends prepared with PA-11 and oligoamides-11 with sulfonamide end groups. Oligoamides-11 with amine end groups were synthesized according to Deleens [2]. The amine end groups are transformed into sulfonamide functions by reaction with the *p*-toluenesulfonyl chloride (PTSC).

EXPERIMENTAL

Elemental analyses were carried out on a Carlo Erba Model 1106 elemental analyzer. The infrared spectra were recorded on a Perkin-Elmer Model 577 spectrophotometer from potassium bromide pellets in the case of oligomers. The NMR spectra were recorded using a Varian NMR spectrometer with TMS or DSS as internal standards. Melting points were determined on a Perkin-Elmer Model DSC_2 differential scanning calorimeter at a heating rate of 20°C/min using an indium standard. End groups were titrated by Waltz and Taylor's method [3]. Limit of error: 3%.

Synthesis of α,ω-Diaminooligoamides-11

All the reactions were carried out in a stainless-steel reactor fitted with a stirrer and swept by dry N_2. A mixture of 11-aminoundecanoic acid and freshly distilled 1,6-diaminohexane was introduced into the reactor. Three purges were necessary. After the last purge the pressure was kept at 0.15 MPA. It was elevated and kept at 1 MPa with one or more successive introductions. The reaction mixture was heated from 150 to 250°C for 30 min. After 5 h at 250°C, it was slowly cooled to room temperature under nitrogen. The mixture was poured into ice water, ground, and dried under vacuum. The experimental conditions are summarized in the Table 1.

The α,ω-dimethyloligoamides-11 were obtained from the ATOCHEM Society.

Synthesis of α,ω-Disulfonamidooligoamide-11 in Dimethylformamide

Dimethylformamide and triethylamine were distilled under reduced pressure. Triethylamine (1.75 cm^3) was introduced into the reactor, then DMF (100 cm^3) and α,ω-diaminooligoamide-11 (No. 1, 10.82 g). *p*-Toluenesulfonyl chloride (PTSC) (9.52 g) was added to reaction mixture. At the end of the reaction, DMF was distilled off under vacuum. The amine salt was washed out with water. The substance was filtered and then dried.

TABLE 1. Experimental Conditions for the Syntheses of α,ω-Diaminooligoamides-11

	Oligomer number		
	1	2	3
11-Aminoundecanoic acid, g	2 820.0	3 470.2	3 060.0
1,6-Diaminohexane, g	435.0	338.3	174.0
Water, cm^3	145	190	144
$\overline{M}_n$ by endgroup titration	865	1 290	2 100
Melting temperature, °C	165.0	163.0	174.5

Synthesis of Iminium Salt

DMF (15.4 g) was introduced into a Pyrex reactor. PTSC (28.13 g) was added during 5 min. The reaction mixture turned red-brown. After 1.5 h at room temperature, the iminium salt, which is a liquid, was characterized.

Syntheses of Sulfonamide Derivatives

N-n-Butyl-p-toluenesulfonamide

PTSC (19.06 g), freshly distilled triethylamine (14 cm^3), and diethyl ether (50 cm^3) were placed in a reactor and stirred. *n*-Butylamine (7 g) was added for 5 min. When the exothermic reaction was over, the mixture was reacted at 25°C for 1.5 h. The mixture was poured into water. The aqueous phase was dried over magnesium sulfate. Diethyl ether was distilled off, and a yellow liquid was obtained.

1,6-Diaminohexanedisulfonamide

PTSC (38.12 g), triethylamine (28 cm^3), and chlorobenzene (70 cm^3) were placed in a Pyrex reactor and stirred. 1,6-Diaminohexane (11.62 g) was progressively added. The mixture was refluxed for 1.5 h and then washed several times with hot water to eliminate the amine chlorhydrate formed. The product was filtered, dried, and then recrystallized from methanol (needles, mp 165°C).

1-Aminooctadecanesulfonamide

1-Aminooctadecane (269.5 g) and PTSC (190.6 g) were added, under stirring to a solution of 75 g sodium hydroxide in 680 cm^3 water, then 300 cm^3 toluene was introduced. The reaction mixture was refluxed to distill off water. The product was dried, washed with hot toluene, and filtered. Toluene was eliminated by heating at 110°C under 17 torr.

Syntheses of Disulfonamide Derivatives of α,ω-Diaminooligoamides-11

The reaction was carried out as reported for 1,6-diaminohexane. The product was progressively added to water and the mixture was stirred with a very efficient stirrer (Ultra-Turrax). The sulfonamide derivatives obtained were dried, then powdered to make the extraction of the amine hydrochlorate easier. The experiments were carried out with the following quantities of α,ω-diaminooligoamides-11: 43.25 g (No. 1), 64.5 g (No. 2), and 105 g (No. 3). The experiments used the same amount of triethylamine (14 cm^3) and PTSC (19.06 g). Molecular weights were equal to 895, 1 300, and 2 300 g/mol, respectively. Yields were 80-95%.

RESULTS AND DISCUSSION

Synthesis and Characterization of α,ω-Diaminooligoamides-11

Samples with different molecular weights were synthesized by polycondensation in bulk of 11-aminoundecanoic acid in the presence of 1,6-diaminohexane as chain limiter. Their melting points were 120, 136, and 160°C, respectively.

Endgroup Titration

These samples had $\overline{M}_n$ equal to 865 ± 26, 1 290 ± 39, and 2 100 ± 63, respectively.

IR Spectroscopy

The IR spectra of diaminooligoamides show few differences from the spectrum of the high-molecular-weight polyamide. Endgroup bands were identified: N–H (3 300 and 3 060 cm^{-1}), ν_{CO} (amide band I) (1 660 cm^{-1}), and ν_{CN} and δ_{NH} (amide band II) (1 560 cm^{-1}).

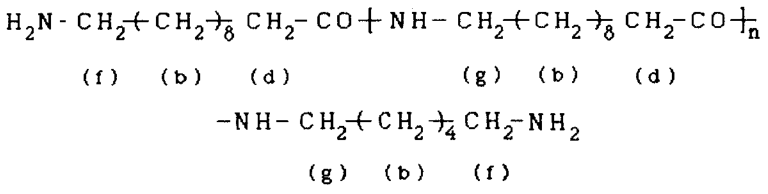
TABLE 2. ^1H NMR Spectra of α,ω-Diaminooligoamides-11

Assignments of protons	Theoretical number of protons	δ,[a] ppm
(*b*)	$16n + 24$	0.85-2.05
(*d*)	$2n + 2$	2.75
(*f*)	4	3.30
(*g*)	$2n + 2$	3.60

[a] δ(ppm, TMS): solvent, CF_3COOD; 40°C; 60 MHz.

^1H NMR

We did not find any reference relative to α,ω-diaminooligamide-11 ^1H NMR spectra in the literature. Our results are reported in Table 2. The assignments of the methylene groups (*f*) were obtained by comparison with the spectrum of 11-aminoundecanoic acid. Our assignment of methylene groups (*d*) and (*g*) fit those published by Holmes, Moniz, and Ferguson [4].



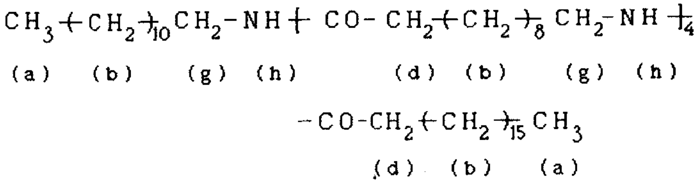
$$H_2N-\underset{(f)}{CH_2}\underset{(b)}{(CH_2)_8}\underset{(d)}{CH_2}-CO\left[NH-\underset{(g)}{CH_2}\underset{(b)}{(CH_2)_8}\underset{(d)}{CH_2}-CO\right]_n$$

$$-NH-\underset{(g)}{CH_2}\underset{(b)}{(CH_2)_4}\underset{(f)}{CH_2}-NH_2$$

By comparing the integrations corresponding to the 4 protons (*f*), to the ($2n + 2$) protons (*d*), and to the ($16n + 24$) protons (*b*), we could determine the values of n, which are reported in Table 3. $\overline{M}_n$ values resulting from ^1H NMR and from endgroup titration are compared in Table 3, which shows good agreement between the results obtained by both methods. Moreover, the nitrogen, carbon, and hydrogen contents could be calculated from the molecular weight values determined by NMR and compared to the experimental values (Table 4).

Characterization of α,ω-Dimethyloligoamide-11

In the same way we characterized an oligoamide-11 with methyl end groups, which was used in plasticization studies. Its structure was analyzed by several techniques:



$$\underset{(a)}{CH_3}\left(\underset{(b)}{CH_2}\right)_{10}\underset{(g)}{CH_2}-\underset{(h)}{NH}\left[CO-\underset{(d)}{CH_2}\left(\underset{(b)}{CH_2}\right)_8\underset{(g)}{CH_2}-\underset{(h)}{NH}\right]_4-CO-\underset{(d)}{CH_2}\left(\underset{(b)}{CH_2}\right)_{15}\underset{(a)}{CH_3}$$

Elemental analysis. Calculated for $C_{74}H_{145}N_5O_5$: C, 75.06; H, 12.25; N, 5.92%. Found: C, 74.9; H, 12.2; N, 5.9%. The IR spectrum is identical to that of PA-11. ^{1}H NMR chemical shifts are reported in Table 5.

TABLE 3. α,ω-Diaminooligoamides-11. Comparison of $\overline{M}_n$ Obtained by NMR Analysis and by Endgroup Titration

Oligomer no.	n	$\overline{M}_{n\,\text{NMR}}$	$\overline{M}_{n\,\text{titr}}$
1	3.4	921 ± 46	865 ± 26
2	5.5	1 305 ± 65	1 290 ± 39
3	12.0	2 495 ± 125	2 100 ± 63

TABLE 4. α,ω-Diaminooligoamides-11. Comparison of Elemental Analyses Calculated for NMR and Found

		C	H	N	O
		No. of atoms			
Oligomer no.		$11n + 17$	$21n + 37$	$n + 3$	$n + 1$
1	Calculated, %	70.8	11.8	9.7	7.2
	Found, %	69.9	12.0	9.4	10.4
2	Calculated, %	71.3	11.7	9.1	7.7
	Found, %	69.8	11.8	8.8	10.9
3	Calculated, %	71.7	11.6	8.4	8.2
	Found, %	71.3	11.6	8.5	8.2

TABLE 5. ^1H NMR Spectrum of α,ω-Dimethyloligoamide-11

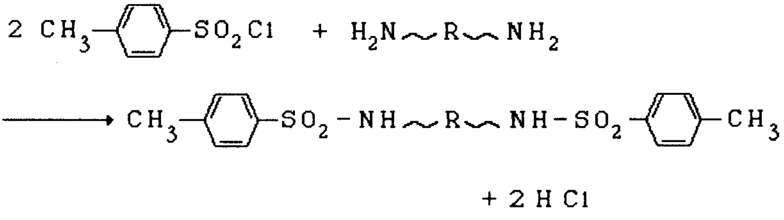
Assignments	δ^a	Multiplicity
(*a*)	0.92	Multiplet
(*b*)	1.30-1.73	Multiplet
(*d*)	2.06	Amount
(*g*)	2.90	Triplet
(*h*)	7.40	Amount

$^a\delta$(ppm, DSS): solvent, DMSO-d_6; 150°C; 60 MHz.

RESULTS AND DISCUSSION

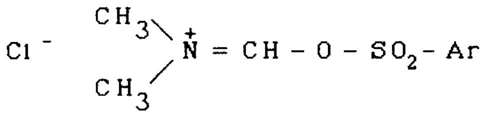
Study of the System α,ω-Diaminooligoamides-11/*p*-Toluenesulfonyl Chloride (PTSC) in DMF

The reaction between PTSC and an α,ω-diamino compound must be carried out in the presence of a proton acceptor to trap hydrogen chloride. We mainly used triethylamine. The first experiments were carried out in DMF, which is a good solvent for α,ω-diaminooligoamide-11. A preliminary experiment showed that PTSC does not react with triethylamine. Unfortunately, side reactions take place, and we did not obtain the expected α,ω-sulfonamidooligoamide-11.



Reaction of DMF with Sulfonyl Chlorides

Albright et al. [5] showed that DMF can react with sulfonyl chlorides to form an iminium salt:

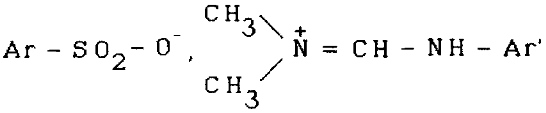


$$Cl^- \quad \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\overset{+}{N}=CH-O-SO_2-Ar$$

(I)

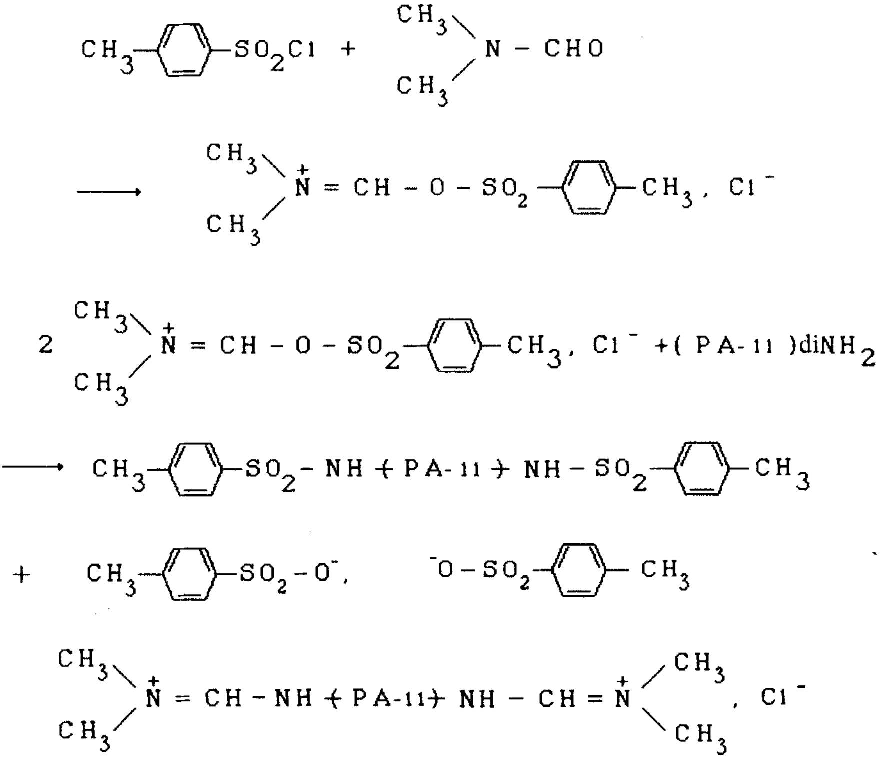
This salt reacts with aryl amines ($Ar'NH_2$) to form sulfonamides (II) and/or formamidines (III). Preferential formation of (II) or (III) apparently depends on the amine basicity, on the nature of the aryl substituents of the amine, and on experimental conditions.

$$Ar - SO_2 - NH - Ar' \qquad \text{(II)}$$



$$Ar - SO_2 - O^-, \quad (CH_3)_2\overset{+}{N} = CH - NH - Ar' \qquad \text{(III)}$$

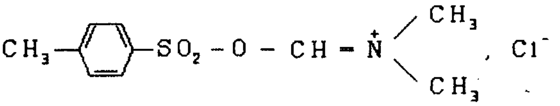
Albright et al. [5] did not establish the structure of (III), and apparently, this has not been done until now. Using Albright's assumptions, we propose the following reaction scheme:



Synthesis and Characterization of the Iminium Salt A

Iminium salt A was obtained by reacting dimethylformamide with *p*-toluenesulfonic chloride (see Experimental part).

Elemental analysis. Calculated for $C_{10}H_{14}NSO_3Cl$: C, 45.54; H, 5.31; N, 5.31; S, 12.14%. Found: C, 45.4; H, 5.7; N, 5.7; S, 12.0%. The IR spectrum shows the presence of the iminium group $-CH{=}\overset{+}{N}<$ at 1 700 cm^{-1}. The characteristics of the ^1H NMR spectrum are reported in Table 6. Elemental analysis, IR, and ^1H NMR spectra fit the expected Structure A.



A

Modification of α,ω-Diaminooligoamides-11 by *p*-Toluenesulfonyl Chloride in Chlorobenzene

Study on Model Compounds

In order to eliminate the side reaction, we replaced DMF with chlorobenzene which is not as good as DMF as a solvent of the oligoamide but which does not react with amines under our experimental conditions. To determine the optimal conditions of the modification of the oligomers, we carried out a preliminary study on low-molecular-weight model diamines using an amine/PTSC molar ratio of unity.

TABLE 6. ^1H NMR Spectrum of the Iminium Salt A

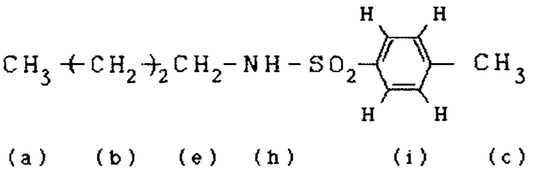
Assignments	δ^a	Multiplicity
(*g*)	2.33	Singlet
(*k*)	3.22	Singlet
(*i*)	7.80	Quadruplet
(*j*)	7.95	Singlet

$^a\delta$(ppm, TMS): solvent, $CDCl_3$; 35°C; 60 MHz.

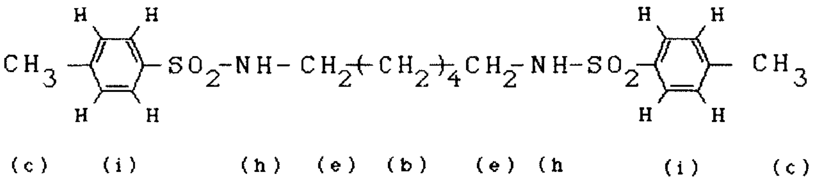
N-Butylaminesulfonamide was synthesized by White et al. [6], 1,6-diaminohexanesulfonamide [7] by Iwata, and 1-aminooctadecanesulfonamide by Cole and McCoy [8].

However, the characterization of these syntheses was very incomplete. In the case of the octadecanesulfonamide, no characterization was reported. The most complete analysis was that of *N*-butylsulfonamide, whose structure was determined by IR in CCl_4 and by ^1H NMR in $CDCl_3$. Only elemental analysis and melting point were indicated.

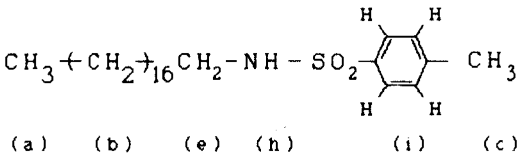
The results of the characterization by elemental analysis. IR spectrum, and ^1H NMR are reported in Tables 7-9.



N-Butyltoluenesulfonamide



1,6-Diaminohexanedisulfonamide



1-Aminooctadecanesulfonamide

Study on α,ω-Diaminooligoamides-11

The reaction between PTSC and the α,ω-diaminooligoamides-11 was carried out in chlorobenzene, and the modified polyamide was characterized by elemental analysis (Table 10) and IR spectra.

TABLE 7. Comparative Values of Elemental Analyses of Sulfonamide Models

	N-Butyltoluenesulfonamide, $C_{11}H_{17}NSO_2$		1,6-Diaminohexaneditoluenesulfonamide, $C_{20}H_{28}N_2S_2O_4$		1-Aminooctadecanetoluenesulfonamide, $C_{25}H_{45}NSO_2$	
	Calculated, %	Found, %	Calculated, %	Found, %	Calculated, %	Found, %
C	58.15	58.1	56.60	56.8	70.92	70.9
H	7.49	7.6	6.60	6.8	10.64	10.7
N	6.17	6.2	6.60	6.6	3.31	3.1
O			15.09	15.0	7.56	7.7
S			15.09	15.5	7.56	7.5

TABLE 8. Sulfonamide Models. Main Characteristics of Infrared Spectra

Assignment	*N*-Butyltoluene-sulfonamide	1,6-Diaminohexane-ditoluenesulfonamide	1-Aminooctadecane-toluenesulfonamide
ν(N–H), cm^{-1}	3 270	3 275	3 285
$\nu_{as}(SO_2)$, cm^{-1}	1 320	1 305	1 325
$\nu_s(SO_2)$, cm^{-1}	1 155	1 147	1 155

TABLE 9. Sulfonamide Models. ^1H NMR Spectra

Assignments	*N*-Butyltoluene-sulfonamide, δ, ppm[a]	1,6-Diaminohexane-ditoluenesulfonamide, δ, ppm[a]	1-Aminooctadecane-toluenesulfonamide, δ, ppm[b]
(*a*)	0.78	–	0.87
(*b*)	1.35	1.2-1.5	1.24
(*c*)	2.50[c]	2.40	2.40
(*e*)	2.85	2.70	2.91
(*h*)	7.25	7.55	4.77
(*i*)	7.80	7.62	7.53

[a] DMSO-d_6, 40°C, 60 MHz.
[b] $CDCl_3$, 40°C, 90 MHz.
[c] Signal masked by DMSO-d_6.

IR spectra show the characteristic H–NSO_2 infrared absorption at 3 300 cm^{-1}. The bands at 1 315 and 1 160 cm^{-1} were attributed, respectively, to antisymmetric and symmetric stretching of SO_2. The frequency of the antisymmetric bands increases with increasing molecular weight of the oligoamide, whereas the opposite effect is observed with the symmetric bands under the same conditions.

TABLE 10. Elemental Analyses of α,ω-Disulfonamidooligoamides-11

	No. 1′, $C_{64}H_{112}N_6S_2O_8$		No. 2′, $C_{86}H_{154}N_8S_2O_{10}$		No. 3′, $C_{141}H_{269}N_{13}S_2O_{15}$	
	Calculated, %	Found, %	Calculated, %	Found, %	Calculated, %	Found, %
C	66.43	66.4	67.80	67.9	69.43	69.1
H	9.69	9.9	10.12	10.4	11.04	11.1
N	7.26	7.3	7.36	7.4	7.47	7.2
O	11.07	10.1	10.51	10.7	9.85	9.9
S	5.53	4.8	4.20	3.6	2.63	2.2

TABLE 11. ^1H NMR Spectra of α,ω-Disulfonamidooligoamides-11

Assignments	Theoretical number	δ^a
(*b*)	$16n + 24$	0.9-2.1
(*c*)	$6a$	2.5
(*d*)	$2n + 2$	2.8
(*e*)	$4a$	3.05
(*f*)	$4(1 - a)$	Not measurable
(*g*)	$2n + 2$	3.6
(*h*)	$n + 2$	
(*i*)	$8a$	7.4-7.85

[a]δ(ppm, TMS): solvent, CF_3COOD; 40°C, 60 MHz.

^1H NMR spectra of the modified compound show that its backbone has the same peaks as those of the spectra of initial diamines; only the end groups are different. The three oligoamides showed identical spectra. Results are summarized in Table 11. To quantify the change of the initial amino end groups into sulfonamide functions, we introduced a parameter a: $a = 1$ when both ends are modified; $a = 0$ when no modification takes place.

It is worth mentioning that proton (*f*) does not give any signal, showing that the modification of amino end groups is quantitative.

We carried out a quantitative study of the spectrum of the product with the lowest molecular weight (No. 1′), assuming that n is not modified during the modification. Comparison of the integrations of all the protons (*c*), (*d*), and (*e*) and that of protons (*c*) only, gave $a = 1.04$ for this compound.

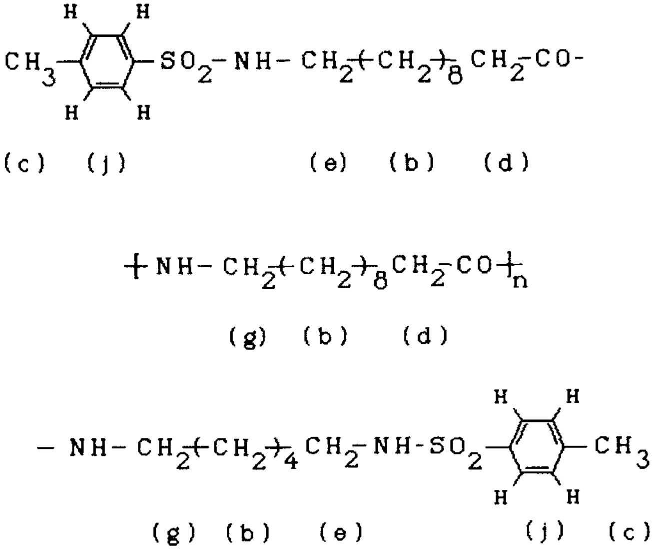
For the other samples, $a = 1.12$ for No. 2′ and 0.93 for No. 3′. These values show unambiguously that, within experimental error, amino end groups were quantitatively modified. From the values of n, we obtained the number-average molecular weights and also the contents of carbon, hydrogen, nitrogen, oxygen, and sulfur. These calculated values are compared to those obtained by elemental analyses in Table 12.

The melting temperatures of the oligomers rise with molecular weight to 167, 169, and 177°C, respectively.

TABLE 12. Comparison of Elemental Analyses Calculated from ^{1}H NMR and Found for α,ω-Disulfonamidooligoamides-11

		C	H	N	O	S
		No. of atoms				
		$11n + 31$	$21n + 49$	$n + 3$	$n + 5$	2
α,ω-Disulfonamidooligoamide-11, 1 210[a]	Calculated, %	66.7	9.8	7.3	10.9	5.2
	Found, %	66.4	9.9	7.3	10.1	4.8
α,ω-Disulfonamidooligoamide-11, 1 610[a]	Calculated, %	68.1	10.2	7.4	10.4	4.0
	Found, %	67.9	10.4	7.4	10.7	3.6
α,ω-Disulfonamidooligoamide-11, 2 590[a]	Calculated, %	69.8	10.7	7.5	9.7	2.3
	Found, %	69.1	11.1	7.2	9.9	2.2

[a] Molecular weight of the oligoamide-11.



No trace of primary amine group was found by titration of the different samples, showing that the oligoamides-11 with primary amino end groups were completely modified.

CONCLUSIONS

These reactive oligoamides were synthesized to carry out a plasticization study of polyamide-11 [1]. Such a study requires oligomers with well-defined structures. We showed that, depending on the solvent, a side reaction can take place, and we defined experimental conditions allowing the preparation of oligomers which have the expected structures.

ACKNOWLEDGMENT

We are extremely grateful to Professor E. Maréchal for the interest shown in this work and for many valuable suggestions.

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Received March 10, 1986
Revision received June 2, 1986