

Synthesis and Properties of Some Polyamides and Polysulfonamides

JEAN-PIERRE SOULIER, BERNARD CHABERT, JACQUES
CHAUCHARD, *Laboratoire de Chimie ler Cycle*, and PHILIPPE
BERTICAT and JEAN-FRANÇOIS MAY, *Laboratoire de Chimie
Macromoléculaire Associé au CNRS, U.E.R. de Chimie-Biochimie,
Université Claude Bernard-Lyon I 43, Villeurbanne, France*

Synopsis

Different polyamides and polysulfonamides were prepared by the interfacial polycondensation method. The influence of the experimental condition was specified. The principal characteristics of polymers are indicated (solubilities, molecular weights, IR spectra, thermal stability). In the case of poly(ethylene 1,3-benzenesulfonamide), a study of the thermal behavior was specially developed.

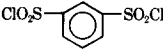


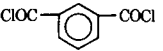
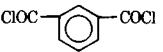
INTRODUCTION

A series of polyamides and polysulfonamides was prepared by the interfacial polycondensation method,¹ in order to study the influence of the group —CONH— and —SO₂NH— and of the chain segments which link them (methylene and benzene groups) on the phenomena of dielectric and mechanical relaxations. This paper presents the different polymers prepared, indicates the experimental conditions, and gives their principal physicochemical characteristics (solubility, IR spectra, molecular weight). Their behavior under the influence of an increase in temperature is also described. Let us specify that several polymers²⁻⁷ have been already prepared, and some of them have been indexed by Livingston.⁸

STUDY OF INTERFACIAL POLYCONDENSATION

The different polymers prepared are listed in Table I. In order to show (regarding their electrical and mechanical properties) the influence of the number of methylene groups on the flexibility of the macromolecular chain having an aromatic cycle, polymers A and B were synthesized. The homologous polyamides C and E were also polymerized, as was an intermediate product D. Finally polyamides containing only methylene groups in their chain and differing only in the number of these groups were prepared (polymers F, G, H, and I) in order to study their relaxations in comparison with the previous products.

TABLE I
Polymers Prepared by Interfacial Polycondensation

Acid dichloride	Diamine	Polymer	
	$\text{NH}_2(\text{CH}_2)_2\text{NH}_2$	$\text{-(O}_2\text{S-}\langle\text{C}_6\text{H}_3\rangle\text{-SO}_2\text{NH}(\text{CH}_2)_2\text{NH)}_n\text{-}$	A
	$\text{NH}_2(\text{CH}_2)_{12}\text{NH}_2$	$\text{-(O}_2\text{S-}\langle\text{C}_6\text{H}_3\rangle\text{-SO}_2\text{NH}(\text{CH}_2)_{12}\text{NH)}_n\text{-}$	B
	$\text{NH}_2(\text{CH}_2)_2\text{NH}_2$	$\text{-(OC-}\langle\text{C}_6\text{H}_3\rangle\text{-CONH}(\text{CH}_2)_2\text{NH)}_n\text{-}$	C
	$\text{NH}_2(\text{CH}_2)_6\text{NH}_2$	$\text{-(OC-}\langle\text{C}_6\text{H}_3\rangle\text{-CONH}(\text{CH}_2)_6\text{NH)}_n\text{-}$	D
	$\text{NH}_2(\text{CH}_2)_{12}\text{NH}_2$	$\text{-(OC-}\langle\text{C}_6\text{H}_3\rangle\text{-CONH}(\text{CH}_2)_{12}\text{NH)}_n\text{-}$	E
$\text{ClOC}(\text{CH}_2)_2\text{COCl}$	$\text{NH}_2(\text{CH}_2)_2\text{NH}_2$	$\text{-(OC}(\text{CH}_2)_2\text{CONH}(\text{CH}_2)_2\text{NH)}_n\text{-}$	F
$\text{ClOC}(\text{CH}_2)_6\text{COCl}$	$\text{NH}_2(\text{CH}_2)_2\text{NH}_2$	$\text{-(OC}(\text{CH}_2)_6\text{CONH}(\text{CH}_2)_2\text{NH)}_n\text{-}$	G
$\text{ClOC}(\text{CH}_2)_6\text{COCl}$	$\text{NH}_2(\text{CH}_2)_6\text{NH}_2$	$\text{-(OC}(\text{CH}_2)_6\text{CONH}(\text{CH}_2)_6\text{NH)}_n\text{-}$	H
$\text{ClOC}(\text{CH}_2)_6\text{COCl}$	$\text{NH}_2(\text{CH}_2)_{12}\text{NH}_2$	$\text{-(OC}(\text{CH}_2)_6\text{CONH}(\text{CH}_2)_{12}\text{NH)}_n\text{-}$	I

Purification of Initial Reagents

Most of the reagents are prepared industrially with an adequate degree of purity (>98%). On the other hand, 1,3-benzenedisulfonyl chloride, isophthalyl chloride, and hexamethylenediamine had to be purified.

The 1,3-benzenedisulfonyl chloride was purified by the method indicated by Arnold, Cantor, and Marvel.⁹ The dichloride is dissolved in benzene, and the organic solution is washed with a 5% solution of sodium bicarbonate and then with water. The solution is then dried over calcium sulfate,¹⁰ treated with activated charcoal, and dried again by passing it through a column of activated alumina. The 1,3-benzenedisulfonyl chloride is precipitated by the addition of pure hexane or heptane.

The isophthalyl chloride is solubilized by heating in petrol ether, treating with active charcoal, and recrystallizing when cold.

The hexamethylenediamine was purified by distillation.

Experimental Conditions and Method of Interfacial Polycondensation

The method of interfacial polycondensation is based on the Schotten-Bauman¹¹ reaction, which takes place at the interface of an aqueous solution of diamine containing an acid acceptor and a solution of an acid dichloride in a nonmiscible solvent. There is a formation of hydrogen chloride following the reaction between the acid chloride and the primary amine.

It is noted that the exact stoichiometry of the reagents is not as critical as in the case of polycondensation in an homogeneous system, and in certain

cases an excess of diamine can even be used as acid acceptor. Some authors¹¹ consider that the reaction takes place near the interface, in the organic phase, which limits the amount of acid dichloride likely to pass into the aqueous phase, thereby considerably reducing the hydrolysis. Finally, although stirring is not necessary, it allows obtaining rapidly the polymer in the form of powder or grains which are easily isolated and washed, and facilitating a more complete reaction between the functional groups.

The reactor used is a 1-liter narrow-neck vessel. Stirring is done with a propeller driven by an Ultra Turrax motor (3,000–10,000 rpm). The vessel is placed in a thermostat which allows the initial reaction temperature to be fixed to within 0.5°C. The thermal exchange is satisfactory, since at the end of the reaction, the increase in temperature of the reactional system does not exceed 2–3°C.

The diamines are solubilized in water. After a study of different water immiscible solvents (CCl₄, CHCl₃, CH₂Cl₂, C₆H₆, etc.), benzene was chosen as the solvent for the acid dichlorides and disulfochlorides because of its high boiling point, which reduces evaporation, and because of its high miscibility with methyl and ethyl alcohols, which facilitates its elimination and the obtention of a pure polymer.

The acid acceptor used was sodium carbonate, dissolved initially in the aqueous solution.

The polycondensation is always achieved with two solutions of the same concentration in order to obtain statistically an equal number of acid and amine functional groups at the end of the macromolecular chain.

For polymer A, the two reagents being highly soluble both in water and benzene, we can use a decinormal solution as indicated by Sundet, Murphey, and Speck.² On the other hand, in view of the low solubility of the isophthalyl chloride in benzene and of the 1, 12-diaminododecane in water, and of the expansion of the polymers which become impregnated with solvent and therefore occupy more space, limiting the possibility of stirring, we had to work with 0.015*M* solutions to prepare the polymer.

During interfacial polycondensation, hydrolysis in the dichlorides and especially the disulfonylchlorides in contact with the aqueous phase is inevitable. It is accentuated by the violent agitation of the bath which increases the area of contact between the two phases and leads to considerable evaporation of the organic solvent.

Disulfonyl chlorides being more easily hydrolyzable than the carboxylic acid dichlorides,¹² the phenomenon is studied more particularly for the 1,3-benzenedisulfonyl chloride by potentiometric determination of the chloride ions appearing in the aqueous phase in the course of an experiment conducted in conditions identical to those used for the preparation of polymer A, but without diamine in the aqueous phase.

There is considerable hydrolysis as soon as stirring is commenced (Fig. 1). However, if the volume of the organic phase is kept constant, either by working at low temperature (6°C) (although the rate of the polycondensation is then slower), or by adding benzene as it evaporates, the extent of hydrolysis is reduced (Fig. 1).

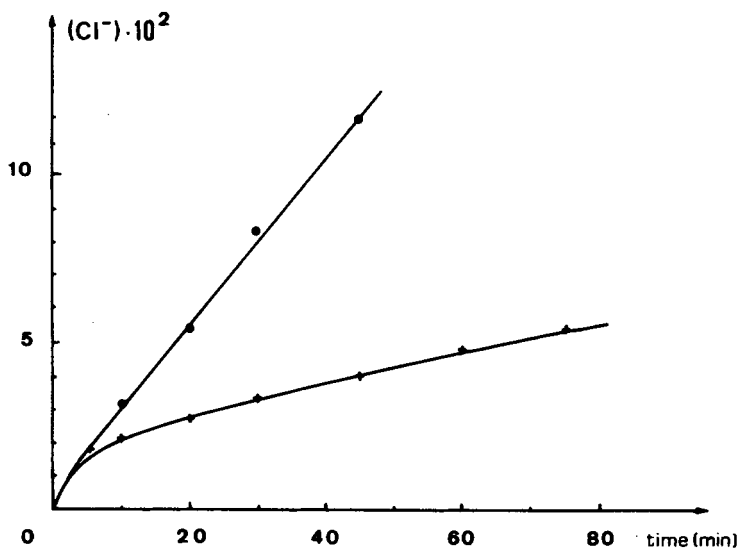


Fig. 1. Hydrolysis, at 25°C, of the 1,3-benzenedisulfonyl chloride: (+) with addition of benzene; (●) without addition of benzene.

Since this blank experiment is an extreme case as far as hydrolysis is concerned, it is apparent that during the course of the preparation of the polymers, the hydrolysis phenomenon of the reagent is considerably reduced by the polycondensation reaction itself. This phenomenon is also influenced by the pH of the aqueous solution,² the hydrolysis being greater in direct relation to the pH value.

Bearing in mind these different factors, often self-contradictory, we defined the optimal conditions and worked at a temperature of 25°C using sodium carbonate as an acid acceptor in order to have an aqueous medium with a pH value of approximately 10.5. Also, since the acid dichloride is the less stable of the two reagents, the organic solution is poured into the aqueous phase under agitation.

As far as the polyamides are concerned, it is generally accepted¹¹ that the time necessary for the obtention of macromolecules of maximal molar weight, by the interfacial method with agitation, is in the region of 10 to 15 min. We established this time for polymer A by the determination of its molecular weight. It is observed that after 40–50 min of preparation, the value of the molecular weight is maximal (Fig. 2), as is also the yield calculated in relation to the total weight of the reagents (Fig. 3).

The difference in the time required for the obtention of macromolecules of maximal molar weight in the case of the polyamide and that of the polysulfonamide can be attributed to the weaker reactivity, with amino groups, of the disulfonyl chloride to the carboxylic acid dichloride.

The polymer, separated from the reactive medium by filtration, is washed in water, in ethyl and methyl alcohols, and then dried at 70–75°C for 12 hr. Polymers A, B, C, and D appear in the form of a white powder, while the

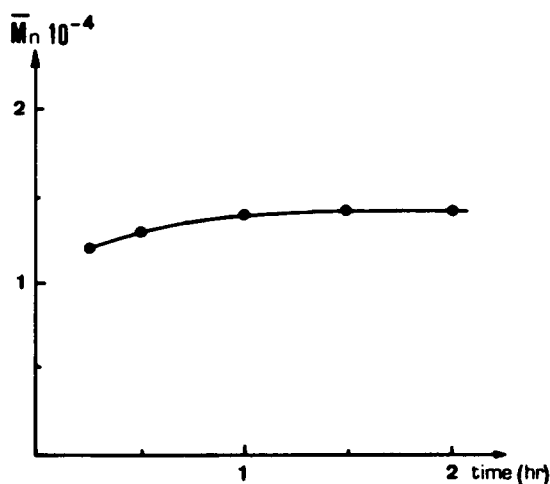


Fig. 2. Number-average molecular weight of samples of poly(ethylene 1,3-benzene sulfonamide) obtained for different times of polycondensation.

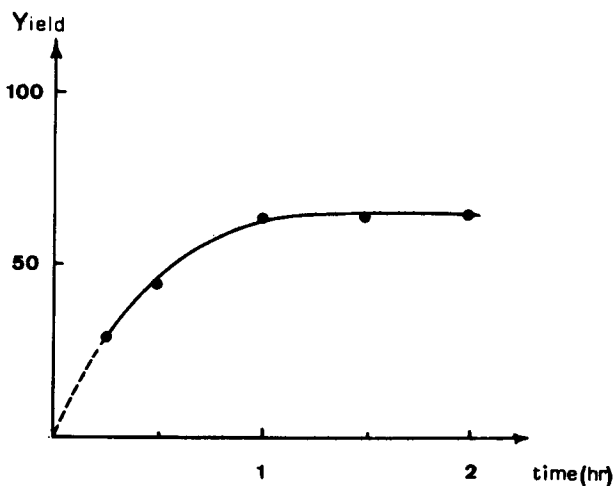


Fig. 3. Preparation of poly(ethylene 1,3-benzenesulfonamide) yield calculated in relation to the total weight of the reagents.

polymer E, also white, appears spongy. Finally, the products F, G, H, and I appear as compact grains relatively hard and colored to varying degrees (grey-brown).

PHYSICOCHEMICAL CHARACTERISTICS OF POLYMERS

Solubility of Aromatic Polyamides and Polysulfonamides

In general, the polysulfonamides are soluble in alkaline solvents.¹¹ However, it is to be noted that, in a cold state, the polysulfonamides studied

TABLE II
 Solubility of Polymers*

Solvents	Polymer A	Polymer B	Polymer C	Polymer D	Polymer E
Sulfuric acid	++	++	++	++	++
Acetic acid	-	-	-	-	-
Formic acid	-	-	±	±	±
N-Methyl-2-pyrrolidone	++	++	+	+	+
HMPT	±	±	±	±	±
Dimethylformamide	+	+	+	+	+
Dimethylformamide + LiCl	++	++	++	++	++
Dimethylacetamide	+	+	-	-	±
Dimethyl sulfoxide	±	±	-	-	-
Tetrahydrofuran	±	+	±	±	±
2,6-Dimethylaniline	+	+	+	+	+
Phenol	±	±	±	±	±
<i>m</i> -Cresol	+	+	+	+	+
<i>m</i> -Xylen	-	-	-	-	-
Chlorobenzene	-	-	-	-	-
Dichlorobenzene	±	±	±	±	±
Methanol	-	-	-	-	-
Ethanol	-	-	-	-	-
Acetone	-	-	-	-	-

* (++) solubility at room temperature; (+) soluble on heating; (±) partially soluble; (-) insoluble.

present, at best, a degree of solubility which is relatively weak (0.5%–1%) in the pure solvents we used (Table II).

It is to be observed that the isophthalyl polyamides, (C, D, E) are not very soluble. Hanus¹³ notes the same phenomenon with polyamides prepared from aromatic dichlorides and aromatic diamines. It will also be noted that for a given type of polymer, the increase in the number of methylenes between —CONH— and —SO₂NH— groups seems to lead to an increase in the solubility which is probably due to a diminution in the number of hydrogen links.

Elemental Quantitative Analysis

Elemental quantitative analysis was carried out on the different polymers, and the results are in good agreement with theoretical values. For example, results are given in Tables III and IV for polymers A and C. Theoretical values are calculated considering that polymers can be written as specified in Table I.

 TABLE III
 Analytical Results for Polymer A

	C, %	H, %	N, %	O, %	S, %
Theoretical	36.6	3.8	10.7	24.4	24.4
Experimental	36.4	3.9	10.8	24.7	23.7

TABLE IV
Analytical Results for Polymer C

	C, %	H, %	N, %	O, %
Theoretical	63.1	5.2	14.7	16.8
Experimental	62.3	5.5	14.1	17.4

Molecular Weight

The molecular weight of the aromatic polymers obtained after a reaction time of 1 hr were measured by determination of the number of amino groups ($-\text{NH}_2$) situated at the end of the chains, using Van Slyke's method⁸ extended to the determination of the amino groups of insoluble polyamides.^{9,10}

Taking account of the stoichiometry of the reagents when they are prepared, it can be allowed that the macromolecular chains are terminated statistically by one amino group and one acid group. This being so, the value of the volume of nitrogen released leads to the following average molecular weights \bar{M}_n : polymer A, 14,000; polymer B, 3,500; polymer C, 16,000; polymer D, 15,000; polymer E, 4,000.

IR Spectra

The IR absorption spectra of all the compounds were determined by tabloid technique with potassium bromide using a Perkin-Elmer spectrophotometer. The spectra obtained for the poly(ethylene 1,3-benzenesulfonamide) and poly(ethylene isophthalamide) are shown in Figures 4A and 4B, respectively. For A, we can note presence of two strong absorption bands at $1340\text{--}1320\text{ cm}^{-1}$ and $1170\text{--}1150\text{ cm}^{-1}$ which is characteristic of the sulfonamide group^{2,17}, and for C, two bands at $1660\text{--}1640$ and $1540\text{--}1520\text{ cm}^{-1}$ corresponding to the amide functions. The two products show absorption bands at $1430\text{--}1420$ and $1640\text{--}1630\text{ cm}^{-1}$ due to the benzenic cycles.

Thermal Properties

The study of the thermal stability of the polymers was done by differential thermal analysis (DTA) with the aid of a BDL microanalyzer Type M2 and thermogravimetric analysis (TGA) with an Adamel apparatus Type C. Table V shows the results obtained in the case of a first rise in temperature for the prepared products.

Studying more precisely polymers A and C by differential thermal analysis, we noted some unusual phenomena regarding the thermal behavior of these polymers. For product A, the DTA curve obtained in an inert atmosphere or in air, with a temperature increase rate of $10^\circ\text{C}/\text{min}$, shows an endothermal peak, the beginning of which is around 150°C . On cooling, no exothermal phenomenon appears which might be evidence of solidification. If heating is continued, decomposition occurs at 320°C , but before

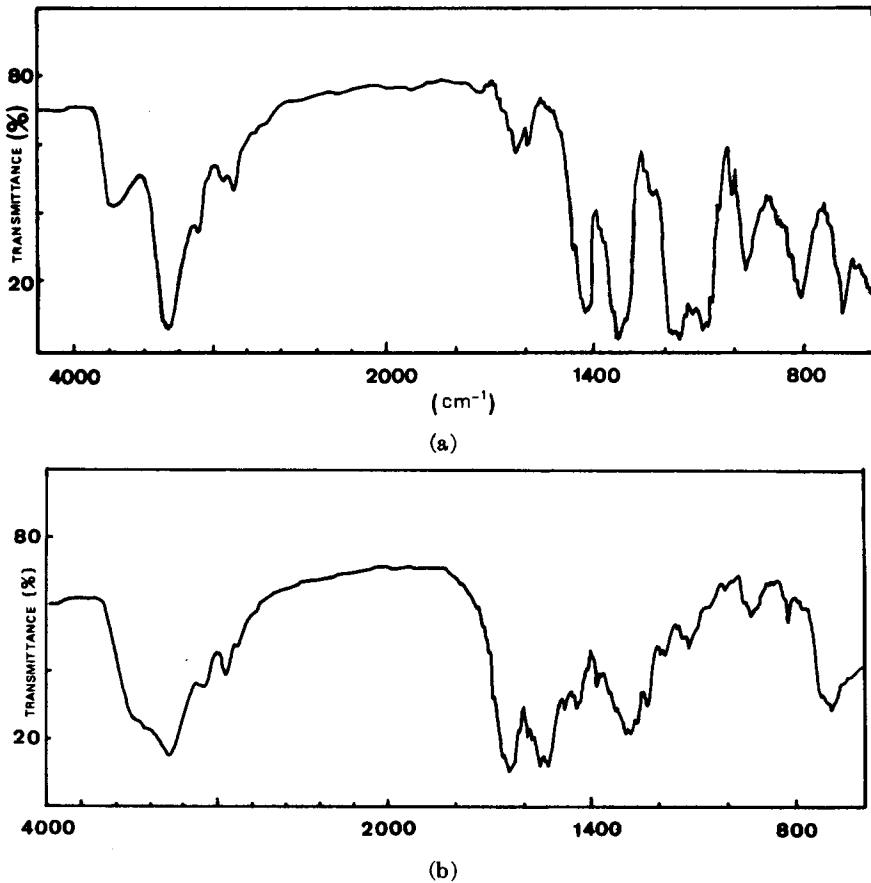


Fig. 4. (a) Infrared spectra of poly(ethylene 1,3-benzenesulfonamide). (b) Infrared spectra of poly(ethylene isophthalamide).

this temperature a second endothermal peak can be seen at around 270–280°C (Fig. 5, curve a).

The TGA curve (Fig. 6, curve A) shows indeed that a beginning of degradation only starts at 320°C. Observation with a Maquenne block shows, at 150°C, a considerable and sudden decrease in the apparent volume of the polymer and the presentation of a sticky state. When the temperature reaches 280°C the product seems to change into a liquid state, at the same time undergoing a light browning which could be due to the beginning of degradation in air.

In order to determine the significance of the first endothermal phenomenon observed (a phenomenon which is not accompanied by a loss in weight measurable by TGA, Fig. 6, curve A), the product, heated at 190°C, is recooled and submitted to a new rise in temperature by DTA. It is noted that the curve no longer shows an endothermal peak at 150°C. The peak at 270°C is not changed; on the other hand, a very clear change in the base-

TABLE V
Thermal Behavior of Polymers

	Polymer								
	A	B	C	D	E	F	G	H	I
DTA under nitrogen softening point (observed with Maquenne block), °C	150	140	295	205	192		274	220	200
Decomposition temp., °C	320	380	385	390	430	300	340	400	420
TGA									
Temperature of beginning of first mechanism, °C	320	380	385	390	410	300	340	405	420
Yield of weight loss during first mechanism	58.5	69	57	65	82	75	73.5	86.3	87
Temperature of beginning of second mechanism, °C	385	530	500	500	510	490	530	520	500
Yield of total weight loss	98.5	95	97	96.5	95	99	98	96.5	99

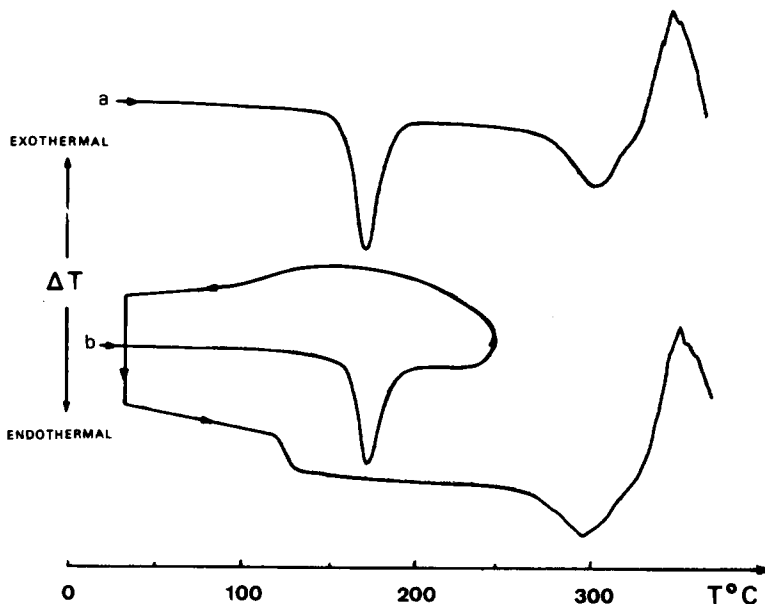


Fig. 5. DTA curves obtained for poly(ethylene 1,3 benzenesulfonamide): Curve a, first rise in temperature up to temperature of decomposition; curve b, successive thermal treatments.

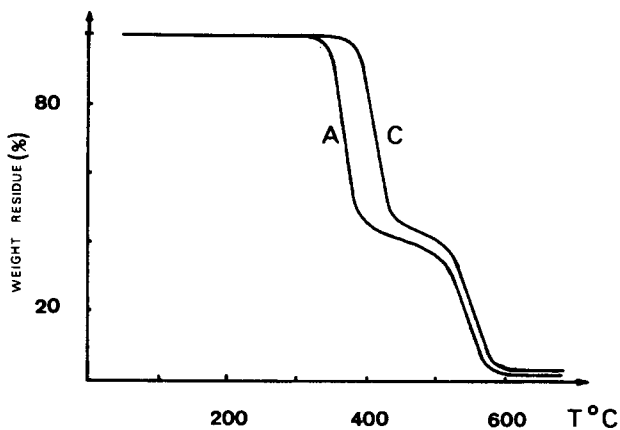


Fig. 6. Curve A, TGA curve obtained for poly(ethylene 1,3-benzenesulfonamide). Curve C, TGA curve obtained for poly(ethylene isophthalamide).

line appears at 119°C. After this thermal treatment, the DTA curve undergoes no further change whatever the reheating, lower than the decomposition temperature, imposed on the polymer.

In general, a modification in the baseline like that observed here at 119°C (Fig. 5, curve b), corresponding to a simple change in the heat capacity of the polymer, is attributed to the phenomenon of glass transition at the

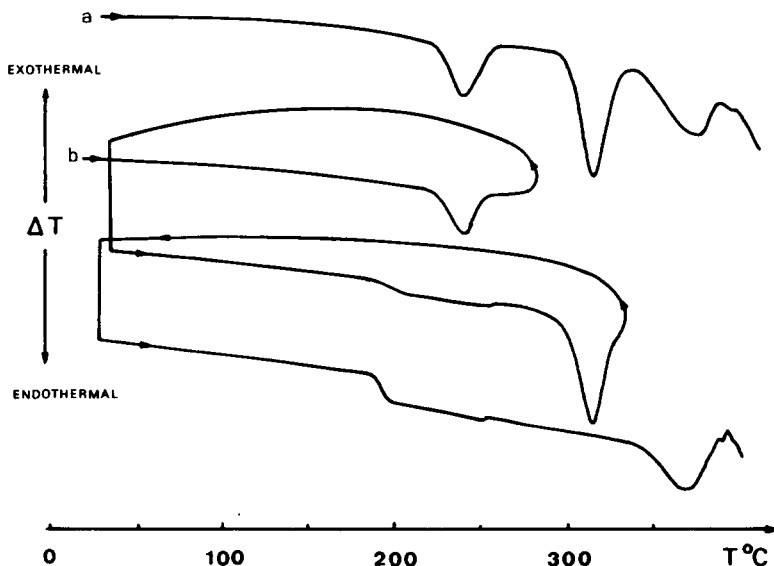


Fig. 7. DTA curves obtained for poly(ethylene isophthalamide): curve a, first rise in temperature up to temperature of decomposition; curve b, successive thermal treatments.

center of the amorphous regions.¹⁸ It may be that this phenomenon is not observed during the first temperature rise because its low intensity, which is in turn due to the size of the apparent volume, leads to poor thermal conductivity.

A release of gas was observed when the product was treated at 150°C. Furthermore, measures of intrinsic viscosities in sulfuric acid give the following results: initial polymer A, $[\eta] = 15$; polymer A treated at 180°C, $[\eta] = 18$.

These observations would lead one to believe that the temperature of 150°C corresponds to the end of the polycondensation of the product. In order to verify this hypothesis, we carried out a determination of the number of the amino groups for an initial sample and for a sample heated at 180°C. This led to the following number-average molecular weights: initial polymer A, $\bar{M}_n = 14,000$; polymer A treated at 180°C, $\bar{M}_n = 50,000$.

The results seem to confirm our hypothesis. However, let us observe that due to the thermal treatment, which caused a slight burnishing of the polymer, a certain transformation of the polymer could lead to a certain extent to a decrease in the number of amino groups.

In conclusion, the irreversible endothermic effect observed at 150°C corresponds to the juxtaposition of the different processes previously shown (polycondensation, release of gas, softening, and contraction).

As for the poly(ethylene isophthalamide), the DTA curve shows three distinct endothermic peaks at 220, 295, and 340°C (Fig. 7, curve a). As

in the case of polymer A, the corresponding exothermal peaks do not reappear on cooling. Furthermore, the peak at 220°C is not accompanied by a softening observable on the Maquenne block.

On the other hand, after the second peak, the product is in a sticky state. Evers and Ehlers¹⁷ observe similar phenomena with other aromatic polymers.

The endothermal phenomenon at 220°C disappears if polymer C has been previously heated at 240–250°C. The same is true for the second process if the product has been heated at 320°C (Fig. 7, curve b).

The decomposition, with considerable loss in weight, of polymer C, shown by DTA and by TGA (Fig. 7 and Fig. 6, curve C), occurs at 340°C in air and at 360°C in nitrogen atmosphere. On the Maquenne block, one observes that up to 295°C, the polymer stays in the form of a white powder. At 300–310°C, the product becomes slightly sticky and starts to turn slightly brown.

As in the case of polymer A, previous thermal treatment of product C leads to the appearance of a glass transition point which is not observable in the initial product. After heating the polymer to 250°C, the glass transition phenomenon, which occurs at 190°C, is not very evident; on the other hand, the thermal analysis of the product heated to 310°C shows a very clear glass transition point at 190°C (Fig. 7 curve b).

Let us observe that for all the polymers studied, thermal decomposition takes place in two stages. In the first stage with product C, at 340–360°C it was possible to show, in particular, the release of CO₂ and NH₃.

In general, for all the polymers this first stage, which occurs at temperatures of 300° to 400°C according to the products, corresponds to a loss in weight of the order of 50% to 90%. The second stage, which appears at temperatures of 400° to 500°C, leads to almost total decomposition, the total loss in weight being about 95–99%.

In conclusion, all the aromatic polyamides and polysulfonamides studied show a softening phenomenon accompanied by a considerable decrease in the apparent volume which is not to be found in the homologous aliphatic polyamides. Thermal treatment carried out at a temperature higher than that of the start of this phenomenon leads to its disappearance.

On the other hand, a very noticeable glass transition occurs in the thermograms of the obtained products.

In order to determine the structure modifications of these polymers when they are heated, a study is being developed with x-rays diffraction, vapor retention in gas–solid chromatography,¹⁹ and the depolarization thermocurrent method.²⁰

References

1. E. L. Wittbecker and P. W. Morgan, *J. Polym. Sci.*, **40**, 289 (1959).
2. S. A. Sundet, W. A. Murphey, and S. B. Speck, *J. Polym. Sci.*, **40**, 389 (1959).
3. N. Masamitsu and U. Minco, *Sen-i Gakkaishi*, **26**(4), 185 (1970); *C.A.*, **73**, 88934y (1970).
4. V. S. Naumov and L. B. Sokolov, *Vysokomol. Soedin., Ser. B*, **12**(3), 241 (1970); *C.A.*, **73**, 15346y (1970).

5. G. S. Kolesnikov, O. Ya. Fedotova, V. V. Trezvov, and V. N. Kuz'micheva, *Vysokomol. Soedin., Ser. A*, **10**(10), 2248 (1968); *C.A.*, **70**, 29424x (1969).
6. K. Tsutomi, I. Mazatsugu, M. Takeda, and F. Kenichi, *Macromol. Syn.*, **3**, 29 (1968).
7. W. B. Black and J. Preston, *Man-Made Fibers*, Sci. Technol., Vol. 2, Interscience, New York, 1968, p. 297.
8. H. K. Livingston, *J. Macromol. Sci. Rev. Macro Chem.*, **C6**(2), 29 (1971).
9. F. E. Arnold, S. Cantor, and C. S. Marvel, *J. Polym. Sci. A1*, **5**, 553 (1967).
10. A. Chalamet, D. E. S. Lyon, 1965.
11. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1968.
12. Y. Imai and H. Okunoyama, *J. Polym. Sci. A1*, **10**, 2257 (1972).
13. M. Hanus, Thesis, Lyon, 1972.
14. D. D. Van Slyke, *J. Biol. Chem.*, **9**, 185 (1911).
15. D. G. Doherty and C. L. Ogg, *Ind. Eng. Chem., Anal. ed.*, **12**, 751 (1943).
16. M. Hanus and G. Vallet, *C.R. Acad. Sci.*, **263**, 708 (1966).
17. R. C. Evers and G. F. L. Ehlers, *J. Polym. Sci. A1*, **5**, 1797 (1967).
18. M. S. Ali and R. P. Sheldon, *J. Polym. Sci.*, **14**, 2619 (1970).
19. K. Ateya, B. Chabert, J. Chauchard, and G. Edel, *C.R. Acad. Sci.*, **274**, 506 (1972).
20. D. Chatain, C. Lacabanne, and M. Maitrot, *Phys. Stat. Sol.*, **13**, 303 (1972).

Received October 23, 1973

Revised February 4, 1974