Evaluation of the Film and Adhesive Properties of Some Block Copolymer Polyhydroxypolyamides from Esterified Aldaric Acids and Diamines*

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ABSTRACT: A number of structurally different block copolymer polyhydroxypolyamides (PHPAs), produced by condensation polymerization of activated aldarates with 1° diamines, were evaluated for their water and methanol solubility and film-forming and adhesive properties. The polymers are composed of a single aldaric acid and a single diamine unit, a single aldaric acid and two diamine units, two aldaric acids and a single diamine unit, or two aldaric acids and two diamine units. The aldaryl monomer units in the polymers were derived from D-glucaric, xylaric, and galactaric (mucic) acids. A number of alkylenediamines and heteroatom (oxygen and nitrogen)-containing diamines were employed as comonomers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 3085–3092, 2000

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INTRODUCTION

Pocius, in his work on adhesives,[1] defined an adhesive as "a material capable of holding together solid materials by means of surface attachment." A common factor that affects the efficiency of all adhesive systems is their ability to form films of uniform thickness between the surfaces of the adherends. Several methods are available to apply films of adhesives, the two major methods being the hot melt and solvent-applied. Hot-melt procedures are limited to the use of adhesives that are stable to high temperatures and also to adherend surfaces that are equally resistant to heat. A shortcoming of solvent-applied adhesives is that, on a commercial scale, their use may require large quantities of flammable solvents. On the other hand, use of nonflammable solvents, such as halogenated hydrocarbons, can pose health and environmental concerns. Consequently, water-soluble environmentally safe adhesives are an important class of adhesives and their use avoids these hazards.[2]

Carbohydrates, commercially available from renewable agricultural resources such as starch, have historically been used as adhesives in the forms of carbohydrate polymers, oligomers, monomers, and degradation products or as derivatives of the above.[3] A large number of these materials

are water soluble and most decompose to products that are deemed environmentally safe. Some of the major routes to carbohydrate-based adhesives are (a) derivatization of hydroxyl groups of carbohydrates with polymerizable functionalities such as allyl groups[3]; (b) treatment of monosaccharides or oligosaccharides with strong acid to form hydroxymethylfurfural, which then polymerizes to an adhesive material[3]; (c) reacting carbohydrates with phenolic resins to give adhesive combinations[4]; and (d) using monosacharide/phenol/urea/formaldehyde mixtures to form adhesives under neutral conditions.[5,6]

For several years, our laboratory has been exploring the preparation and potential utility of polymers formed from carbohydrate starting materials, polymers referred to as polyhydroxypolyamides (PHPAs).[7–14] These polyamides are formed from the condensation polymerization of esterified aldaric acids with 1° diamines. The purpose of the study described here was to begin correlating film-forming and adhesive properties of different PHPAs as a function of their primary structures. The variability in the diacid monomer structure results from a change in the carbon chain length and the stereochemistry of the chiral, hydroxy-bearing carbons. The esterified activated diacid monomers (aldarates) selected for this study were as follows: methyl-D-glucarate-1,4-lactone (**1**), an equilibrium mixture of methyl xylarate-1,4-lactone and dimethyl xylarate (**2**), and dimethyl galactarate (**3**).

Although diamine monomer structures can differ in a number of ways, the diamines chosen for this study were limited to alkylenediamines of different lengths, a branched alkylenediamine, and some heteroatom containing diamines. The diamine monomers employed were *alkylenediamines* – ethylenediamine (**4**), tetramethylenediamine, (**5**) hexamethylenediamine (**6**), and dodecamethylenediamine (**7**); *a branched alkylenediamine*-2-methylpentamethylenediamine (**8**); and *heteroatom(s)-containing diamines* - 4-aza-4-methylheptamethylenediamine (**9**), 3,6-dioxaoctamethylenediamine (**10**), 3-azapentamethylenediamine (**11**), and 4-azaheptamethylenediamine (**12**):
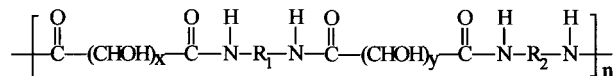
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EXPERIMENTAL

General Procedure for the Synthesis of Block Copolymer Polyamides Utilizing Esterified Xylaric Acid, a Second Esterified Aldaric Acid, and One Diamine

To methanol (50 mL) was added aldarate **2** (0.25M methanol solution, 8.0 mL, 2.0 mmol) and the appropriate diamine (4.0 mmol). The reaction mixture was stirred for 1–3 h at room temperature and then 25.0 mL of a methanol solution of aldarate **3** (476 mg, 2.0 mmol) containing triethylamine (10 drops) or a methanol solution (10 mL) of aldarate **1** (412 mg, 2.0 mmol) was added. After the addition of **1** or **3,** the reaction mixture was stirred for an additional 6 h at room temperature. The reaction mixture was then concentrated under reduced pressure and the product used without further purification.

General Procedures for the Synthesis of Block Copolymer Polyamides Utilizing One Esterified Aldaric Acid Monomer and Two Diamines

To a solution of aldarate **1, 2,** or **3** (4.00 mmol) in methanol (50 mL) was added the appropriate heteroatom diamine or branched alkylenediamine (2.0 mmol) and the reaction mixture was stirred at room temperature for 1–3 h; a second diamine (2.0 mmol), not restricted to a branched alkylene or heteroatom diamine, was added and the reaction mixture was then stirred at room temperature for an additional 6 h. The reaction mixture was concentrated and the product was used without further purification.

General Procedure for the Synthesis of Block Copolymer Polyamides Utilizing Esterified Glucaric Acid, Esterified Galactaric Acid, and One Diamine

To a solution of aldarate **1** (2.0 mmol) in methanol (50 mL) was added the appropriate diamine (4.0 mmol). The reaction mixture was stirred for 1–3 h at room temperature and a solution of aldarate **3** (2.0 mmol) in methanol (25.0 mL) containing triethylamine (10 drops) was added. After completion of the addition of aldarate **3,** the reaction mixture was stirred for an additional 6 h at room temperature and concentrated and the product was used without further purification.

General Procedures for the Synthesis of Block Copolymer Polyamides Utilizing Esterified Xylaric Acid, a Second Esterified Aldaric Acid, and at Least Two Diamines

To a solution of aldarate **2** (2.0 mmol) in methanol (50 mL) was added the appropriate heteroatom(s)-containing diamine or branched alkylenediamine (2.0 mmol) and the reaction mixture was stirred at room temperature for 1–3 h. To this solution was added either aldarate **3** (2.0 mmol) in methanol (25 mL) containing triethylamine (10 drops) or aldarate **1** (2.0 mmol) in methanol (10 mL). The reaction was stirred for at least an additional 2 h at room temperature. A second diamine (2.0 mmol), not restricted to a branched alkylene or heteroatom(s)-containing diamine, was then added and the reaction mixture stirred at room temperature for an additional 6 h. The reaction mixture was concentrated and the product was used without further purification.

General Procedures for the Synthesis of Block Copolymer Polyamides Utilizing Esterified Glucaric Acid, Esterified Galactaric Acid, and at Least Two Diamines

To a solution of aldarate **1** (2.0 mmol) in methanol (50 mL) was added the appropriate heteroatom(s)-containing diamine or branched alkylenediamine (2.0 mmol) and the reaction mixture was stirred at room temperature for 1–3 h. To this solution was added aldarate **3** (2.0 mmol) in methanol (25.0 mL) containing triethylamine (10 drops). The reaction was stirred for at least an additional 2 h at room temperature. A second diamine (2.0 mmol), not restricted to a branched alkylene or heteroatom(s)-containing diamine, was then added and the reaction mixture stirred at room temperature for an additional 6 h. The reaction mixture was concentrated and the product was used without further purification.

General Procedure for the Synthesis of Block Copolymer Polyamides Utilizing Esterified Glucaric Acid or Esterified Xylaric Acid and at Least One Diamine
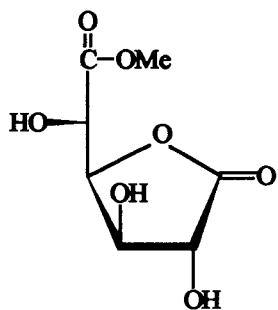
To a solution of aldarate **1** or **2** (4.0 mmol) in methanol (50 mL) was added the appropriate diamine (4.0 mmol). The reaction mixture was then stirred for 6 h at room temperature. The reaction mixture was concentrated and the product used without further purification.

General Procedure for the Synthesis of Block Copolymer Polyamides Utilizing Esterified Galactaric Acid and at Least One Diamine
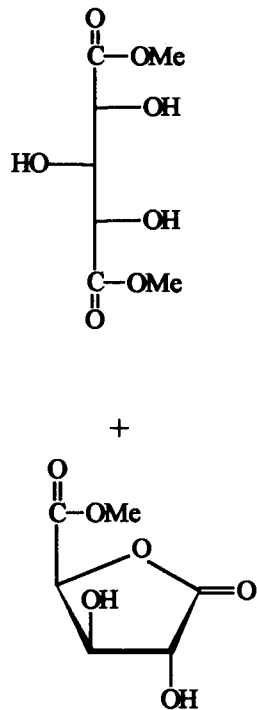
To a solution of aldarate **3** (4.0 mmol) in methanol (50 mL) containing triethylamine (10 drops) was added the appropriate diamine (4.0 mmol). The reaction mixture was heated to reflux for 4 h. The product precipitate from the reaction was separated by vacuum filtration and washed with additional methanol (10 mL). The polymer was then used without further purification.
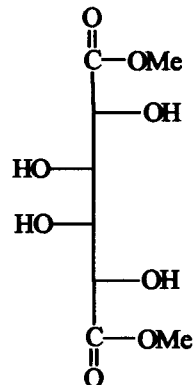
RESULTS AND DISCUSSION

The aldarates and diamines were polymerized using one of the following combinations: (1) a single aldarate with a single diamine, (2) a single aldarate with two diamines, (3) two aldarates with a single diamine, or (4) two aldarates with two diamines. A general polymer structure is represented as **I**, where x and y can be 3 or 4, with the five-carbon acid component being the *meso-xylaryl* unit and the six-carbon diacid components being the *D-glucaryl* or *meso-galactaryl* units.

1

2

3

$H_2N(CH_2)_nNH_2$

	n
4	2
5	4
6	6
7	12

$$CH_3$$
$$H_2NCH_2CHCH_2CH_2CH_2NH_2$$

8

$$CH_3$$
$$H_2NCH_2CH_2CH_2NCH_2CH_2CH_2NH_2$$

9

$$H_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$$

10

$$H$$
$$H_2NCH_2CH_2NCH_2CH_2NH_2$$

11

$$H$$
$$H_2NCH_2CH_2CH_2NCH_2CH_2CH_2NH_2$$
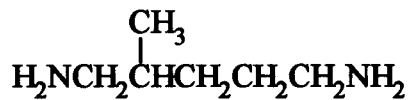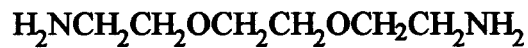
12

Table I   Polyhydroxypolyamides Prepared from Dialkyl Aldarates or Alkyl Aldarate Ester/Lactone(s) and 1 ° Diamines

First Aldarate	Second Aldarate	First Diamine	Second Diamine	Product
1		4		Poly(ethylene D-glucaramide) (**13**)
1		5		Poly(hexamethylene D-glucaramide) (**15**)
1		7		Poly(dodecamethylene D-glucaramide) (**16**)
1		8		Poly(2′-methylpentamethylene D-glucaramide) (**17**)
1		9		Poly(4′-aza-4′-methylheptamethylene D-glucaramide) (**18**)
1		10		Poly(3′,6′-dioxaoctamethylene D-glucaramide) (**19**)
2		8		Poly(2′-methylpentamethylene xylaramide) (**20**)
2		9		Poly(4′-aza-4′-methylheptamethylene xylaramide) (**21**)
2		10		Poly(3′,6′-dioxaoctamethylene xylaramide) (**22**)
3		6		Poly(hexamethylene galactaramide) (**23**)
3		7		Poly(dodecamethylene galactaramide) (**24**)
3		8		Poly(2′-methylpentamethylene galactaramide) (**25**)
3		9		Poly(4′-aza-4′-methylheptamethylene galactaramide) (**26**)
3		10		Poly(3′,6′-dioxaoctamethylene galactaramide) (**27**)
3		11		Poly(3′-azapentamethylene galactaramide) (**28**)
2	1	6		Poly(hexamethylene xylaramide, hexamethylene D-glucaramide) (**29**)
2	1	8		Poly(2′-methylpentamethylene xylaramide, 2‴-methylpentamethylene D-glucaramide) (**30**)
2	1	9		Poly(4′-aza-4′-methylheptamethylene xylaramide , 4‴-aza-4″-methylheptamethylene D-glucaramide) (**31**)
2	1	10		Poly(3′,6′-dioxaoctaamethylene xylaramide, 3‴,6‴-dioxaoctamethylene D-glucaramide) (**32**)
2	1	11		Poly(3′-azapentamethylene xylaramide, 3‴-azapenta-methylene D-glucaramide) (**33**)
2	1	12		Poly(4′-azaheptamethylene xylaramide, 4‴-azahepta-methylene D-glucaramide) (**34**)
2	3	8		Poly(2′-methylpentamethylene xylaramide, 2‴-methylpentamethylene galactaramide) (**35**)
2	3	9		Poly(4′-aza-4′-methylheptamethylene xylaramide, 4‴-aza-4‴-methylheptamethylene galactaramide) (**36**)
2	3	10		Poly(3′,6′-dioxaoctaamethylene xylaramide, 3‴,6‴-dioxaoctaamethylene galactaramide) (**37**)
2	3	11		Poly(3′-azapentamethylene xylaramide, 3‴-azapenta-methylene galactaramide) (**38**)
2	3	12		Poly(4′-azapentamethylene xylaramide , 4‴-azapenta-methylene galactaramide) (**39**)
2	8	6		Poly(2′-methylpentamethylene xylaramide, hexa-methylene xylaramide) (**40**)
1	8	6		Poly(2′-methylpentamethylene D-glucaramide, hexa-methylene D-glucaramide) (**41**)
3	9	4		Poly(4′-aza-N-methylheptamethylene galactaramide, ethylene galactaramide) (**42**)
3		9	10	Poly(4′-aza-4′-methylheptamethylene galactaramide, 3‴,6‴-dioxaoctamethylene galactaramide) (**43**)
1	3	8		Poly(2′-methylpentamethylene D-glucaramide, 2‴-methylpentamethylene galactaramide) (**44**)
1	3	9		Poly(4′-aza-4′-methylheptamethylene D-glucaramide, 4‴-aza-4″-methylheptamethylene galactaramide) (**45**)
1	3	10		Poly(3′,6′-dioxaoctaamethylene D-glucaramide, 3‴,6‴-dioxaoctaamethylene galactaramide) (**46**)
1	3	11		Poly(3′-azapentamethylene D-glucaramide, 3‴-aza-pentamethylene galactaramide) (**47**)
1	3	12		Poly(4′-azaheptamethylene D-glucaramide, 4‴-aza-heptamethylene galactaramide) (**48**)
2	1	10	8	Poly(3′,6′-dioxaoctaamethylene xylaramide, 2‴-methylpentamethylene D-glucaramide) (**49**)
2	3	10	8	Poly(3′,6′-dioxaoctaamethylene xylaramide, 2‴-methylpentamethylene galactaramide) (**50**)
1	3	10	8	Poly(3′,6′-dioxaoctaamethylene D-glucaramide, 2‴-methylpentamethylene galactaramide) (**51**)

The diamines come from the group of compounds **4–12**. The specific combinations used are listed in Table I. The prepared polymers were then tested for their water solubility, ability to form films, and adhesive characteristics (Table II). The aldarate/diamine condensation polymerizations were carried out in methanol at room to solvent reflux temperatures by the addition of the 1° diamine(s) to a methanol solution of the aldarate(s). When two 1° diamines were used, the

Table II   Film-forming and Adhesive Characteristics of Polymers 13–51

	Solubility in Water	Film Appearance	Adhesion Strength	
			Hot melt	Solvent-applied
13	Yes	Cracked	Not tested[a]	Not tested[a]
14	Yes	Cracked	Not tested[a]	Not tested[a]
15	No	Opaque	Not tested[a]	Not tested[a]
16	No	Opaque	Not tested[a]	Not tested[a]
17	Yes	Transparent	+[d]	+[1]
18	Yes	Transparent	+[e]	0
19	Yes	Transparent	+[e]	+[4]
20	Yes	Transparent	+[e]	+[3]
21	Yes	Transparent	0[b]	+[6]
22	Yes	Transparent	0[b]	+[2]
23	No	Opaque	Not tested[a]	Not tested[a]
24	No	Opaque	Not tested[a]	Not tested[a]
25	No	Opaque	Not tested[a]	Not tested[a]
26	Yes	Cracked	Not tested[a]	Not tested[a]
27	Yes	Cracked	Not tested[a]	Not tested[a]
28	Yes	Transparent	0[b]	
29	Yes	Transparent	0[b]	
30	Yes	Transparent	+[d]	+[4]
31	Yes	Transparent	+[e]	+[4]
32	Yes	Transparent	+[e]	+[4]
33	Yes	Transparent	+[e]	
34	Yes	Transparent	+[e]	
35	Yes	Transparent	+[d]	+[2]
36	Yes	Transparent	0[b,c]	+[1]
37	Yes	Transparent	+[d]	+[6]
38	Yes	Transparent	+[e]	
39	Yes	Transparent	0[b,c]	
40	Yes	Transparent	0[b]	
41	Yes	Transparent	0[b]	
42	Yes	Cracked	Not tested[a]	Not tested[a]
43	Yes	Cracked	Not tested[a]	Not tested[a]
44	Yes	Transparent	0[b,c]	0
45	Yes	Transparent	+[d]	+
46	Yes	Transparent	+[c]	+[4]
47	Yes	Transparent	+[d]	
48	Yes	Transparent	+[d]	
49	Yes	Transparent	0[b]	+[5]
50	Yes	Transparent	0[b]	+[3]
51	Yes	Transparent	0[b]	+[1]

Superscripts 1–6 indicate qualitative but increasing effort to separate glass slides.

[a] Only polymers forming transparent films were analyzed for their adhesive properties; 0 indicates no or slight adhesion; + indicates adhesion.

[b] Cardboard surfaces were easily separated.

[c] Separated with light force with no tearing of the cardboard.

[d] Moderate force required to separate, but the cardboard did not tear.

[e] Cardboard pieces could not be separated without tearing.

following order of addition was employed: Heteroatom(s)-containing diamines were added before branched alkylenediamines, which were added before alkylenediamines. When two al- darates were used, the order of addition was as follows: Methanol-esterified xylarate was added before methyl-D-glucaro-1,4-lactone, which, in turn, was added before dimethyl galactarate.

These orders of addition were intended to enhance the solubility of the oligomer intermediates and, therefore, enhance the incorporation of all the monomeric structural units prior to the precipitation of the polymeric product.

The polymers were analyzed for their ability to form films by first dissolving them in distilled water. Several drops of the aqueous solution were then placed on a microscope slide and the slide was warmed to 60°C to evaporate the solvent. Results from attempts to form films and adhesives from the polyhydroxypolyamides (13–51, Table I) are given in Table II. Film-forming capabilities were used as a screening method for adhesive analyses, that is, only compounds forming transparent films were further tested for their adhesive characteristics.

The polymers were evaluated for their adhesive capabilities by either the solvent-applied or hot-melt method. In the solvent-applied method, several drops of an aqueous solution of the polymer were placed between two glass slides oriented at 90°. The slides were then warmed to about 60°C to slowly evaporate the solvent. After the slides cooled to room temperature, they were then manually separated. Estimated adhesive strengths ranged from no adhesion (0) and minimal effort to separate the slides to greatest effort to separate the slides ($+^1$ to $+^6$). The superscripted numbers 1–6 (Table II) qualitatively indicate the increasing effort required to separate the glass slides.

To estimate the hot-melt adhesive properties of the polymers, a small amount (25–50 mg) of the polymer was placed between two pieces of cardboard, oriented at 90°. The cardboard was then heated until the polymer liquefied. The cardboard was allowed to cool to room temperature and pieces were then pulled apart. The results are presented in Table II: 0 indicates no or slight adhesion, + indicates adhesion, and superscripted b–e indicate a range of adhesion from cardboard surfaces being easily separated to separation of cardboard pieces with tearing.

Although these evaluations are qualitative, the data presented in Table II suggest that film-forming and good adhesive characteristics are clearly dependent on the aldarate(s)/diamine(s) combinations. Applications of more accurate ASTM procedures for evaluating the film-forming ability[15] and hot-melt adhesion characteristics[16–17] are being considered for some of the better film-forming/adhesive polymers. The most effective PHPAs are those derived from condensing xylarate or glucarate monomers with branched alkylene or heteroatom(s) containing diamines; for example, D-glucarate derivatives 17 and 19, xylarate derivative 20, and xylarate/D-glucarate derivatives 31–32. As the data in Table II indicate, all of the polymers that formed transparent films were water-soluble. However, it is also observed that good water solubility does not necessarily confer film-forming or adhesive capabilities.

The film-forming and adhesive trends can be correlated with conformational preferences of the parent diacids. Galactaric acid and derivatives thereof adapt extented or zigzag conformations.[18] The preferred extended conformation is a result of the absence of any destabilizing 1,3-dihydroxyl interactions in the galactaric acid configuration. In contrast, D-glucaric[19] and xylaric acid monomers[20] both have destabilizing 1,3-dihydroxy interactions, which results in the carbohydrate structural subunit adopting bent or nonextended conformations. The apparent crystalline character of the solid polygalactaramides suggests that the conformationally extended *galactaryl* monomer combined with the typically extended alkylene unit allows for both effective intermolecular hydrogen bonding and van der Waals interactions between the polymer chains. Consequently, these polymers show poor film-forming and adhesive properties. Incorporating bent (nonextended) D-glucaric and xylaric acid monomer units in the polymer primary structure makes it more difficult for effective intermolecular interactions between the polymer chains, thus increasing the amorphous character of the polymers and improving their film-forming and adhesive characteristics. Surprisingly, it was found that a combination of bent (*xylaryl*) and extended (*galactaryl*) monomer units with a common heteroatom diamine (3,6-dioxaoctamethylenediamine (10) gave a block copolymer (37) with improved adhesive properties over that of the parent simple copolymers 22 and 27.

CONCLUSIONS

Incorporation of extended (*galactaryl*) diacid monomers into PHPAs suggests an apparent increase in polymer crystallinity due to increased intermolecular hydrogen bonding between polymer chains. This was accompanied by a decrease in polymer water solubility and increase in polymer melting point (causing decomposition of the polymer in a hot-melt application). Use of bent

(e.g., *glucaryl* or *xylaryl* configuration) diacids gave rise to a decrease in intermolecular interactions and enhancement in both film-forming and adhesive characteristics. Introduction of saturated hydrocarbon structural units into the polymer primary structure appears to increase polymer crystallinity, presumably via increased van der Waals attractive interaction between the alkylene portions of the polyamide backbone. The use of diamines containing heteroatom(s), however, does not favor these interactions and decreases the polyamide crystallinity, resulting in materials that have improved film-forming and adhesive properties. Finally, those polyamides with adequate film-forming and adhesive properties were water soluble and had a melting point significantly below the temperature at which decomposition of the polymer began.

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