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Synthesis of N-Methylated Polyamides and Copolyamides

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ABSTRACT

N-Methylated polyamides and copolyamides derived from sebacic acid, N,N'-dimethylethylenediamine, and ethylenediamine were synthesized. Both interfacial polycondensation and melt polycondensation were examined, with the interfacial generally giving the higher molecular weights. The choice of organic solvent was important in the copolyamide synthesis with hexane giving random copolyamides and the more polar chloroform yielding copolyamides with a more blocklike structure, comparable to that obtained from the melt. The softening point of the N-methylated polyamide was between 65-75°C.

INTRODUCTION

This paper is concerned with the synthesis of N-methylated polyamides and copolyamides with flexible backbone chains. N-Alkylated polyamides were first synthesized in the 1940's and were reported to be low melting, amorphous polymers with good elastic properties(1-5). This is in contrast to unsubstituted polyamides which are known to be highly crystalline, high

melting materials. This difference is in part due to the fact that the hydrogen bonding found between the chains of the unsubstituted polyamides is not present in N-alkylated polyamides(2,4).

N-Alkylated polyamides have received relatively little attention compared to unsubstituted polyamides because their properties preclude their use in the preparation of strong fibers. The solubility and low melting points of these polymers, coupled with their thermal stabilities, make these polymers ideal candidates for other uses such as plasticizers, binders, or as soft blocks in elastomeric block copolymers(1-16). It has been reported that it is difficult to find a nonsolvent for some N-alkylated polyamides(8). The polyamides are soluble in most organic solvents and can be expected to interact strongly with a wide range of materials.

The majority of the work on N-alkylated polyamides has been done in an attempt to elucidate the effect of hydrogen bonding on polyamides. The two major methods of synthesis used have been polymerization of prepolymer nylon salts in the melt and interfacial polycondensation of diacid chlorides and diamines. Of the two methods, interfacial polycondensation has generally given the higher molecular weights, but gives poorer yields and is synthetically more difficult to work up. Both synthetic routes resulted in soluble polyamides with the expected reduced melting points caused by the reduction of hydrogen bonding.

Most of the previous work involved the synthesis of N-alkylated polyamides containing rigid aromatic rings in the backbone thereby increasing the transition temperatures. If N-alkylated polyamides were synthesized with flexible backbone chains, this would cause a reduction in the glass transition temperature and the melting point of the polymers. We report here the synthesis of the considerably more flexible N-methylated polyamides and copolyamides derived from sebacic acid, N,N'-dimethylethylenediamine, and ethylenediamine. Both melt polycondensation and interfacial polycondensation were examined.

EXPERIMENTAL

The diamines and the acid chloride were distilled under Argon prior to use. Sebacic acid was recrystallized twice from ethanol/water and dried over P_2O_5 . Chloroform was purified by washing with H_2SO_4 and water, drying over $CaCl_2$, and distilling. Hexane was purified by washing with H_2SO_4 , HNO_3 , and water, drying over $CaCl_2$, and distilling. Benzene was purified by washing with H_2SO_4 until clear and then distilling.

The interfacial polycondensation of the methylated polyamide was carried out in a 2-l resin kettle by adding sebacyl chloride (11.95g, 0.050 mole) in 500ml organic solvent to the aqueous phase consisting of N,N'-dimethylethylenediamine (4.41g, 0.050 mole) and sodium hydroxide (4.00g, 0.100 mole) and stirring rapidly for 5 minutes. The resulting polymer was filtered, washed thoroughly with water, and dried under vacuum. The copolyamides were synthesized as above with the exception that the aqueous phase contained both the ethylenediamine and the N,N'-dimethylethylenediamine along with sodium hydroxide.

The melt polycondensation of the methylated polyamide was carried out by first preparing the nylon salt by dissolving an equimolar mixture of sebacic acid and N,N'-dimethylethylenediamine in ethanol and heating at reflux for one hour. The solution was cooled, the salt filtered, washed with cold ethanol, recrystallized twice from ethanol, and dried under vacuum. The salt was transferred to a polymerization tube whose atmosphere was then exchanged with Argon and sealed under vacuum. The polycondensation was then carried out by heating the sealed tube for 3 hours at $210^\circ C$ and then heating an additional 18 hours under vacuum. The copolyamides were prepared as above by first preparing the prepolymer nylon salts, mixing the salts together, and carrying out the polycondensations at $250^\circ C$ for the same time periods.

The model compound studies were conducted exactly like the copolymerizations using 1 mole N,N'-dimethylethylenediamine and 1 mole ethylenediamine to 2 moles decanoyl chloride.

The viscosities were measured in TFA at 30°C in the Ubbelohde Viscometer. The NMRs' of all polymers were carried out in TFA in a Varian EM360A, 60MHz spectrometer. The softening points were recorded as the temperature range from the point of initial flow to complete sample flow on a Reichert, Austria melting point apparatus and DuPont 990 Thermal Analyzer.

RESULTS

All of the homopolymers prepared by interfacial polycondensation had approximately the same softening point. The differences caused by varying the organic solvent can be seen in the viscosities and the yields (Table 1). Hexane and benzene gave polymers with similar viscosities but with different yields due to the increased solubility of the polymer in the benzene as compared to the hexane. Only the precipitated polymer which was filterable with a medium porosity sintered glass funnel was collected with these two solvents. The viscosity and percent yield of the homopolymer from chloroform was quite different from that obtained from the other two solvents. This is due to the complete solubility of the polymer in this solvent at the reaction concentration. This made it necessary to separate the chloroform layer and strip the solvent to collect the polymer.

TABLE 1. Poly(N,N'-dimethylethylene sabacamide)

Polymerization Technique	Solvent System	Percent Yield	Softening Point(°C)	^a [η]
interfacial	CHCl ₃ /H ₂ O	92.5	68-73	.110
interfacial	hexane/H ₂ O	47.3	68-71	.216
interfacial	benzene/H ₂ O	24.3	65-70	.188
melt		89.0	b	.106

^a Measured in trifluoroacetic acid at 30°C.

^b Oil, solidifies slowly on standing.

The result is a larger yield and lower viscosity due to the isolation of the low molecular weight fraction along with the high molecular weight fraction which is primarily collected by filtration in the other two solvents. The melt polycondensation yielded a polymer which was initially a viscous liquid at room temperature, but solidified on standing after several days.

Both melt and interfacial polymerization gave copolyamides with compositions identical to that contained in the monomer feed (Tables 2,3,4). The viscosities of the copolyamides generally

TABLE 2. Melt Polymerization of Methylated and Unmethylated Ethylenediamine With Sebacic Acid

% Methylated Diamine	% Yield	Softening Point (°C)	$[\eta]^a$
0	92.3	275-280	b
25	99.3	245-250	.181
50	79.7	195-210	.153
75	96.0	50-80	.131
100	89.0	c	.106

^a Measured in trifluoroacetic acid at 30 C.

^b Insoluble in trifluoroacetic acid.

^c Oil, solidified losely on standing.

TABLE 3. Interfacial Polymerization of Methylated and Unmethylated Ethylenediamine With Sebacyl Chloride In Hexane/H₂O

% Methylated Diamine	% Yield	Softening Point (°C)	$[\eta]^a$
25	58.0	212-216	.143
50	70.6	130-145	.158
70	71.2	105-110	.316
100	47.3	68-71	.216

^a Measured in trifluoroacetic acid at 30°C.

TABLE 4. Interfacial Polymerization of Methylated and Unmethylated Ethylenediamine with Sebacyl Chloride In $\text{CHCl}_3/\text{H}_2\text{O}$

% Methylated Diamine	% Yield	Softening Point ($^{\circ}\text{C}$)	$[\eta]^a$
25	57.6	250-253	.191
50	45.6	193-198	.219
75	25.0	85-90	.210
100	92.5	68-73	.110

^a Measured in trifluoroacetic acid at 30°C .

decreased as the methylation percent increased in the melt polymerization but increased as the methylation percent increased in the interfacial polymerization. When the percent methylation was 50 percent or less, chloroform gave polymers with larger viscosities than hexane, but when the percent methylation was further increased, hexane gave the polymers with the higher viscosities. Interfacial polycondensation generally resulted in higher molecular weights, but lower yields than the melt polycondensation.

DISCUSSION

It was not surprising to find that the polyamides prepared interfacially had higher viscosities than those prepared via the melt. Interfacial polymerization does not require the monomer purity or exactness of stoichiometry that melt polymerization requires.

The decrease in viscosity with the increase in percent methylation in the melt is probably due to the much greater condensation rate of primary diamines versus secondary diamines(17). With the interfacial systems, the reverse trend seems to indicate that the methylated diamine was reacting faster. To confirm this

reversed trend, a model compound study was undertaken using 2 moles of the monofunctional decanoyl chloride to 1 mole of both N,N'-dimethylethylenediamine and ethylenediamine and running the reaction under conditions identical to that used in the copolymerizations. In both hexane and chloroform, the N,N'-dimethylated diamide was obtained in better than 90% yield, indicating that at least initially, the methylated diamine is reacting faster. This type of reactivity difference of diamines to an acid chloride in interfacial systems has been observed by Ogata, et. al. (18). He credited their differences in partition coefficients into the organic phase, where interfacial polymerizations are known to occur, as the controlling factor. The difference in the partition coefficients of the N,N'-dimethylethylenediamine and the ethylenediamine into the hexane and chloroform is probably quite different and is the likely cause of the methylated diamine reacting faster.

In the plot of melting point versus percent methylation for the copolyamides (Fig. 1), we would expect to find a concave upwards curve if the methylated and nonmethylated units were randomly situated throughout the system. This is what is found in the hexane/water interfacial system suggesting that this system does indeed give a random copolymer, despite the diamine reactivity difference. When chloroform/water is used as the interfacial solvent system, however, a convex upwards curve is found. On going from 0 percent to 50 percent methylation, only an approximately 70°C drop in T_m is realized whereas a nearly 110°C reduction in T_m occurs when the methylation percent is further increased from 50 to 75 percent. The same results are found with the copolyamides synthesized from the melt, indicating that the structures of the respective copolyamides are fairly similar. Saotome and Komoto observed the same convex upwards curves for a different set of alkylated copolyamides and suggested that this could only be explained by a block copolymer structure (8). It appears that both the melt and interfacial polycondensation using chloroform gave block copolyamides.

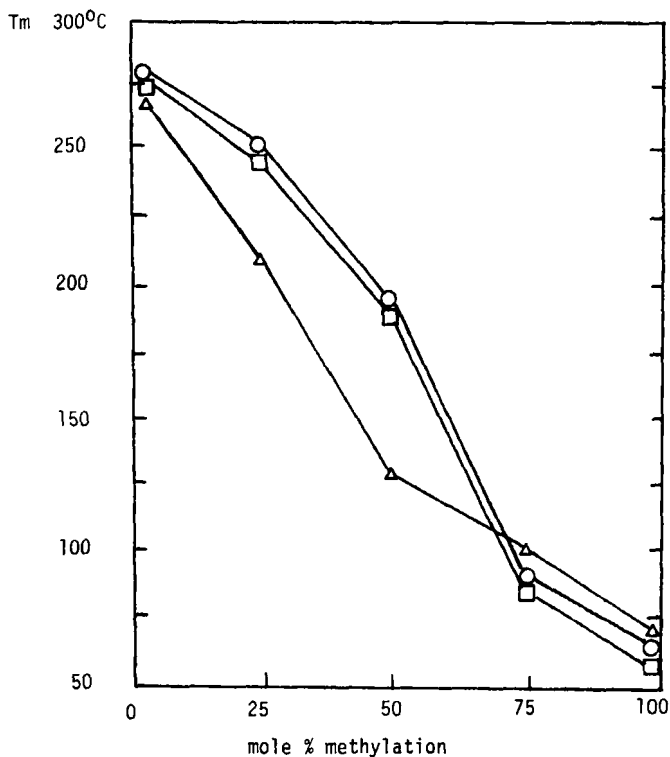


Fig. 1. Effect of methylation on the melting points of copolyamides.
 ○ Interfacial polymerization in $\text{CHCl}_3/\text{H}_2\text{O}$. □ Melt polymerization.
 △ Interfacial polymerization in hexane/ H_2O .

The formation of blocks in the melt can be explained by the higher condensation rate of the primary amine as compared to the secondary amine (17). This rate difference would result in chains of unsubstituted polyamides being produced in the initial stages of the reaction followed by further condensation of the unused secondary amine to form the block structure.

With the chloroform interfacial system, the formation of blocks is probably a result of the reaction of the secondary diamine in the initial stages of the reaction, due to its greater partition coefficient. With the hexane interfacial system, the

reactivity difference between the diamines was not sufficient enough to cause block formation and therefore a random copolyamide resulted.

It is possible, therefore, to synthesize block copolyamides by both the melt and by interfacial polycondensation with the interfacial method in $\text{CHCl}_3/\text{H}_2\text{O}$ giving higher viscosities but lower yields. It is also possible to synthesize random copolyamides by interfacial polymerization in hexane/ H_2O .

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