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SOME PROPERTIES OF AROMATIC AND ARYL-ALIPHATIC POLYAMIDES PREPARED BY INTERFACIAL POLYCONDENSATION-V*

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POLYAMIDES based on aromatic primary diamines and terephthalic acid have a high heat resistance, their melting points are very high and in a number of cases are above the temperature of degradation. This latter property complicates processing and is a hindrance to their technical application.

It is known that N-alkylation, by lowering the packing density and the strength of the intermolecular bonds, brings about a substantial change in the properties of the polymers, in particular raising the solubility and lowering the melting point. However the lower reactivity of aromatic secondary diamines and their high oxidizability does not allow polyterephthalamides to be made from these by polycondensation in the melt and the polymer cannot be made by substitution of the acid by an ester. In one of the first communications [1] we described some polymers of this type, prepared by interfacial polycondensation of terephthalic chloride and N-alkylated diamines of the diphenylmethane and ditolylmethane series. The interesting properties of this type of polymer, combining a high melting point (up to 300°) with good solubility in a number of readily available solvents, and also the impossibility of preparing them by other methods, led us to make a more detailed study of some of the special features and kinetics of this reaction when secondary aromatic diamines are used.

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In this communication an account is given of the results of a study of the size of the substituent on the nitrogen atom, the concentration of the reactants, the pH of the medium and the nature of the organic solvent on the properties of polyterephthalmides of the diphenylmethane series. Some properties of the polymers and peculiarities of the reaction when the corresponding primary diamine, 4,4'-diaminodiphenylmethane, is used are also given for comparison.

EXPERIMENTAL

The N-alkylated diaminodiphenylmethanes (N,N'-dimethyl-N,N'-diethyl-,N,N'-dipropyl and N,N'-dibutyl) were synthesized by condensation of the corresponding alkyl anilines with formaldehyde in an acidic medium [2, 3]. For final purification the ethyl and propyl derivatives were redistilled twice *in vacuo* and the methyl and butyl derivatives after redistillation *in vacuo* were recrystallized from cyclohexane. The constants of the diamines are given in the Table.

Diamine	М .р., °С	B.p., °C	n_D^{20}
4,4'-diaminodiphenylmethane	89-90	216 - 222/2 - 3	
N,N'-dimethyl-4,4'-diaminodiphenylmethane	55	213 - 216/1	
N.N'-diethyl-4,4'-diaminodiphenylmethane		225 - 228/1	1.6073
N,N'-dipropyl-4,4'-diaminodiphenylmethane	_	253 - 257/3 - 4	1.5891
N,N'-dibutyl-4,4'-diaminodiphenylmethane	44	255 - 256/2	

CONSTANTS OF SYNTHESIZED DIAMINES

Terephtalyl chloride was purified by two recrystallizations from heptane: m.p. 81°.

The polycondensation reaction was carried out at 20° by the method described previously [1], with a stirrer speed of ~4000 rev/min and a reaction time of 20 minutes. After removal of the solvent by steam distillation the polymer was filtered off, washed with hot aqueous methanol (30%) and water, and then dried in a vacuum desiccator at room temperature. The yield of polymer and the specific viscosity in solution in ethylene chlorohydrin (5 g per 1000 ml) were determined. The specific viscosity of polymers based on the primary diamine was determined with a solution in concentrated sulphuric acid (at the same concentration). However the specific viscosities of the N-substituted polyamides in ethylene chlorohydrin and sulphuric acid were very close, enabling comparison to be made with sufficient accuracy.

RESULTS AND DISCUSSION

The study of the effect of the concentration of the reactants on the yield and viscosity of the polymers shows that unlike the unsubstituted 4,4'-diaminodiphenylmethane (DPhM), which gives a polymer of high viscosity only when the concentration of reagents is very low, with the N-alkylated diaminodiphenylmethanes the viscosity of the polymer increases with increasing concentration of the reagents up to 0.4-0.5 mole/l. without giving a sharp maximum (Fig. 1, curves 3. 4 and 5), The curve for N,N'-dimethyl-DPhM is somewhat different, it has a sharp maximum at a concentration of 0.1 mole/l. (Fig. 1, curve 2). It should be noted that because of the formation of a thick, sticky gel that enveloped

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the stirrer immediately and prevented normal stirring it was difficult to carry out the reaction with N,N'-dimethyl-DPhM in benzene, and although this led to the formation of a polymer of higher molecular weight than that obtained in other solvents ($\eta_{sp}=0.45-0.5$ in the concentration region of 0.2-0.25 mole/l.), because of the irreproducibility of the conditions in this solvent we were unable to determine the dependence of viscosity on concentration. Consequently the curves for N,N'-dimethyl-DPhM, free base and hydrochloride (Fig. 1, curves 2



FIG. 1. Dependence of the specific viscosity of N-alkylated polyterephthalamides on the concentration of the reactants taken in equimolar ratios: 1-from 4,4'-diaminodiphenylmethane, organic phase benzene; 2-from N,N'-dimethyl-4,4'-diaminodiphenylmethane, organic phase CCl₄; 3-from N,N'-diethyl-4,4'-diaminodiphenylmethane, organic phase benzene; 4-from N,N'-dipropyl-4,4'-diaminodiphenylmethane, organic phase benzene; 5from N,N'-dibutyl, 4,4'-diaminodiphenylmethane, organic phase benzene; 5from the hydrochloride of N,N'-dimethyl-4,4'-diaminodiphenylmethane, organic phase CCl₄.

and 6) were plotted for solutions in carbon tetrachloride, which undoubtedly has some effect, though it does not alter the general nature of the relationship.

On the whole, with the introduction of an alkyl substituent and increase in the size of the latter there is a gradual shift in the region of optimal concentrations toward the higher concentration side, and simultaneously with an increase in size of the substituent the absolute value of the viscosity decreases. This is evidently associated with the increase in steric hindrance and also with the decrease in reactivity of the diamines as the size of the alkyl substituent increases. Substitution of the free base by the hydrochloride does not alter the shape of the curve or the position of the maximum, but leads to the production of polymers of lower viscosity as we observed previously in a study of the polycondensation of unsubstituted aromatic diamines.

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Taking into account the great importance of the nature of the solvent we studied the dependence of the specific viscosity on the reagent concentration in systems where the organic solvent dissolved the polymer to different extents. This showed that the greatest yield of polymer, of highest viscosity, was obtained in solvents that dissolved the polymer (benzene, carbon tetrachloride). In systems where the solvent dissolves only the starting materials (heptane, cyclohexane) the viscosity of the polymer falls, though the general shape of the curve and the region of optimal reagent concentrations varied little. It should be noted however that the latter fact could also be the result of the different solubility of the reagents, particularly of the diamine, in the organic phase.

The statement in the literature that there is an optimal solvent-nonsolvent ratio for interfacial polycondensation [4] prompted us to verify this idea for the case of the N-alkylated polyterephthalamides, which are of some interest in this respect because they have unusually good solubility for polyamides. Taking as an example the reaction of N,N'-dimethyl-DPhM with terephthalyl chloride we studied the effect of the composition of a two-component organic phase on the properties of the polymer formed. The solvent systems chosen were benzene-CCl₄, benzene-cyclohexane and benzene-heptane. The concentration of the reagents was the same in all cases (0.2 mole/l.).

The results, presented graphically in Figure 2 do not support the above statement. In all cases there was a fall in viscosity and yield over the entire range of



FIG. 2. Dependence of the yield and viscosity (lower curves) of polydiphenylmethaneterephalyl-N,N'-dimethylamide on the composition of a twocomponent organic phase. Concentration of reactants 0.2 mole/l., component A-benzene, component $B: 1-\text{CCl}_4: 2-\text{cyclohexane}; 3-n$ -heptane.

ratios of the pairs of solvents studied. In the interval from 70:30 to 30:70 the change in the proportion of the second component had very little effect, but in the extreme regions, particularly for small additions of the second component to the benzene, the yield, and to a greater extent the viscosity, fall sharply. Evidently in this case it is not the solvent power of these solvents and mixtures that is of

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decisive importance, but other physico-chemical factors. However we are not at present able to provide an explanation of this phenomenon.

We have previously pointed out the great importance of the pH of the medium on the viscosity of polyamides based on aromatic diamines and sebacyl chloride. A study of the effect of additions of alkalis and acids on the interfacial polycondensation of DPhM and its N-alkylated derivatives with terephthalyl chloride showed that in this case the optimal quantity of alkali is somewhat lower than when sebacyl chloride is used [5].

It is seen from Figure 3 that for unsubstituted DPhM this quantity is approximately half an equivalent and for its N-alkylated derivatives the quantity varies



FIG. 3. Variation of the viscosity (a) and yield (b) of N-alkylated polyterephthalamides with the addition of alkali and acid. Concentration of reactants 0.2 mole/l., organic phase benzene. Numbers on curves as in Fig. 1.

between 0.5 and 1.5 equivalents the optimal quantities giving a fairly sharp maximum (except N,N'-dipropyl-DPhM, which gives a rather smoothed out curve). This is obviously explained by the lower rate of hydrolysis of terephthalyl chloride in comparison with sebacyl chloride, and hence the need of a smaller quantity of alkali in the inorganic zone to combine with the hydrolysis products that retard the polycondensation reaction. In any case there is no doubt that in addition to the basicity of the diamine the nature of the acid chloride, especially its rate of hydrolysis, has a marked effect on the optimal pH value (i.e. on the quantity of added alkali or acid).

It is interesting to note that the shift in the optimal pH of the medium toward the acid side with increase in the size of the substituent on the nitrogen, which occurs for the reaction of N,N'-dialkyl substituted diamines of the ditolylmethane series with fumaric acid chloride [6], was not observed in this case.

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CONCLUSIONS

A study has been made of the effect of reactant concentration on the interfacial polycondensation of 4,4'-diaminodiphenylmethane and its N,N'-dialkyl derivatives (dimethyl, diethyl, dipropyl and dibutyl) with terephthalyl chloride. It is shown that the optimal concentrations increase with increasing size of the substituent and the maximal viscosity values fall. It was found that in the reaction of secondary aromatic diamines with terephthalyl chloride the optimal quantities of HCl acceptor are from 0.5 to 1.5 equivalents. It is shown that polymers of highest viscosity are obtained when the organic phase is a solvent capable of dissolving the polymer formed (benzene, CCl_4). In this case the use of a solvent-nonsolvent mixture does not bring about an increase in the molecular weight of the polymers.

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SYNTHESIS OF PHOSPHORUS-CONTAINING POLYESTERS BY POLYTRANSESTERIFICATION*

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UP TO the present time phosphorus-containing polyesters have been prepared mainly by the reaction of phosphinic acid chlorides with various glycols and dihydric phenols [1, 2]. Polyesters have also been prepared by the polymerization of cyclic phosphinic [3] and phosphoric [4] esters. In a number of cases it was shown that during the reaction a definite equilibrium is set up between the cyclic esters and the linear polyesters [5].

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