

Copolyamides Derived from Brassylic Acid

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Synopsis

Polyamides were prepared from C_6 to C_{12} diamines with brassylic acid, a linear C_{13} dicarboxylic acid, derived from Crambe seed oil. One distinct characteristic of these polymers is their low moisture adsorption as compared to nylon 66 and nylon 6. To modify the properties of these nylons, multi-component copolyamides were prepared from hexamethylene diamine and mixtures of brassylic acid with adipic, terephthalic, or isophthalic acids. It was found that the melting points of the copolyamides were changed by the choice and the levels of the diacids used. The melting point-composition curves all show a eutectic minimum. The glass transition temperature of nylon 6,13 is also changed by the incorporation of other diacids. Water adsorption of nylon 6,13 increases with increased substitution of brassylic acid by other diacids in the order of adipic > isophthalic \geq terephthalic. Mechanical properties of some copolyamides are in the same range as the commercial nylon 11 and nylon 12. The low moisture absorption, reduced fabrication temperature, and the wide range of properties obtainable through copolymerization make copolyamides derived from brassylic acid potentially suitable as specialty tubing, powder coatings, and molded machine parts. They will be commercially viable when brassylic acid becomes available on a large scale and is competitively priced.

INTRODUCTION

Recently, a family of new polyamides with low water absorption was developed by Wolff et al.^{1,2} at USDA, Northern Regional Research Laboratory, Peoria, Illinois. These polyamides, nylons 13, 13,13, and 6,13, are all derived from the plant *Crambe abyssinica*, a new oilseed crop first planted commercially in 1965. The changing economics of petroleum has presented an opportunity to explore naturally renewable materials as sources of industrial plastics.

Crambe seed is rich in oil. The seed remaining after hull removal contains about 45% oil and 30% protein.³ Crambe seed oil, like other vegetable oils, is mainly a triester of glycerol with long-chain fatty acids. However, 55% to 60% of the acids in the Crambe oil is erucic acid, a C_{22} straight-chain monosaturated acid. The only other source for this C_{22} straight-chain acid, to a lesser extent, is rapeseed oil. Ozonolysis¹ of the erucic acid provides brassylic acid, a linear C_{13} dicarboxylic acid and pelargonic acid. Even though brassylic acid is not now in volume production, it has potential as a raw material for polyamides,^{1,2} lubricants,^{4,5} or plasticizers.^{6,7}

This paper describes some homo- and copolyamides derived from brassylic acid and their physical properties.

EXPERIMENTAL

Chemicals. Brassylic acid was supplied by USDA, Peoria, Illinois. The diacid, 95% pure, was recrystallized from toluene, mp 112°C. All other chemicals were obtained commercially.

Preparation of Polymers. The method described by Coffman and co-workers⁸ was used. A neutral nylon salt was prepared from a diamine and a diacid. The polyamide was made by heating the salt, first under nitrogen atmosphere and then under reduced pressure, to a high degree of polymerization. To prepare copolyamides, two salts were weighed separately to give the correct mole ratio and then polymerized as above. The melting points and elemental analysis of the nylon salts prepared in this work are listed in Table I.

Characterization of Polymers. Solution viscosities were measured in 0.5% *m*-cresol solution at 25°C. Melting points were measured by observing polymer particles between cross polarizers on a hot-stage microscope (Thomas Model 40). The melting point was taken as the temperature at which the last trace of birefringent crystallinity disappeared. Glass transition temperatures were measured with a Perkin-Elmer DSC-2 at a heating rate of 20°C/min. The midpoint in the baseline shift was taken as T_g .

Water adsorptions were determined by the method described by Beaman and Cramer.⁹ Films were melt pressed on a Carver laboratory press. Water absorption was determined on films 6–7 in.² in area and 3–6 mils thick. The films were first dried to constant weight in vacuo and then immersed in water for 24 hr at room temperature. The films were then weighed immediately after all surface water was removed.

Mechanical Properties. The polymers were compression molded as $6 \times 6 \times \frac{1}{6}$ in. sheets at a temperature (205°C) near their melting points. These were then cut to give test specimens for property measurements. ASTM procedures were used for measuring tensile strength and elongation (D-882), flexural modulus (D-790), tensile impact (D-1822-61T), and heat distortion temperature under 264 psi (D-468).

RESULTS AND DISCUSSION

Table II lists physical properties of homopolyamides obtained from brassylic acid and a series of aliphatic diamines. The diamines used were hexamethylene, octamethylene, decamethylene, and dodecamethylene diamines. The melting points and glass transition temperatures of the polyamides decreased with increase in the number of carbon atoms in the diamine. All the polyamides of brassylic acid had very low moisture absorption, in the range of 1.0% to 1.6%. The values are much lower than the 6% moisture absorption for nylon 66.

TABLE I
Melting Points and Analyses of Nylon Salts

Nylon Salts ^a	mp, °C	Empirical formula	C, %		H, %		N, %	
			Calcd	Found	Calcd	Found	Calcd	Found
6,6	193	C ₁₂ H ₂₆ O ₄ N ₂	54.9	54.7	9.99	9.82	10.7	10.7
6,T	275	C ₁₄ H ₁₂ O ₄ N ₂	59.6	59.2	7.80	8.10	9.92	9.83
6,ip	212	C ₁₄ H ₁₂ O ₄ N ₂	59.6	59.0	7.80	7.63	9.92	9.65
6,13	172	C ₁₉ H ₄₀ O ₄ N ₂	63.3	63.2	11.1	11.2	7.78	7.78
8,13	147	C ₂₁ H ₄₄ O ₄ N ₂	64.8	64.9	11.3	11.8	7.20	7.26
10,13	154	C ₂₃ H ₄₈ O ₄ N ₂	66.3	66.6	11.5	11.5	6.72	6.28
12,13	162	C ₂₅ H ₅₂ O ₄ N ₂	67.5	67.5	11.7	11.5	6.30	5.83

^a The nylon salts are designated by the following code: the first number shows the number of carbon atoms in the diamine, the second shows the number of carbon atoms in the diacids; terephthalic acid is denoted by T, and isophthalic acid, by ip.

TABLE II
Physical Properties of Nylons of Brassylic Acid

Nylons	η_{inh} (0.5% in <i>m</i> -cresol)	mp, °C	T_g , °C	Water absorbed, %
13,13 ^a	0.82	175	41	0.87
12,13	1.00	175	42	1.01
10,13	0.52	176	45	1.18
8,13	0.52	192	46	1.36
6,13	0.84	208	51	1.61
6,6	1.20	260	54	5.76

^a From USDA.

To modify the properties of the fatty nylons, multicomponent copolyamides were prepared from hexamethylenediamine and mixtures of brassylic acid with adipic, terephthalic, or isophthalic acid. The melting point curves of the copolyamides show typical eutectic composition (Fig. 1). The replacement of brassylic acid in nylon 6,13 by the other diacids decreased the melting point of the copolyamide at first. After passing through the eutectic minimum, increased substitution raised the melting point. Incorporation of isophthalic or adipic

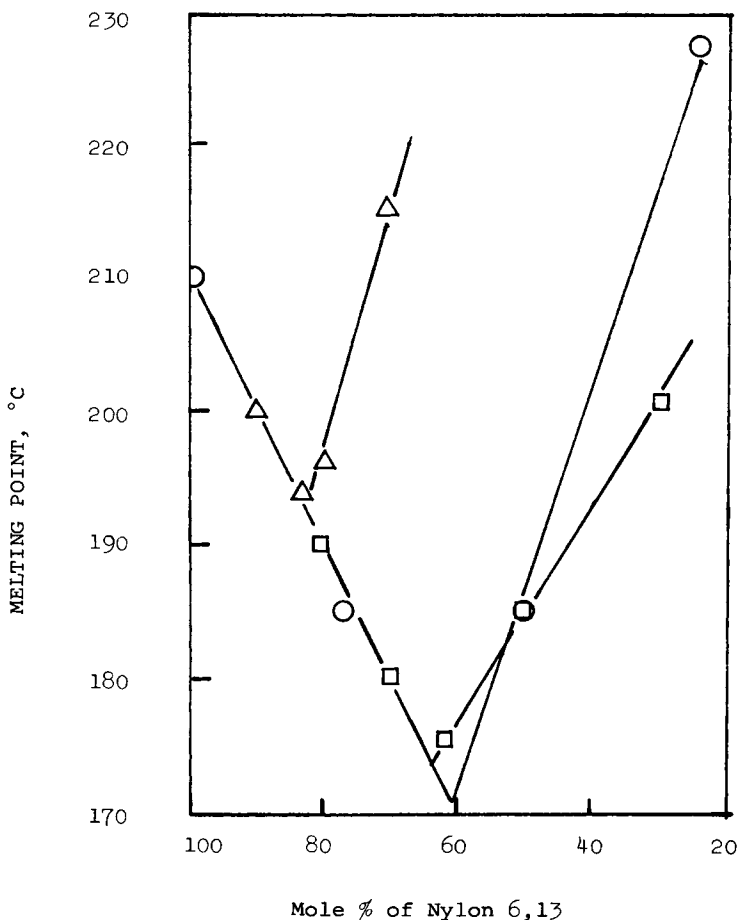


Fig. 1. Melting point vs composition of copolyamides nylons 6,13/6,6 (O), 6,13/6,ip (□), 6,13/6; (Δ).

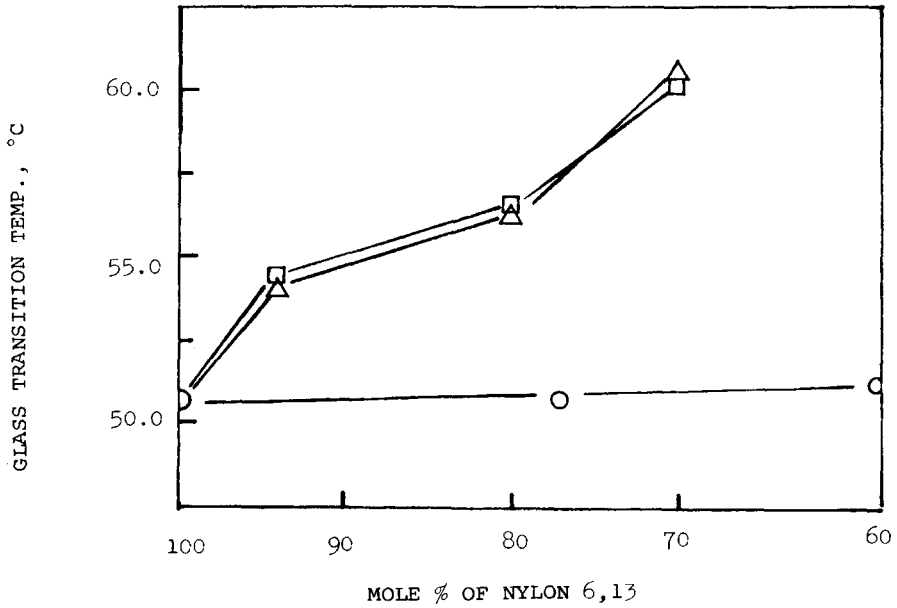


Fig. 2. Glass transition temperature vs composition of copolyamides nylons 6,13/6,6 (O), 6,13/6,ip (□) 6,13/6,T (Δ).

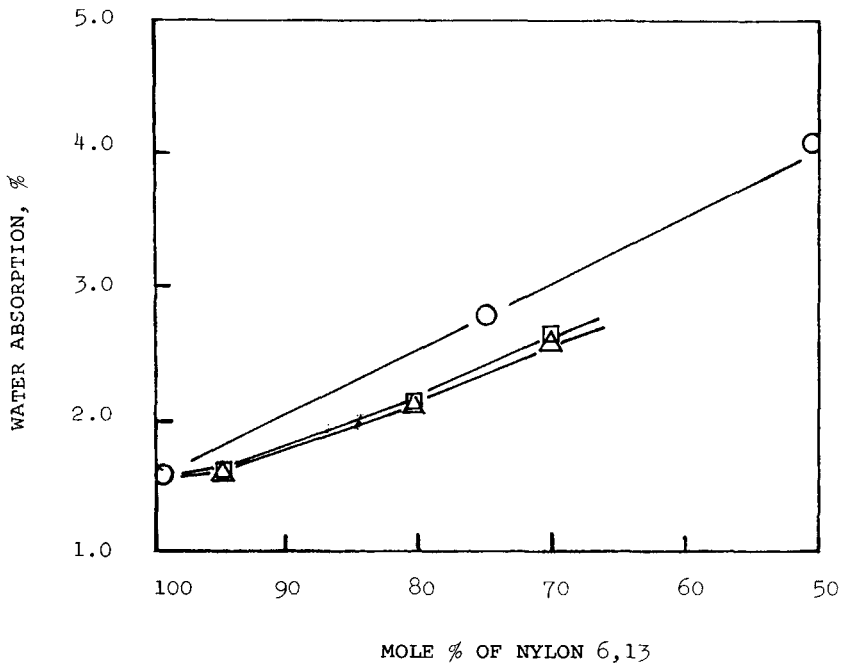


Fig. 3. Water absorption vs. composition of copolyamides nylons 6,13/6,6 (O), 6,13/6,ip (□) 6,13/6,T (Δ).

acid is more effective in lowering of the melting points than terephthalic acid. The minimum melting point of about 170°C occurs at 60–65 mole-% brassylic acid in both isophthalic and adipic acid systems. By contrast, the terephthalic acid system has a minimum melting point of about 195°C at 85 mole-% brassylic

TABLE III
Properties of Selected Copolyamides

Properties	Nylon 6,13/6, ip/6,T (80/8/12 by mole)	Nylon 6,13/6,6 (77/23 by mole)	Nylon 11 ^a	Nylon 12 ^b
Melting points, °C	185	184	186	175
Tensile strength, psi				
at yield	8700	7400	7000	6800
at break	6800	7200	6200	6800
Elongation at break, %	180	390	210	300
Stiffness, ×10 ⁵ psi	1.52	2.61	1.72	2.05
Tensile impact, ft-lb/in. ²	35	23	63	62
DTL, 264 psi, °C	53	47	46	50
Water absorption, %	2.04	2.74	1.38	1.34

^a From Rilsan, Grade BMNO.

^b From Mobay, Grade L-1801.

acid. However, there were no differences in T_g between the para and meta diacid systems (Fig. 2). In general, only a few degrees increase in T_g were obtained with increased substitution of brassylic acid. Figure 3 shows a good linear relationship between the water absorptions and compositions as previously reported in other copolyamide systems.⁹ Moisture sensitivity of nylon 6,13 increased with increasing substitution of brassylic acid by other diacids in the order of adipic > isophthalic ≥ terephthalic acid.

Some of the significant physical properties of the copolyamides are listed in Table III. Two commercial specialty nylons compression molded under the same conditions are included for comparison. Properties such as tensile strength, elongation, stiffness, and DTL of the nylons containing brassylic acid are quite similar to those of the commercial nylons. Tensile impact of nylons 11 and 12 is higher. The values of water absorption are slightly increased because the long-chain fatty acid, brassylic acid, was replaced 20 to 30 mole-% by isophthalic/terephthalic or adipic acid.

CONCLUSIONS

Homopolyamides of brassylic acid have low water absorption which makes them suitable for uses under varying conditions of humidity. Their physical properties such as melting point, mechanical properties, etc., can be modified readily by copolymerization as demonstrated in this work. Nylons derived from brassylic acid could be attractive as specialty thermoplastics when the monomer becomes available on a commercial scale.

Two papers concerning scale-up synthesis of brassylic acid¹⁰ and of nylon 13,13¹¹ have been recently published while this manuscript was in preparation.

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