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The synthesis and characterization of polyethylene succinamide (polyamide 24)

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Summary

The current paper presents the synthesis of a new polyamide, polyethylene succinamide (polyamide 24), via interfacial and solution-solid phase polycondensation. The resulting product was characterized by means of elementary analysis, infrared spectrometry, ^{1}H-nuclear magnetic resonance, intrinsic viscosity and differential carolimetry. The effects of polymerization conditions on molecular weight of the product and the solubility of polyamide 24 in a number of commonly used solvents were also studied.

Introduction

Silk fibroin is a fibrous protein or polypeptide, which has been used as a fabric material for thousands of years and has been widely preferred for its stiffness, smoothness and excellent permeability. Chemically, silk fibroin can be termed as a kind of polyamide 2, a polyamide with highest content of amide groups. Studies on silk fibroin have been focused at spinning mechanism, structure, morphology, simulative synthesis and application as a functional polymer[1]. A conclusion has been reached that the unique properties of silk compared with synthetic fibers are attributed to its crystalline and morphological structure, and more intrinsically, to its chemical structure.

On the other hand, the category of synthetic polyamide has been largely expanded since the first synthetic polyamide, nylon 66, was synthesized by Carothers in the late 1920s[2]. Over the past six decades, Nylon, Perlon, Nomex, Kevlar, etc., have become known worldwide and come to be utilized in our daily life.

To date, the synthetic polyamides with the highest amide content are polyamide 46 and polyamide 4. The lamellar structure and morphology of polyamide 46 and polyamide 4 crystals were investigated by Atkins et al[3,4]. It was concluded, based on electron diffraction and X-ray diffraction data, that the macromolecular chains of these two polyamides folded by a new mechanism, in which amide groups were incorporated in the fold, rather than alkane segments as in other chain-folded nylons. The folds exhibited similarity with the β-bend in proteins[5].

Therefore, it can be predicted that polyamide 24, which is closer to silk fibroin in terms of chemical structure and amide content (see Figure 1), may be a bridge between synthetic nylons and natural silk fibroin, and may lead to better understanding of the performance-structure relationship in silk fibroin.

The current paper presents the synthesis of polyamide 24 through interfacial polycondensation and solution-solid phase polycondensation, and characterization of the resulting polymer.

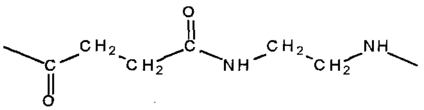

Figure 1 Chemical structure of polyamide 24

Experimental

Synthesis

Interfacial polycondensation A solution of succinyl dichloride (SDC, Shanghai No. 1 Reagent Factory, distilled under reduced pressure before use) in dried chloroform, carbon tetrachloride, benzene and toluene was added dropwise to an aqueous solution of ethylenediamine (EDA, Jincheng Chemicals, Co., distilled before use) containing NaOH, under vigorous stirring. The product is a white powder.

Solution-solid phase polycondensation The succinic acid ethylenediamine salt was prepared and purified to ensure equimolarity. The salt was dissolved in water to reach a concentration of 60%. The solution was charged into an autoclave and purged with nitrogen. At first, the system was kept at 150°C for 2-4 hours and then, the system was heated to 200°C to reach a pressure of 10-15 atms. After 3-5 hours, the temperature was raised to 250°C, while the steam in the system was gradually released. The reaction mixture was then kept under reduced pressure for 1-2 hours. Finally, the system was cooled to room temperature under nitrogen. The product was a yellowish solid.

Characterization

The product resulting from both interfacial and solution-solid phase polycondensation was purified by dissolving it in dichloroacetic acid and then precipitated with methanol. The purified product was characterized by means of elementary analysis, infrared spectroscopy, ^{1}H-nuclear magnetic resonance, intrinsic viscosity in dichloroacetic acid at 25°C and differential scanning calorimeter. The solubility of the product in 14 commonly used solvents was studied.

Results and Discussion

Interfacial polycondensation

Interfacial polycondensation is a heterogeneous polycondensation method, and is essentially diffusion controlled. So it is necessary to carry out the reaction under vigorous stirring, so that the interface is continuously refreshed and the diffusion of diamine from aqueous phase into organic phase is not blocked by the formed polymer. Sodium hydroxide is added to the aqueous phase to neutralize the hydrogen chloride formed in the polycondensation, so as to prevent the formation of amine salt which is inert in the polycondensation under conditions adopted for interfacial method. The organic solution containing succinyl chloride is added dropwise to minimize monomer deactivation caused by hydrolysis.

Effect of organic solvent The selection of organic solvent often affects interfacial polycondensation in two ways: (i) The solvency for the aqueous phase monomer would affect its concentration at the polycondensation loci; (ii) The solvency for the formed polymer or oligomer would affect the reactivity of the species. Therefore, the best solvent should be the one that is a good solvent for both the aqueous phase monomer and the formed polymer, at least the low molecular weight fraction. In the current work, four organic solvents, carbon tetrachloride, benzene, toluene and chloroform, were used. It can was found that only the system with chloroform, which has the greatest polarity, gave a relatively satisfactory result, yet the yield was quite low (< 40%) because of rapid hydrolysis of succinyl chloride.

Effect of monomer concentration Interfacial polycondensation is a hetero-geneous technique, and so the result of the reaction is mainly affected by the monomer concentration at the reaction loci, instead of the overall concentration within the system. The effect of monomer concentration on the intrinsic viscosity of the product in systems using chloroform as the organic solvent was studied, and the results are given in Figure 2. For each of the three sets of data, a maximum can be observed. Normally, in a polycondensation system, the degree of polymerization, X_n, is given by the following equation:[6]

$$X_n = \frac{1+\gamma}{1-\gamma} \tag{1}$$

where γ is the ratio of monomer concentration. Equation (1) is replaced by equation (2) in interfacial polycondensation systems, where β is the ratio of diffusion constant of the two monomers, C_A and C_B are the overall concentrations of monomer A and B, respectively.

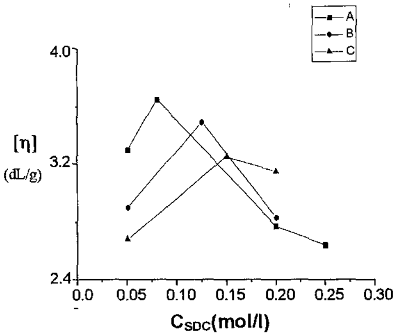

Figure 2 Effect of monomer concentration on [η]. Line A: C_{EDA}=0.10mol/l; Line B: C_{EDA}=0.15mol/l; Line C: C_{EDA}=0.20mol/l

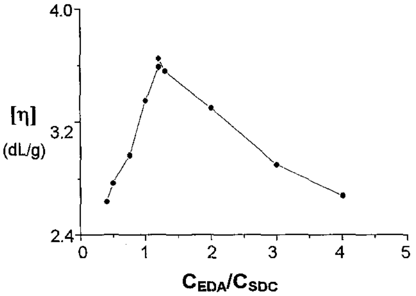

Figure 3 Effect of monomer concentration ratio on [η].

$$X_n = \frac{1+\beta\ C_A/C_B}{1-\beta\ C_A/C_B} \tag{2}$$

Thus, the data in Figure 2 can be replotted in terms of monomer concentration ratio, as shown in Figure 3. The maximum is observed when $C_{SDC}/C_{EDA}=1:1.2$.

Solution-solid phase polycondensation

The monomers used in the preparation of polyamide 24 are succinic acid and ethylenediamine. The boiling point of ethylenediamine is 118°C, so a relatively low reaction temperature , 150°C, was used at the initial stage, to prevent deamination of the monomer. After a moderate degree of polymerization was reached, the reaction temperature was raised to 200°C, while the polycondensation was still taking place in solution under a pressure of 10-15atms for 3-5 hours. Then the system was heated to 250°C and the steam was gradually released, so that the reaction went on by solid phase polycondensation. The equilibrium constant of polycondensation between amine and acid at 250°C is about 300, and so reducing the pressure to 100mmHg would further remove water from the system and ensure a high degree of polymerization.

Characterization

Elementary analysis The contents of carbon, hydrogen, nitrogen and oxygen were measured by elementary analysis, the results being listed in Table 1. The data agreed well with the values calculated according to the proposed structure of polyamide 24.

Infrared spectrum The infrared spectrum of the product resulting from solution-solid phase polycondensation was shown in Figure 4. The peak assignment is listed in Table 2. It can be seen that the IR spectrum of the product is consistent with that proposed for polyamide 24, with characteristic absorptions at 1641cm^{-1} (amide I), 1554cm^{-1} (amide II), 1305cm^{-1} (amide III), and 707cm^{-1} (amide IV). A comparison with some commercial polyamides is also given in Figure 4. The wavenumbers of corresponding peaks are almost the same, but it can be noted that the intensity of the peak at 2943cm^{-1} decreases with the number of methylene groups between each two amide groups along the chemical repeat unit.

Table 1 Result of elementary analysis

element	meas. cont.(%)	calc. cont.(%)
C	50.5	50.7
N	20.0	19.7
H	7.2	7.0
O	22.3	22.5

Table 2 The peak assignment of IR spectrum

wave number (cm^{-1})	assignment
3292	N-H stretching
3089	overtone of N-H in plane bending
2943	C-H stretching
1641	C=O stretching, Amide I
1554	N-H in plane bending, Amide II
1305	C-N stretching, Amide III
707	N-H out of plane bending, Amide IV

^{1}H-Nuclear magnetic resonance The proton magnetic resonance spectrum of the product resulting from solution-solid phase polycondensation is given in Figure

5. The absorption at 2.9966ppm corresponds to the four protons in the two methylene groups between imino groups, and that at 2.2368ppm corresponds to the four protons in the methylene groups between the carbonyl groups. The area ratio of the two peaks is 40.2:40.0., which agrees well with the proposed chemical structure of polyamide 24, and meanwhile, eliminates the possibility of crosslinking, which might occur during the polycondensation at a relatively high temperature. It should be noted that the proton in the imino group is not observed here, because of rapid exchange with the trace proton contained in CF_3COOD.

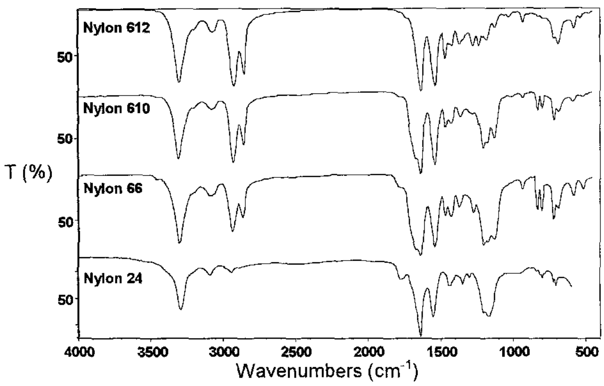

Figure 4 IR comparison of polyamide 24 and some commercial nylons

Intrinsic viscosity Intrinsic viscosity of products from both interfacial and solution-solid phase polycondensation in dichloroacetic acid were measured at 25°C. Molecular weight were estimated using the Mark-Houwink equation of polyamide 66, as given in equation (3):[7]

$$[\eta] = 0.05 + 0.0352M^{0.551} \qquad (3)$$

The intrinsic viscosity of products resulting from solution-solid phase polycondensation ranged from 40 to 60dL/g depending on reaction temperature and reaction time. The molecular weight of the products estimated with equation (3) were found in the range of 5.3×10^3 to 1.1×10^4.

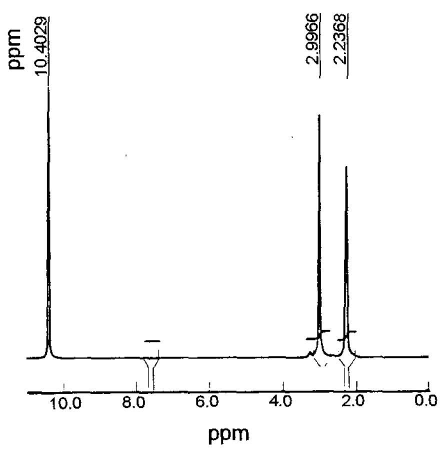

Figure 5 ^{1}H-NMR spectrum of polyamide 24

Table 3 The solubility of PA 46, PA 24 and PA 2

solvent	PA 46	PA 24	PA 2
CH_3OH	-	-	-
C_2H_5OH	-	-	-
$CHCl_3$	-	-	-
Benzene	-	-	-
Toluene	-	-	-
Phenol	-	-	-
m-Cresol	-	-	-
DMSO	-	-	-
DMF	-	-	-
CH_3COOH	-	-	-
HCOOH	+	+*	-
$CHCl_2COOH$	+	+	+
CF_3COOH	+	+	+
9M LiBr Aqueous Solution	-	+*	+

- : insoluble; + : soluble; * partly soluble

Solubility The solubility of polyamide 24 in 14 commonly used solvents were tested by immersing powder of polyamide 24 in the solvent at 25°C for two weeks, and measured the weight of residual, results are shown in Table 3. It can be seen that the new polymer, polyamide 24, is not soluble in most of the common solvents for synthetic polymers, and even not soluble in meta-cresol, a strong solvent which is usually used to dissolve hydrogen-bonding polymers, e. g., commercial polyamides, but dissolves in dichloroacetic acid and trifluoroacetic acid. It is interesting to note that polyamide 24 is only partially soluble in formic acid and aqueous solution of lithium bromide with a concentration of 9M. The former is a good solvent for most of the commercial aliphatic polyamides and the latter is a good solvent for silk fibroin. It was later determined that, in both cases, the soluble part corresponded to the low molecular weight fraction of polyamide 24.

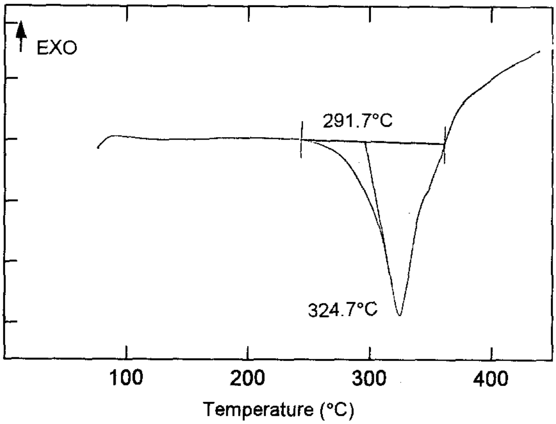

Figure 6 DSC curve of polyamide 24

Thermal behavior The thermal behavior of polyamide 24 as measured by DSC is shown in Figure 6. A vacuum dried sample was measured at a heating rate of 10°C/min. The diagram resembles that of β-form silk fibroin[8]. No transition, but only a endothermic peak at 324.7°C was observed. The endothermic peak was later confirmed to be the degradation of polyamide 24 by TGA analysis. This is similar to β-form silk fibroin which showed a degradation peak at 283°C, and may be an evidence of strong intermolecular hydrogen bonding[8].

Conclusion

Polyamide 24, a new polyamide with a high content of amide groups, was synthesized by both interfacial and solution-solid phase polycondensation. The product was characterized by infrared spectrum, ^{1}H-nuclear magnetic resonance, intrinsic viscosity, solubility and thermal behavior. Polyamide 24 showed some similar properties to both silk fibroin and commercial polyamides in respect to infrared absorption, solubility and thermal behavior. The relationship of these similarities to the crystalline structure and morphology of polyamide 24 will be further investigated in future studies.

Acknowledgement

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