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Z. K. Brzozowski[a]; A. Grabowska-rostek[a]; Z. Przybysz[a]
[a] Technical University of Warsaw, Warsaw, Poland

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Polyamides from Aromatic Bisamines-Chloral Derivatives and Terephthaloyl Chloride by Polycondensation in Solution

ZBIGNIEW K. BRZOZOWSKI, ALICJA GRABOWSKA-ROSTEK, and
ZOFIA PRZYBYSZ

Technical University of Warsaw
Warsaw, Poland

ABSTRACT

New aromatic polyamides from the bisamines 2,2-bis(p-aminephenyl)-1,1,1-trichloroethane (Bisamine I), 2,2-bis(p-aminephenyl)-1,1-dichloroethylene (Bisamine II), and terephtaloil chloride were synthesized by means of several methods. It was found that low-temperature solvent polycondensation is optimum for obtaining polymers with the best properties, which are predominantly better in the case of polyamides based on Bisamine II.

INTRODUCTION

In opposition to preliminary research [1] and from the results of previous work [2] concerned with the interfacial polycondensation of bisamines-chloral derivatives, the possibility of getting a better yield by way of polycondensation in solution is proposed. This possibility is also confirmed by Morgan [3]. The reason is the very high reaction rate of interfacial polycondensation in the case of polyamides which do not give polymers with high molecular weights. In this work, polycondensation in solution, which gives a lower reaction rate, is studied.

EXPERIMENTAL

Materials

2,2-Bis(p-aminophenyl)-1,1,1-trichloroethane (Bisamine I, mp 166-167°C) was obtained according to previous work [2]. The reaction consists of the following stages: condensation between chloral and benzene in acid medium, nitration, catalytic reduction.

2,2-Bis(p-aminophenyl)-1,1-dichloroethylene, (Bisamine II, mp 146-147°C) was obtained from 2,2-bis(p-nitrophenyl)-1,1,1-trichloroethane by the detachment of hydrogen chloride in ethanol by means of KOH and the reduction of the nitrocompound formed according to previous work [2]. Bisamine II with the same melting point can also be obtained by the direct action of KOH on Bisamine I in methanol. Both methods were proposed by Kirkwood and Philips [4, 5].

Terephthalic acid chloride (mp 82-84°C) was obtained by the action of thionyl chloride on terephthalic acid.

Synthesis of Aromatic Polyamides

The syntheses of aromatic polyamides based on the polycondensation of Bisamines I and II with terephthalic acid chloride were carried out by the solutions method according to the instructions given by Matwielagiwili and co-workers [6].

The solution of bisamines (0.010 mol) in 20 mL of the solvent was poured into a three-necked flask equipped with a mixer and a thermometer and put into the cooling bath. During the mixing the system was cooled by means of Dry Ice and acetone to -15°C, and during 10-15 min solid terephthalic acid chloride was added and afterwards the temperature was kept constant at -15 ± 2°C. The solution was mixed for 30 min and the temperature was gradually increased to 0°C. The system was then heated to 10°C and kept at this temperature for 1.5 h. Then the temperature was increased to room temperature (18°C) and mixing was continued for 4 h. A viscous, yellow solution was obtained. The polyamide was precipitated by pouring the contents of the flask into water with intensive mixing. The precipitate was filtered off and washed with ethanol, water, and again with ethanol. Polymer was dried at room temperature for 24 h and then at 60°C under vacuum for 8 h. The polyamide obtained was a pale yellow powder.

During experiments with different solvents it has been found that aromatic polyamides of higher molecular weight are obtained in better yield when dimethylacetamide (DMAA) is used as the solvent than in the case of dimethylsulfoxide (DMSO). During the experiment on the influence of different parameters on the reduced viscosity of the polymer, DMAA was used.

TABLE 1. The Influence of the Acceptor of Hydrogen Chloride

Amine	Solvent	The amount of the acceptor (triethylamine) (mole)	Reduced viscosity, t = 20°C, DMF	Yield (%)
Bisamine I	DMAA	-	0.3050	78.65
		0.020	0.4841	97.00
Bisamine II	DMAA	-	0.3191	97.79
		0.020	0.5136	86.79
		0.030	0.3485	79.46

RESULTS AND DISCUSSION

Influence of the Acceptor of Hydrogen Chloride

The reactions which proceeded according to the experimental part of Ref. 6 were carried out with triethylamine added first to the cooled solution of bisamines and the later addition of terephthalic acid chloride. The results are given in Table 1.

When the reaction was carried out without an acceptor for the evolved hydrogen chloride or in the presence of an acceptor in an amount higher than the stoichiometry, polyamide of lower reduced viscosity was obtained compared with the case when the reaction was carried out with 0.020 mol of an acceptor. However, the viscosity decrease was not large because the DMAA used in the reaction may also act as an acceptor of hydrogen chloride.

Influence of the Addition of Metal Salts

One method of modification of the high molecular weight of polyterephthalamides is based on the increase of the dissolving power of the reaction medium of the amide type by dissolving a metal salt into it. The literature [6, 7] gives several examples of the application of such salts, e.g., LiCl, $ZnCl_2$, $AlCl_3$, $SbCl_3$, $CaCl_2$, and $HgCl_2$ for the synthesis of aromatic polyamides by low-temperature polycondensation in solution.

In our work, salts not mentioned in literature were used; $SnCl_2$ and $SnCl_4$. The results are shown in Table 2.

The experiments showed that stannous chloride has a greater influence on the value of the reduced viscosity of polyamides obtained with Bisamine I and Bisamine II than does stannic chloride although

TABLE 2. The Influence of the Addition of Metals Salts

Ordinal number, PA	Amine	Salt	Amount of the salt (g)	Reduced viscosity, t = 20° C DMF	H_2SO_4	Yield (%)
1	Bisamine I	$SnCl_2$	0.6	0.9591	0.9665	98.87
2		$SnCl_2$	0.8	0.3239	0.1295	99.55
3		$SnCl_2$	0.4	0.1332	0.1295	97.62
4		$SnCl_4$	0.6	Insoluble	0.5584	93.25
5		$SnCl_4$	0.8	0.2017	0.2100	92.13
6		$SnCl_4$	0.4	0.3242	0.3281	94.38
7		-	-	0.3723	0.3884	77.50
8	Bisamine II	$SnCl_2$	0.6	0.7409	0.7469	97.79
9		$SnCl_2$	0.8	0.2366	0.2863	97.79
10		$SnCl_2$	0.4	0.1175	0.1420	95.82
11		$SnCl_4$	0.6	Insoluble	0.4831	89.73
12		$SnCl_4$	0.8	0.2021	0.2104	92.14
13		$SnCl_4$	0.4	0.2026	0.2010	91.25
14		-	-	0.4786	0.4804	79.05

0.6 g of stannic chloride increases the viscosity of polyamides in comparison with polyamides obtained without salt, but the increase is not large.

On the other hand, application of 0.6 g (10.36% by weight in the case of Bisamine I and 11.07% by weight in the case of Bisamine II) of stannous chloride causes a radical increase of the reduced viscosity of both polyamides.

Investigation of the Structure and Properties of Aromatic Polyamides

Solubility

The results of the experiments are shown in Table 3. Aromatic polyamides are insoluble in common solvents.

TABLE 3. Solubility

Ordinal number, PA	Solvent	Result[a]	Ordinal number, PA	Solvent	Result[a]
1	Toluene	-	13	Acetone	-
2	Methanol	-	14	Cyclohexenone	+
3	$CHCl_2$-$CHCl_2$	-	15	Styrene	-
4	Dioxane	-	16	CH_2Cl_2	+ -
5	Benzene	-	17	$CHCl_3$	+ -
6	p-Xylene	-	18	Ethylene dichloride	+ -
7	Chlorobenzene	-	19	Nitrobenzene	-
8	HCOOH	-	20	N,N-dimethylformamide	+
9	n-Butyl acetate	-	21	N,N-dimethylacetamide	+
10	Ethyl acetate	-	22	Concentrated H_2SO_4	+
11	CCl_4	-			
12	CH_3COOH anhydrous	-			

[a] + = soluble; - = insoluble; + - = swelling.

TABLE 4

Ordinal number, PA	Method of polycondensation	Medium	Bisamine	Temperature of destruction (°C)	Softening point (°C)
1	Interfacial	Acidic	I	281, darkens	360
2	Interfacial	Basic	I	290, darkens	360
3	In solution	Basic	I	298, darkens	360
4	Interfacial	Acidic	II	302, darkens	360
5	In solution	Acidic	II	339, darkens	360

Softening Point

The softening points of the polyamides obtained were determined in a melting point capillary. The results are given in Table 4.

The values of the softening points are higher than 360° C. Polyamides obtained by polycondensation in solution and with Bisamine II and terephthalic acid chloride have a higher thermoresistance. A somewhat smaller thermoresistance is seen in the case of polyamides obtained from Bisamine I, which can be explained by the detachment of hydrogen chloride during intensive heating.

Reduced Viscosity

The reduced viscosity was determined by means of Ostwald viscometer in N,N-dimethylformamide (DMF) and concentrated H_2SO_4 at 20° C.

Behavior in a Flame

Aromatic polyamides burn in a flame but immediately self-extinguish after being removed from it. It was observed that the polyamides do not melt and undergo destruction during heating on a spatula.

Foil-Forming Properties

It was discovered that when a nonsolvent (water) is poured into a vessel containing a concentrated solution of polyamide, a polyamide film is formed on the side walls. This proves the foil-forming properties of polyamides. The practical utilization of foils is troublesome because of the lack of low-boiling solvents of aromatic polyamides.

IR Investigations

The IR spectra were obtained on UR-60 instrument (Carl Zeiss, Jena) by the KBr method. They are presented in Figs. 1-4. The characteristic absorption peaks of the IR spectra were studied to determine the presence of functional groups [8, 9]. It is possible to find analogous characteristic absorptions bands for definitie frequencies. Absorption at 3420-3310 cm^{-1} corresponds to the stretching oscillations of NH groups of polyamides. The band at 3030 cm^{-1} points to the presence of C–OH of the aromatic ring. A strong absorption at 1660 cm^{-1} indicates C=O group. A 1600-1520 cm^{-1} band corresponds to the stretching oscillations of aromatic rings. The band at 1270-1020 cm^{-1} is characteristic of the deformation vibrations of the aromatic rings substituted at the 1,4 position. Strong absorption at 960 cm^{-1} confirms the presence of $C{=}CCl_2$ groups and their deformation vibrations [10]. The band at 780-620 cm^{-1} corresponds to the valency oscillations of the $C{-}CCl_3$ group. In conclusion, the infrared spectrum analysis shows that the structure of the compounds obtained corresponds to the proposed formulas.

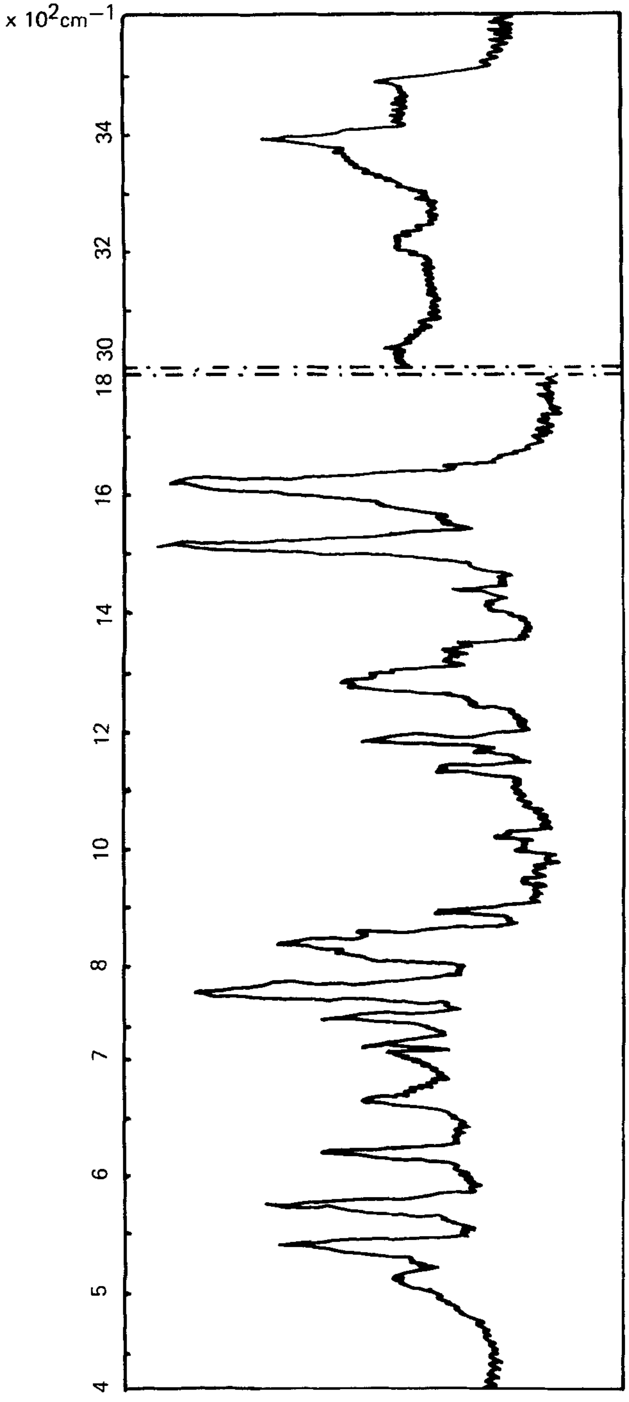


FIG. 1. IR Spectrum of 2,2-bis(p-aminophenyl)-1,1,1-trichloroethane (Bisamine I).

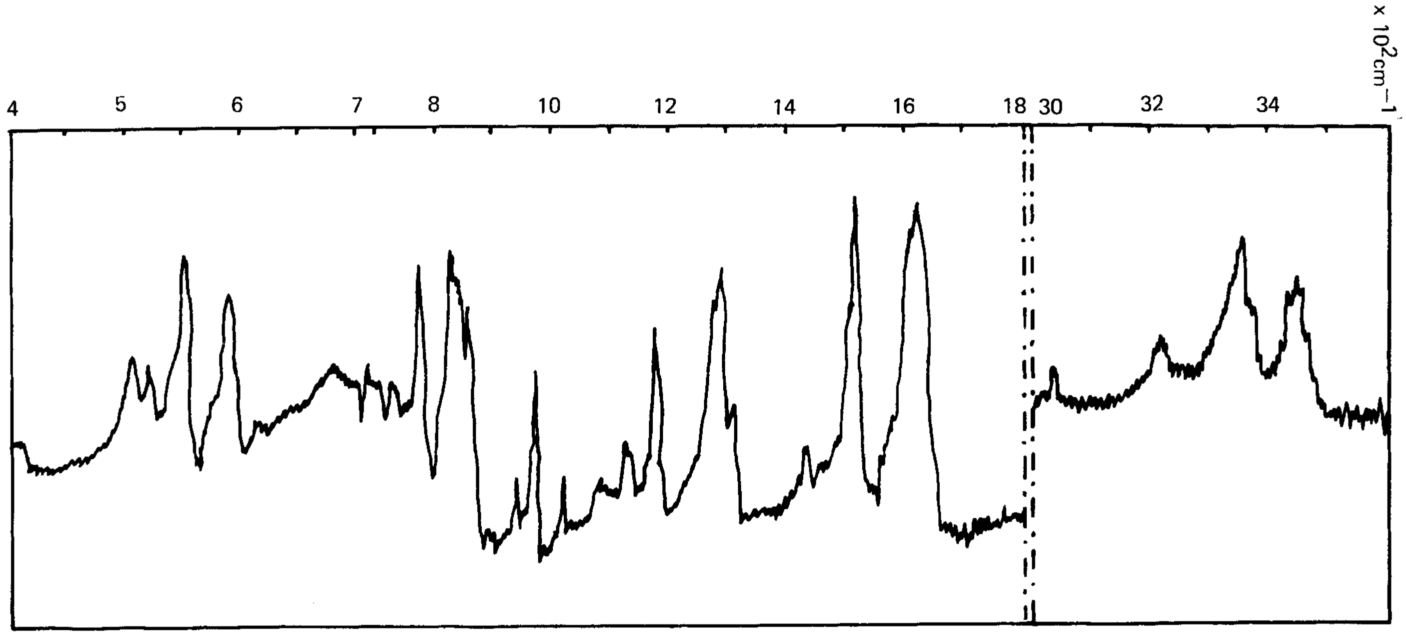


FIG. 2. IR spectrum of 2,2-bis(p-aminophenyl)-1,1-dichloroethylene (Bisamine II).

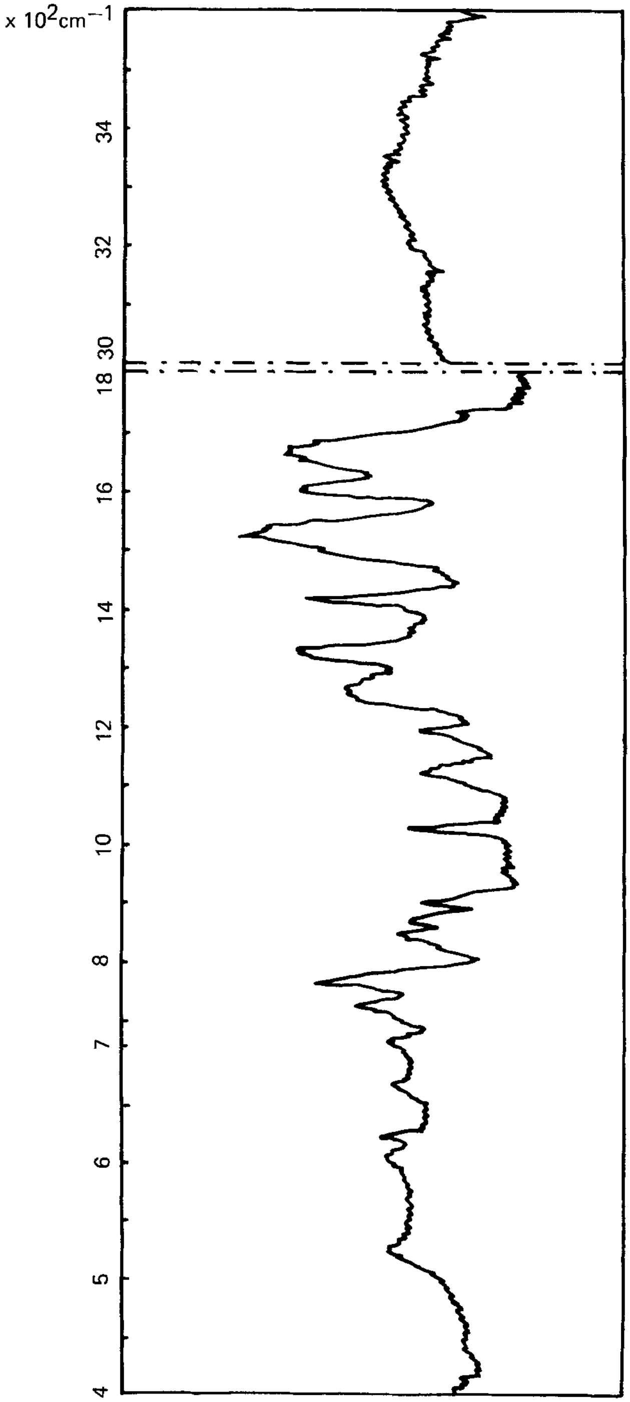


FIG. 3. IR spectrum of polyamide obtained from Bisamine I and terephthalic acid chloride.

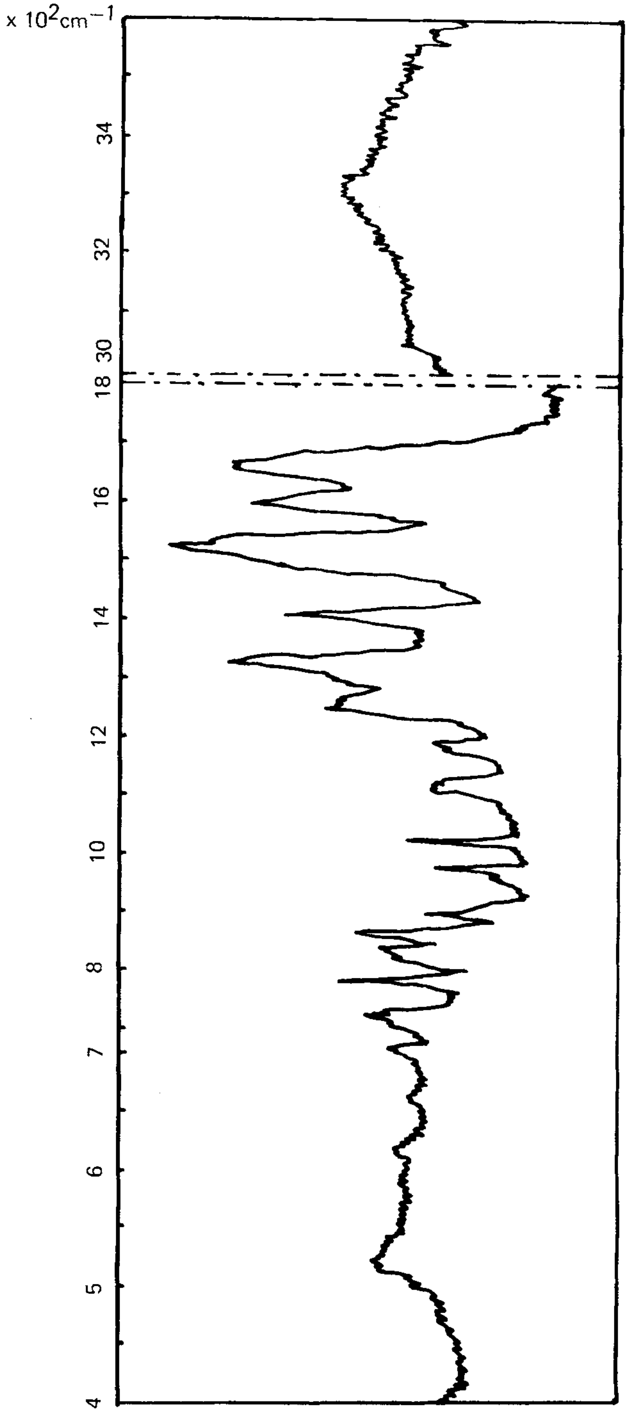
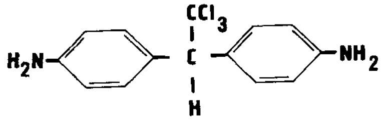
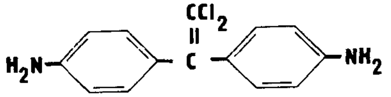


FIG. 4. IR spectrum of polyamide obtained from Bisamine II and terephthalic acid chloride.

The structure of these compounds can be presented as

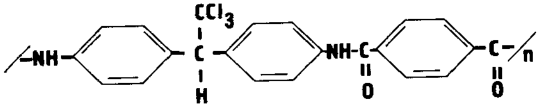


for the 2,2-bis(p-aminophenyl)-1,1,1-trichloroethane, Bisamine I

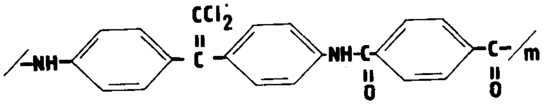


for the 2,2-bis(p-aminophenyl)-1,1-dichloroethylene, Bisamine II

And the corresponding polyamides can be



for the Bisamine I and terephthalic acid chloride



for the Bisamine II and terephthalic acid chloride

CONCLUSIONS

The investigation of the polycondensation of Bisamine I and Bisamine II with terephthalic acid chloride proved that low-temperature polycondensation in solution is the best method of obtaining aromatic polyamides of higher molecular weight. It is especially advantageous to carry out the reaction in the presence of $SnCl_2$ (10-11% by weight) which increases the solubility of N,N-dimethylformamide.

The polyamides thus obtained are characterized by high softening points and very good thermoresistance, higher in the case of a macrocompound based on Bisamine II.

Polyamides of higher molecular weights are obtained with Bisamine II.

The polyamides obtained from Bisamines I and II are sparingly soluble polymers and have foil-forming properties.

An important feature is their self-extinguishing properties.

Because of their high thermoresistance and chemoresistance, those macrocompounds may be of great practical importance. Investigation concerning their application to fiber production should be carried out.

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