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Polyamides from Aromatic Bisamines·Chloral Derivatives and Terephthaloyl Chloride by Interfacial Polycondensation

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ABSTRACT

Investigations on a new class of polyamides obtained by interfacial polycondensation from amine-chloral derivatives, e.g., 2,2-bis(p-aminophenyl)-1,1,1-trichloromethane or 2,2-bis(p-aminophenyl)-1,1-dichloroethylene and terephthaloyl chloride, have been carried out. It was found that the interfacial process proceeds in the most advantageous way in acidic medium at 0°C using equivalent volume amounts and equimolar concentrations of methylene chloride and water phases in the presence of a stoichiometric quantity of triethylamine as the hydrogen acceptor.

INTRODUCTION

As a result of complex research work concerned with the utilization of chloral's derivatives in the synthesis of polymers [1-8], the proposition of using them to synthesize polyamides was taken into consideration. Generally, aromatic polyamides are solid substances which in many cases have higher melting temperatures than that of destruction. The presence of aromatic systems in polyamide molecules causes their rigidity, hardness, thermoresistance, and thermostability. In our case they are also noninflammable [9].

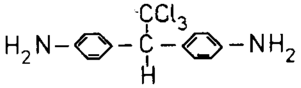

FIG. 1. Bisamine I.

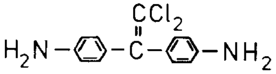

FIG. 2. Bisamine II.

EXPERIMENTAL

The polyamides were synthesized on the basis of the following diamides.

2,2-Bis(p-aminophenyl)-1,1,1-trichloroethane (Bisamine I). The formula is shown as Fig. 1.

2,2-Bis(p-aminophenyl)-1,1-dichloroethylene (Bisamine II). The formula is shown as Fig. 2.

And terephthalic acid chloride.

Preparation of These Substances

Bisamine I (mp 166-167° C) was obtained according to the scheme [10, 11] shown in Fig. 3. The reaction consists of the following stages: condensation between chloral and benzene in acidic medium, nitration, catalytic reduction.

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 nitro compound formed according to the scheme shown in Fig. 4. Bisamine II can also be obtained by the direct action of KOH on Bisamine I in methanol. The Bisamine II so prepared has the same melting point as that obtained by the reduction of the dinitro compound. Both methods were proposed by Kirkwood and Philips [10, 11].

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

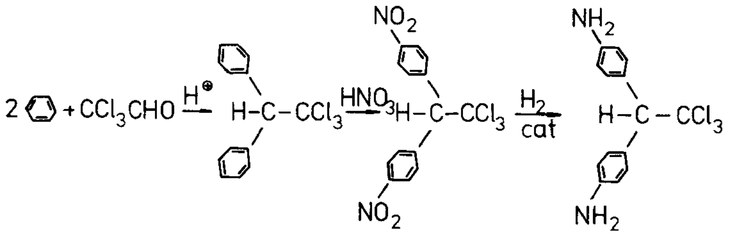

FIGURE 3.

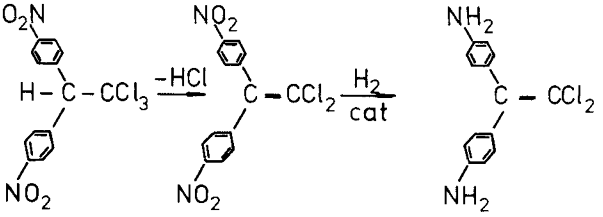

FIGURE 4.

Synthesis of Aromatic Polyamides

Processes of the synthesis of aromatic polyamides based on the polycondensation of Bisamine I and II with terephthalic acid chloride were carried out by interfacial polycondensation. Polycondensation of polyamides on the two-phase boundary may run in one of two ways, depending whether the character of the medium is basic or acidic.

In basic medium the reaction for Bisamine I was carried out analogously to the synthesis of polyarylates [5]. Results were not satisfactory because of the low reduced viscosity (0.091) of the polyamide obtained.

Then several reactions of interfacial polycondensation in acidic medium for Bisamines I and II were executed according to the description in a USSR patent [12], and the influence of different parameters on the yield of the reaction and the reduced viscosity of the polymer were examined.

A solution of 0.011 mol of bisamine in 150 mL of 0.25% HCl was poured into a three-necked flask equipped with a thermometer, a dropper, and a mixer and was cooled down by means of Dry Ice to 0° C. Simultaneously, 0.011 mol of terephthalic acid chloride was dissolved in 225 mL of organic solvent. The solution was cooled to

TABLE 1. Influence of Organic Solvent

Amine	Solvent[a]	Reduced viscosity, t = 20°C, DMF	Yield (%)
Bisamine I	Toluene, μ = 0.37 D	0.1845	31.46
	Methylene chloride, μ = 1.5 D	0.2637	73.03
	Carbon tetrachloride, μ = 0	0.0938	44.08
	Tetrachloroethane, μ = 0	0.2226	40.45
	CH_2Cl_2 + 10 mL DMF	0.3937	35.95
	CH_2Cl_2 + 20 mL DMF	0.3419	33.70
	CH_2Cl_2 + 30 mL DMF	0.3210	16.85

[a] DMF = N,N-dimethylformamide; μ = dipole moment.

0°C and then it was dropped by dropper into the flask, keeping the temperature constant at 0-1°C. The content of the flask was mixed for 4 h, allowing the temperature to increase to room temperature (20°C). The pale yellow precipitate was filtered off on a Büchner funnel; washed with ethanol, water, and again with ethanol, and dried by air to constant weight.

RESULTS AND DISCUSSION

Influence of the Organic Solvent

In our work the following solvents were used for dissolving terephthalic acid chloride: toluene, methylene chloride, carbon tetrachloride, tetrachloroethane, and mixtures of 225 mL CH_2Cl_2 + 10 mL DMF, 225 mL CH_2Cl_2 + 20 mL DMF, and 225 mL CH_2Cl_2 + 30 mL DMF.

The aromatic polyamides are soluble in N,N-dimethylformamide (DMF). A small amount of DMF added to the system allows the maintenance of two phases and at the same time it should theoretically cause an increase of molecular weight as a result of the increase of solubility of the macrocompound. The results of the experiment are shown in Table 1. The highest value of the viscosity of polyamide was

TABLE 2. Influence of the Concentration of the Reacting Substances

Concentration of Bisamine I in the aqueous phase (mol)	Concentration of terephthaloyl chloride in the organic phase (mol)	Reduced viscosity, t = 20° C, DMF	Yield (%)
0.0667	0.049	0.2637	73.03
0.1334	0.098	0.2591	73.32
0.2001	0.147	0.2508	72.20

obtained when 10 mL of DMF was added to 225 mL of methylene chloride, which is in agreement with theoretical expectation. Unfortunately, this reaction runs with a small yield. When a higher amount of DMF is added to the system, the reduced viscosity of the polyamide and the yield of the reaction decreases. This may be caused by the fact that DMF dissolves not only polyamides in the organic phase, but also, even more, in the aqueous phase which disturbs the interfacial mechanism of the polyreaction. DMF present in the system is not only a solvent for the polymer but also acts as an acceptor of hydrogen chloride, and that is the reason why the viscosity of the polyamide decreases.

When methylene chloride, the solvent with the greatest dipole moment of all the solvents listed above, was used alone, the polyamide was obtained with the highest yield. It appears from this fact that a polyamide of high molecular weight can be obtained in good yield when a polar solvent, immiscible with water, is used. This conclusion is confirmed by the high values of reduced viscosity obtained when DMF, which is a strongly polar solvent, was present in the system.

For further investigation, methylene chloride was used as the solvent for terephthalic acid chloride.

Influence of the Concentration of the Reacting Substances

The reactions were always carried out with the same quantities of the solvents, i.e., 225 mL of CH_2Cl_2 and 150 mL of 0.25% HCl, and the quantities of the reacting substances were reduced to maintain a constant ratio between them. The results are shown in Table 2.

The experiment proved that the viscosity of the polyamides and the efficiency of the reaction are not dependent on the concentration of the reacting substances in the system, within the errors of measurements.

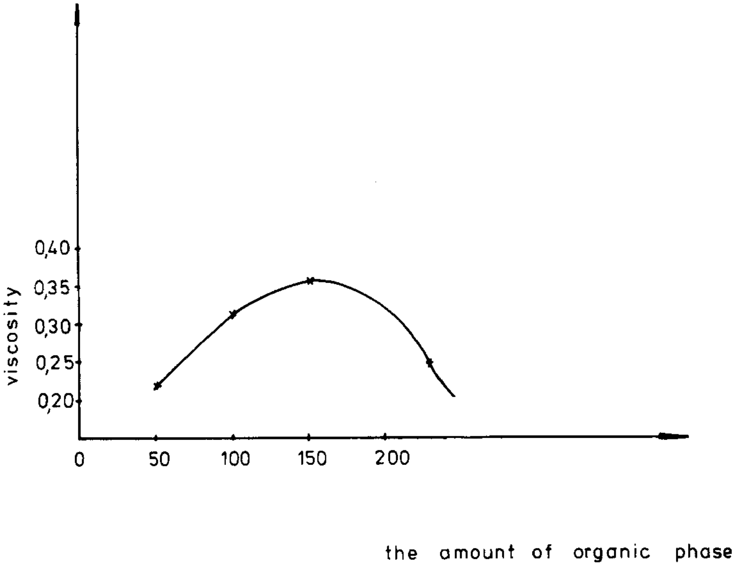

FIGURE 5.

Influence of the Temperature

An increase of temperature, which causes an increase in the reaction rate, often leads to a rise in the molecular weight of the polymer. However, in our case an increase of the temperature to 18°C caused acceleration of the hydrolysis of terephthalic acid chloride and decreased the reduced viscosity of the polyamide. For the polyamide obtained at 18°C with Bisamine I, the reduced viscosity was 0.0850 and the yield of the reaction was 31%.

Influence of the Amount of Organic Phase

The synthesis of polyamides was carried out while maintaining the amount of the aqueous phase constant and changing the amount of the organic phase. The following quantities of methylene chloride were used: 225, 150, 100, and 50 mL. The results of the experiments are shown in Fig. 5 and Table 3.

The investigation of the influence of the amount of organic phase was carried out for polyamides obtained with Bisamine I.

The greatest value of reduced viscosity for polymer was obtained when the volumes of both phases were the same. Such reaction runs also gave the greatest yield. It is evident that in the case of interfacial

TABLE 3. Influence of the Amount of Organic Phase

Amine	Amount of aqueous phase (mL)	Amount of organic phase (mL)	Reduced viscosity, t = 20° C, DMF	Yield (%)
Bisamine I	150	225	0.2637	73.03
	150	150	0.3723	77.50
	150	100	0.3212	75.50
	150	50	0.2210	47.00
Bisamine II	150	150	0.3786	79.05

polycondensation of aromatic polyamides it is fundamental not only to use equimolar quantities of the reacting substances but also the same molar concentrations. Polyamide with Bisamine II was synthesized according to the above conclusion. The value of the reduced viscosity for such a polymer is higher and the yield of the reaction is greater than for the polyamide obtained from Bisamine I.

Influence of the Acceptor of Hydrogen Chloride

The results of the experiments shown in Table 4 illustrate that the addition of triethylamine, which acts as an acceptor of hydrogen chloride, considerably increases the molecular weight of the polyamide so that its viscosity increases. The best results were obtained when equimolar quantities of triethylamine, compared with evolved HCl, were used. When the amount of triethylamine added to the system was smaller, a part of the HCl remained in the system and gave protons to the amine group of the bisamine. It causes the formation of bisamine hydrochloride which is inactive. The excess of acceptor in comparison to evolved hydrogen chloride also leads to a decrease of the viscosity of the polyamide. As the polycondensation runs, the concentration of bisamine decreases. At a certain moment it will be so small that the triethylamine present in the system, may interact with bisamine and inhibit the growth of the polyamide chain.

The yield of the reaction varies in the same direction as the viscosity of the polyamide.

CONCLUSIONS

From data given in the tables and in the diagrams, it can be concluded that interfacial polycondensation in acidic medium proceeds in

TABLE 4. Influence of the Acceptor of Hydrogen Chloride

Amine	Amount of triethylamine (mol)	Reduced viscosity, t = 20°C DMF	Reduced viscosity, t = 20°C H_2SO_4	Yield (%)
Bisamine I	0.011	0.6289	0.6307	83.08
	0.022	0.8313	0.8384	90.21
	0.044	0.7021	0.7082	81.65
	0.000	0.3723	0.3884	77.50
Bisamine II	0.011	0.2378	0.5130	81.87
	0.022	0.6180	0.6092	86.82
	0.044	0.2390	0.2179	80.38
	0.000	0.3786	0.3804	79.05

the most advantageous way when methylene chloride is used as the organic phase with the same volume as the aqueous phase; at 0°C; with an equimolar concentration of the reacting substances; and in the presence of a stoichiometric quantity of an acceptor of hydrogen chloride (i.e., triethylamine in our case).

This polycondensation reaction was then studied by another method on the basis of these results. Solution polycondensation and its experimental results are the subject of another article [13].

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