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### Linear Unsaturated Polyamides and Polyhydrazides

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## Linear Unsaturated Polyamides and Polyhydrazides

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### ABSTRACT

Polyhydrazides and polyamides were prepared from hydrazine, piperazine, or substituted piperazines and muconic or  $\alpha,\alpha'$ -dimethylmuconic acid chlorides by interfacial and solution polymerization. Low-temperature solution polymerization was preferred for polyhydrazides, and the interfacial technique for the piperazines. Polymers of dimethylmuconic acid exhibited better properties than those of muconic acid, e.g., molecular weight, film strength, and solubility. Optical properties, such as transparency, color, refractive index, and birefringence, were also determined and compared to aromatic polyamides and hydrazides.

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## INTRODUCTION

Unsaturated polyamides have been used as reverse osmosis membranes and as crosslinking resins, particularly where the thermal properties of analogous polyesters were inadequate. Many papers and several review articles have appeared on these subjects, the latest in 1979 [1]. Much of the literature describes the synthesis, characterization, and physical properties of dozens of combinations of unsaturated diacids and diamines. Because most of these polymers are readily synthesized to high molecular weight and can be processed into colorless, transparent films and fibers by casting or, in some cases, extruding, they were prime candidates for certain optical applications [2].

The optical devices of greatest utility require polymer films which exhibit birefringence values exceeding 0.4. Unfortunately, birefringence data could not be found in the literature, and hence, we did not have any precedents upon which to base our research. Initially, we postulated that unsaturated polyamides and polyhydrazides would be useful optical materials and would exhibit high birefringence for several reasons: first, polymers could be synthesized which are linear and rigid; second, the conjugation, and hence the color, of the materials could be extended or shortened as required; third, the electron distribution could be made symmetric about the polymer backbone with negligible off-axis contributions; fourth, the unsaturation itself would provide highly polarizable electrons.

Coincidentally, the specific polymers we chose for this study had not been previously synthesized, and we will, therefore, give the synthesis and physical properties of each.

## EXPERIMENTAL

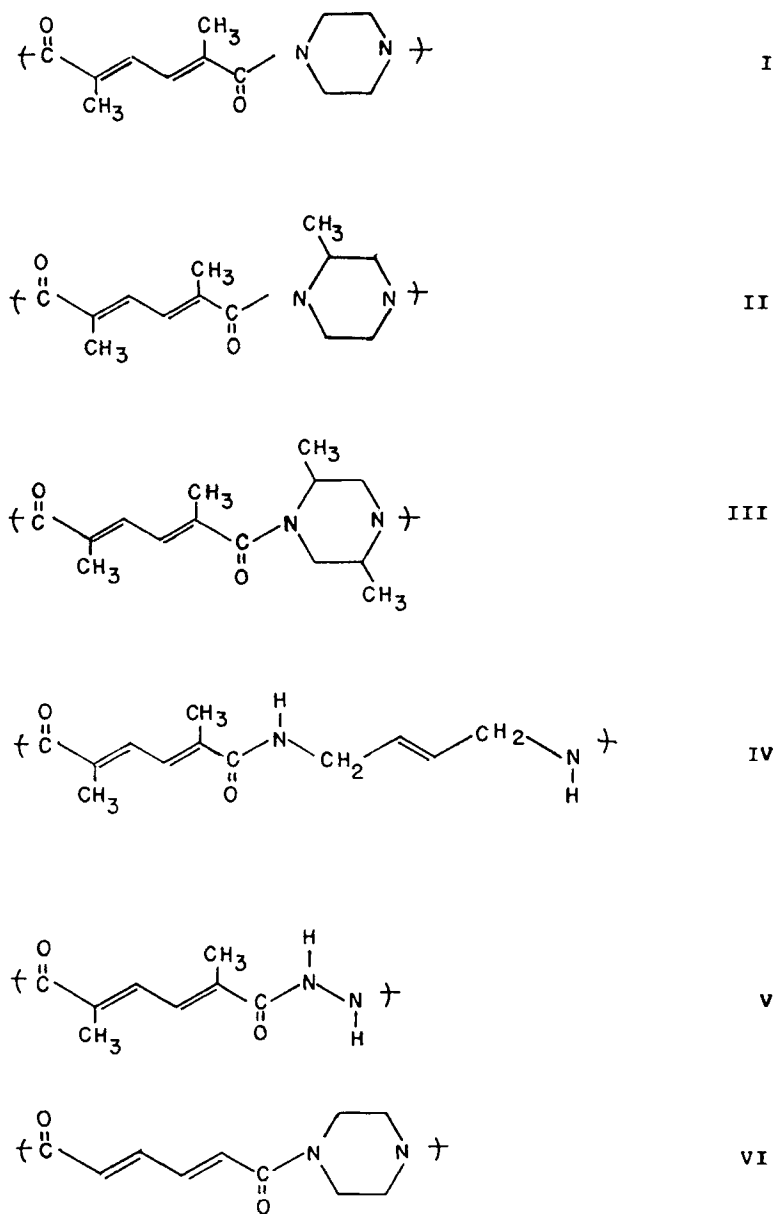
Most of the polymers prepared for this study were synthesized several times by either interfacial or low-temperature solution techniques. The procedures listed below represent the best results for each polymer as determined by viscosity measurements. The molecular structures of the polymers are shown in Table 1, and some of their physical and optical properties are listed in Table 2.

The polymer structures were confirmed by IR spectroscopy (Perkin-Elmer 727),  $^{13}\text{C}$ -nuclear magnetic resonance (Varian FT-80), and elemental analysis (Galbraith Labs).

The inherent viscosities ( $\eta_{inh}^{30}$ , 0.5 dL/g) were determined in an Ubbelohde viscometer. The data are listed in Table 2.

The glass-transition temperatures were determined by differential scanning calorimetry (Du Pont 910) of powders and, where possible, by thermomechanical analysis (Du Pont 943) of films. The onset of

TABLE 1. The Molecular Structures of the Polymers Prepared for This Study



(continued)

TABLE 1 (continued)

	VII
	VIII
	IX

degradation was measured by thermogravimetric analysis (Du Pont 951). The data are listed in Table 2.

Refractive index and birefringence measurements were made on a Zeiss polarizing microscope by Becke line analysis.

### Monomer Preparation

Muconic and  $\alpha,\alpha'$ -dimethylmuconic acid chlorides were obtained by reacting the commercially available diacids (the former from Aldrich Chemical Co., the latter from Frinton Laboratories) with  $\text{PCl}_5/\text{POCl}_3$ .

Muconic acid chloride was purified by sublimation at 60–65°C, 0.10 torr. The resulting fluffy, tan sublimate (yield: 62.9%) melted at 94.5–97.5°C.

Analysis: Calculated for  $\text{C}_6\text{H}_4\text{Cl}_2\text{O}_2$ : C, 40.26%; H, 2.25%; Cl, 39.61%; O, 17.88%. Found: C, 40.10%; H, 2.33%; Cl, 39.43%.

TABLE 2. Physical and Optical Properties

Polymer	$\eta_{inh}^{30}$ , dL/g <sup>a</sup>	$T_g$ , °C <sup>b,c</sup>	$T_d$ , °C <sup>d</sup>		$n_d^e$	$\Delta n^f$
			N <sub>2</sub>	Air		
I	3.20 (TFA) 1.51 (TFE)	180 <sup>b,c</sup>	415	360	1.58	0.05
II	3.10 (TFA) 3.80 (TFE)	180 <sup>b,c</sup>	415	310	1.59	0.17
III	2.67 (TFE)	171 <sup>b,c</sup>	415	315	1.53	0.18
IV	0.55 (TFA) 1.12 (L/D)	120 <sup>b,c</sup>	370	326	g	g
V	2.55 (L/D)	185 <sup>b</sup>	345	325	1.68	0.23
VI	0.78 (TFA)	170 <sup>b,c</sup>	400	305	g	g
VII	0.91 (TFA)	ND <sup>h</sup>	380	325	g	g
VIII	i	175 <sup>b</sup>	400	325	g	g
IX	0.61 (TFA)	ND <sup>h</sup>	350	318	g	g

<sup>a</sup>0.5% Polymer w/v in parentheses: TFA, trifluoroacetic acid; TFE, trifluoroethanol; L/D, 5% LiCl/dimethyl acetamide (w/v).

<sup>b</sup>Differential scanning calorimetry (5°C/min).

<sup>c</sup>Thermomechanical analysis (5°C/min).

<sup>d</sup>Onset of degradation (10°C/min).

<sup>e</sup>Refractive index (Becke line).

<sup>f</sup>Birefringence experimental maximum (Becke line).

<sup>g</sup>Films too scattering to measure accurately.

<sup>h</sup>Not detectable.

<sup>i</sup>Partially insoluble.

$\alpha, \alpha'$ -Dimethylmuconic acid was recrystallized from hexane. The details of its characterization are given elsewhere [3].

The piperazine homologs are commercially available (Aldrich Chemical Co.) and were purified by recrystallization [4].

trans-1,4-Diamino-2-butene·2HCl was synthesized by first reacting 1,4-dibromo-2-butene with potassium phthalimide in dimethylformamide; hydrolysis of the diimide by refluxing in concentrated HCl/glacial acetic acid for 6 days yielded a white solid in 83.27% yield.

Analysis: Calculated for C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>Cl<sub>2</sub>: C, 30.20%; H, 7.60%; Cl 44.58%; N, 17.61%. Found: C, 30.16%; H, 7.59%; N, 17.23%.

Hydrazine dihydrate was obtained from Aldrich Chemical Co. It was purified by refluxing with an equal weight of NaOH pellets for 2 h and then distilled in a  $N_2$  atmosphere (bp  $115^\circ C$ ).

### Poly (Piperazino) $\alpha, \alpha'$ -dimethylmuconamide (I)

A solution of 6.80 g (0.0789 mol) piperazine and 15.06 g (0.142 mol) sodium carbonate in 230 mL water was added to a blender. The contents were stirred rapidly, and 14.71 g (0.0710 mol)  $\alpha, \alpha'$ -dimethylmuconic acid chloride in 315 mL chloroform was added. The contents were stirred for 10 min. The product was filtered and washed with acetone and then ether, followed by drying for 18 h in a vacuum oven ( $55^\circ C/15$  torr). Yield was 14.41 g of a white polymer.

Molecular structure was confirmed by infrared and  $^{13}C$ -nuclear magnetic resonance analysis. The proton-decoupled CMR ( $CF_3COOD$ ) showed  $\gamma$  (TMS): 176.5 (amide-C), 135.2 ( $\alpha$ -C), 127.8 ( $\beta$ -C), 48.5 and 44.2 (piperazino-C's), 14.8 ( $\alpha$ - $CH_3$ ).

Polymeric films were prepared by puddle casting a solution of the polymer in trifluoroethanol solvent onto a glass plate, and after evaporation of solvent, immersing the slide in water. Colorless, slightly hazy films were obtained. The films were soaked in water to remove solvent and cut into strips for stretching between the jaws of a mechanical stretcher. Stretching in steam to an elongation of 170% provided strips having a birefringence of 0.05.

Analysis: Calculated for  $(C_{12}H_{16}N_2O_2)_n$ : C, 65.43%; H, 7.32%; N, 12.71%; O, 14.53%. Found: C, 64.55%; H, 7.47%; N, 12.74%.

### Poly (2-Methylpiperazino) $\alpha, \alpha'$ -dimethylmuconamide (II)

A solution of 2.04 g (0.0203 mol) 2-methylpiperazine and 4.31 g (0.0407 mol) sodium carbonate in 50 mL water was added to a blender and stirred vigorously. A solution of 4.21 g (0.0203 mol)  $\alpha, \alpha'$ -dimethylmuconic acid chloride in 40 mL chloroform was added to the blender. The reaction mixture was stirred for 5 min. After chloroform evaporation, hexane and acetone were added while stirring. The resulting white chunklike solid was washed with acetone and ether and dried in a vacuum oven ( $55^\circ C/15$  torr) for 18 h. The yield was 2.27 g of a white solid.

Polymer films were prepared by puddle casting solutions of the polymer in a chloroform/methanol solvent onto a glass plate and immersing in water to provide a transparent, flexible, and colorless film. The refractive index was 1.59.

Films were prepared in the usual manner. Strips were cut and mounted between the jaws of a mechanical stretcher. Separate strips

were stretched under different conditions as follows: in air at 200°C to an elongation of 231%, in steam to 320% elongation, in boiling dimethylacetamide to 200% elongation, and in boiling o-dichlorobenzene to 170% elongation. Birefringence results were as follows: 0.16 (air), 0.12 (steam), 0.17 (dimethylacetamide), and 0.15 (o-dichlorobenzene).

Analysis: Calculated for  $(C_{13}H_{18}N_2O_2)_n$ : C, 66.64%; H, 7.74%; N, 11.95%; O, 13.65%. Found: C, 66.01%; H, 7.61%; N, 11.81%.

Poly(2,5-Dimethylpiperazino) $\alpha, \alpha'$ -dimethylmuconamide (III)

An aqueous solution of 1.30 g (0.0114 mol) 2,5-dimethylpiperazine and 2.18 g (0.0205 mol) sodium carbonate in 60 mL water was added to a blender. An additional 15 mL chloroform was added to the blender while rapidly stirring. To the stirring contents was added 2.13 g (0.0103 mol)  $\alpha, \alpha'$ -dimethylmuconic acid chloride in 65 mL chloroform. The product had a gel-like character which was lost upon washing with hexane. After washing with acetone and then ether, the product was dried for 18 h in a vacuum oven (50°C/15 torr). Yield was 2.32 g of a white fibrous solid.

Polymeric films were prepared by puddle casting a solution of the polymer in a chloroform/methanol solvent mixture onto a glass plate, and after evaporation of solvent, immersing the slide in water. Colorless, slightly hazy films were obtained. The refractive index was 1.53. The films were cut into strips. Different strips were stretched under the following conditions: in air at 200°C to 38% elongation, in steam to 172% elongation, in boiling dimethylacetamide to 150% elongation, and in boiling o-dichlorobenzene to 147% elongation. Birefringence values were obtained as follows: 0.04 (in air), 0.18 (in steam), 0.09 (in dimethylacetamide), and 0.04 (in o-dichlorobenzene).

Analysis: Calculated for  $(C_{14}H_{20}N_2O_2)_n$ : C, 67.74%; H, 8.06%; N, 11.29%; O, 12.90%. Found: C, 68.01%; H, 7.70%; N, 10.79%.

Poly(trans-2-Butenylene) $\alpha, \alpha'$ -dimethylmuconamide (IV)

An aqueous solution of 3.05 g (0.019 mol) 1,4-diamino-2-butene dihydrochloride and 4.55 g (0.0383 mol) potassium hydroxide in 80 mL water was added to a blender. To the blender was added 40 mL carbon tetrachloride, and the contents were rapidly stirred. To the stirring contents was added 2.65 g (0.012 mol)  $\alpha, \alpha'$ -dimethylmuconic acid chloride in 70 mL carbon tetrachloride. The reaction mixture thickened immediately. After stirring for 10 min the reaction mixture was filtered off and washed with ether and then acetone. The product was dried for 18 h in a vacuum oven (60°C/15 torr). The yield was 1.75 g of a white, slightly fibrous, solid polymer.



Polymeric films were prepared by puddle casting a solution of the polymer in trifluoroethanol solvent onto a glass plate, and after evaporation of solvent and immersing the slide in water, colorless, translucent films having a slightly elastic character were obtained.

Analysis: Calculated for  $(C_{12}H_{16}N_2O_2)_n$ : C, 65.43%; H, 7.32%; N, 12.72%; O, 14.53%. Found: C, 66.18%; H, 6.83%; N, 11.55%.

### Poly- $\alpha, \alpha'$ -dimethylmuconic Hydrazide (V)

To a round-bottomed flask, equipped with an addition funnel, mechanical stirrer, and nitrogen inlet tube, was added 0.333 g (0.0131 mol) hydrazine and 25 mL N-methylpyrrolidone. The contents were cooled to 0°C in a cooling bath and a solution of 2.14 g (0.0131 mol)  $\alpha, \beta'$ -dimethylmuconic acid chloride in 6 mL tetrahydrofuran was added dropwise. An additional 5 mL N-Methylpyrrolidone, utilized to rinse the addition funnel, was added to the reaction flask. The temperature of the contents was observed to rise to 3°C and then drop to 0°C. After addition of 1.52 g (0.0204 mol) lithium carbonate, the reaction mixture was stirred at 0°C for 45 min. During this time a light yellow solution was produced. The cooling bath was removed, and the temperature rose to 25°C over a 20-min period. The reaction mixture was warmed gradually to 50°C; heating and stirring were continued for 1 h. The reaction mixture was poured into a mixture of ice and water in a blender, and a yellow fibrous solid was formed. The mixture was filtered and washed in the blender three times with water, three times with methanol, and three times with ether. The resulting product was dried for 18 h in a vacuum oven (78°C/15 torr) to yield 1.72 g of a yellow, fibrous solid polymer.

The molecular structure was confirmed by infrared analysis. Inspection of the ultraviolet/visible spectrum of the polymer (in 5% w/v lithium chloride/dimethylacetamide) showed a  $\lambda_{\max}$  of 298 nm ( $\epsilon = 12\,000$ ) and a peak at 390 nm ( $\epsilon = 4\,300$ ).

Films were prepared by casting solutions of the polymer in a 5% w/v solution of lithium chloride and dimethylacetamide onto glass plates. The concentration of polymer ranged from 1.0 to 5% w/v. In each instance the glass plate carrying the puddle-cast polymer solution was immersed in water (after evaporation of solvent). The polymer films were observed to gel, and an unoriented film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone, and dried in a vacuum oven at 90°C and 15 torr. The refractive index was 1.68.

Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. Different strips were stretched under differ-

ent conditions as follows: in air at 200°C to an elongation of 21%, in steam to 30% elongation, and in boiling o-dichlorobenzene to 20% elongation. Birefringence results were 0.146 (air), 0.234 (steam), and 0.146 (p-dichlorobenzene).

Analysis: Calculated for  $(C_8H_{10}N_2O_2)_n$ : C, 57.83%; H, 6.02%; N, 16.87%; O, 19.28%. Found: C, 57.67%; H, 6.01%; N, 16.59%.

#### Poly (Piperazino)muconamide (VI)

An aqueous solution of 0.897 g (0.0104 mol) piperazine and 2.21 g (0.0208 mol) sodium carbonate in 30 mL water was added to a blender. After addition of 10 mL water and 10 mL chloroform, the blender contents were vigorously stirred. To the blender was added 1.86 g (0.0104 mol) muconic acid chloride in 50 mL of chloroform, and the reaction mixture was stirred for 10 min. The resulting polymeric product was filtered, washed with acetone, and washed with ether. The product was dried in a vacuum oven for 18 h (40°C/15 torr). The resulting product (2.00 g) was a white powder.

Polymeric films were formed by puddle casting a solution of the polymer in trifluoroethanol onto a glass plate and immersing the plate into water. Brittle and translucent films resulted.

Analysis: Calculated for  $(C_{10}H_{12}N_2O_2)_n$ : C, 62.49%; H, 6.29%; N, 14.59%; O, 16.65%. Found: C, 62.71%; H, 6.15%; N, 14.23%.

#### Poly (2-Methylpiperazino)muconamide (VII)

An aqueous solution of 1.26 g (0.126 mol) 2-methylpiperazine and 2.53 g (6.024 mol) sodium carbonate in 50 mL water was added to a blender. Thereupon 10 mL chloroform was added, and the contents were vigorously stirred. To the blender was added 2.14 g (0.0120 mol) muconic acid chloride in 70 mL methylene chloride. The reaction mixture was stirred for 5 min. The gel-like product was filtered, washed with acetone, and washed with ether. After drying in a vacuum oven for 18 h (45°C/15 torr), the resulting white powder weighed 1.49 g.

Polymeric films were prepared by puddle casting a solution of the polymer in trifluoroethanol onto a glass slide and immersing the slide into water. The resulting films were translucent and slightly brittle.

Analysis: Calculated for  $(C_{11}H_{14}N_2O_2)_n$ : C, 64.06%; H, 6.84%; N, 13.59%; O, 15.52%. Found: C, 63.78%; H, 6.59%; N, 13.31%.

#### Poly (2,5-Dimethylpiperazino)muconamide (VIII)

An aqueous solution of 1.26 g (0.0110 mol) 2,5-dimethylpiperazine and 2.32 g (0.0220 mol) sodium carbonate in 45 mL water was added

to a blender. Thereupon 7 mL chloroform was added and the contents were vigorously stirred. To the blender was added 1.97 g (0.011 mol) muconic acid chloride, and the reaction mixture was stirred for 5 min. Hexane was added to the reaction mixture to precipitate the polymer and to eliminate the gel-like character of the product. The product was filtered, washed with acetone, and washed with ether. It was dried in a vacuum oven for 18 h (50°C/15 torr). The resulting polymer (1.24 g) was a very pale yellow powder which was insoluble in all solvents tested.

### Poly(trans-2-Butenylene)muconamide (IX)

An aqueous solution of 2.12 g (0.0379 mol) potassium hydroxide and 3.01 g (0.0189 mol) 1,4-diamino-2-butene dihydrochloride in 75 mL water was placed in a blender. To the blender was added 40 mL methylene chloride, and the contents were vigorously stirred. A solution of 2.26 g (0.0126 mol) muconic acid chloride in 70 mL methylene chloride was added all at once to the stirring contents of the blender. Stirring was continued for 5 min. The reaction product was filtered, and the polymer was washed with acetone, then with ether. The polymer was dried in a vacuum oven for 18 h (60°C/15 torr). The yield was 1.629 g of a white polymer.

The molecular structure was confirmed by infrared and  $^{13}\text{C}$ -nuclear magnetic resonance analysis. This proton decoupled CMF ( $\text{CF}_3\text{COOD}$ ) showed  $\gamma$  (TMS): 170.6 (amide-C), 142.5 ( $\alpha$ -carbon), 129.7 and 128.9 (correspond to the  $\beta$ -C of the diacid and the vinyl-C of the diamine—the exact assignment cannot be made), 43.9 ( $\text{CH}_2$ ).

Polymeric films were formed by puddle casting a solution of the polymer in trifluoroethanol onto a glass plate and immersing the plate into water. The resulting films were colorless, mechanically weak, and translucent. Exposure to ambient light for about 24 h produced a dark yellow color.

Analysis: Calculated for ( $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_2$ ): C, 62.49%; H, 6.29%; N, 14.57%; O, 21.25%. Found: C, 62.11%; H, 6.39%; N, 14.25%.

## RESULTS AND DISCUSSION

### Polymer Synthesis

Interfacial polymerization is the preferred procedure for the polyamides of this work. Either sodium carbonate or sodium hydroxide was used as the acid acceptor, and  $\text{CHCl}_3$  or  $\text{CCl}_4$  was used as the solvent. An equimolar amount of diamine, or a slight excess, relative to acid chloride was used. The correct amount of diamine was determined

empirically by measurement of the inherent viscosity of the resulting polymer, and the amount varied from polymer to polymer.

Low-temperature solution polymerization is the method of choice for polydimethylmuconic hydrazide (V). Lithium carbonate was used as the acid acceptor, and N-methylpyrrolidone with LiCl was found to be the best solvent. Unfortunately, a polymerization technique could not be found for polymuconic hydrazide. All attempts to synthesize this polymer by either method failed because the product precipitated from the solution at the early stages of reaction. The resulting yellow solid could not be redissolved, thus making characterization impossible. This polyhydrazide was probably more sensitive to room light than the muconic-acid-containing polyamides, e.g., VI-IX, because its absorption band tails into the visible region of the spectrum. We postulate that a high degree of crosslinking is the cause of the insolubility. This observation implies that polydimethylmuconic hydrazide, which, although it is yellow, is a very tractable material, is much less susceptible to crosslinking. Presently, we have no explanation for this behavior, and the literature makes no distinction between methyl-substituted and unsubstituted polyene diacid-containing polymers in regard to crosslinkability.

### Solubility

All of the polymers made from dimethylmuconic acid are more soluble (as high as 12% w/v) in a wider variety of solvents, e.g., strong acids, m-cresol, and  $\text{CH}_3\text{OH}/\text{CHCl}_3$ , than muconic acid-containing polymers. This difference in solubility is reflected in the molecular weight, as indicated by the inherent viscosity (Table 2) of the various polymers. Interestingly, the viscosity values, and perhaps the solubility, of our dimethylmuconic polyamides are higher than either fumaric or monomethylfumaric/piperazine and dimethylpiperazine polymers [6, 7]. This suggests that a high degree of methyl substitution on polyene diacids may significantly enhance the solubility of polymers composed of these relatively insoluble materials.

We also observed solubility enhancement with increasing methyl substitution on the piperazine ring. A similar effect was noted in fumaric acid/piperazine polyamides [6, 7].

In addition, symmetry of the polymer backbone also plays a role in solubility. For example, polymers containing 2-methylpiperazine (II and VII), the least symmetric of the diamines, exhibited greater solubility, and consequently higher viscosity, than any of the other piperazine-containing polymers.

The dimethylmuconic acid polymers containing butenediamine and hydrazine exhibited solubility in LiCl/amide solvents in analogy to terephthalic acid polymers of these diamines [8, 9].

## Thermal Properties

A comparison of the thermal properties of our polymers with the literature revealed that the onset of degradation, i.e., fragmentation, is in the range expected for unsaturated polyamides, namely, 300-350°C in air and 350-420°C in nitrogen. The relatively low glass transitions, e.g., < 200°C, exhibited by the majority of these polymers (I-VI and VIII) were surprising. Typically, unsaturated aliphatic polyamides exhibit either high softening points or decomposition at the melt, or they are completely infusible.

## Optical Properties

The major purpose of this investigation was the determination of the optical properties, particularly birefringence, of unsaturated, non-aromatic polyamides and polyhydrazides. The birefringence of a polymer is dependent on several interrelated properties, such as morphology, density, orientation, absorptivity, and polarizability. We hypothesized that three of these properties could be readily manipulated. The first is orientation, as indicated by elongation, which is highly dependent on processing variables. The second and third properties are absorptivity and polarizability, which depend completely on molecular structure. Because of our interest in lenticular and interference polarizers and polarizing beam splitters [2], only those polymers which formed nonscattering films were extensively studied.

Films were obtained by puddle casting a solution of polymer onto a glass plate, evaporating or extracting the solvent in a polymer nonsolvent, e.g., water, and removing the film from the glass plate by differential swelling in a nonsolvent. The polymer films were cut into strips, placed in a mechanical stretcher, and dried. The infrared spectrum and the isotropic refractive index of the films were measured (Table 2). In addition, film strips were stretched in a variety of nonsolvent/plasticizers (at elevated temperature) or in air (200°C), and the extent of elongation and birefringence were measured (Table 3).

Films obtained from polymers comprised of dimethylmuconic acid and the piperazines (I-III) and hydrazine (V) ranged from highly scattering to very slightly scattering, depending on solvent and casting conditions. The scattering may be the result of semicrystalline morphology or voids. The literature indicates that identical film properties are exhibited by polymers comprised of fumaric or methylfumaric acid and the piperazines [6, 10]. It also indicates that polymers containing fumaric acid and linear aromatic diamines [11], and also linear aromatic polyhydrazides [12], have a high propensity for crystallization and void formation. Because Polymers I-III and V are soluble in a variety of solvents, casting variables could be manipulated until the correct combination of solvent and evaporation rate was discovered which produced relatively scatter-free films. Unfortunately, the

TABLE 3. Film Stretching Variables and Birefringence

Polymer	Casting solvent	Stretching medium	Percent elongation	Birefringence
I	TFE	Air (200°C)	5	a
		Steam	170	0.05
		o-Dichlorobenzene (179°C)	3	a
II	CHCl <sub>3</sub> /MeOH	Air (200°C)	231	0.16
		Steam	220	0.12
		DMAC (165°C)	200	0.17
		o-Dichlorobenzene (179°C)	170	0.15
III	CHCl <sub>3</sub> /MeOH	Air (200°C)	38	0.04
		Steam	172	0.18
		DMAC (165°C)	150	0.09
		o-Dichlorobenzene (179°C)	147	0.04
IV	LiCl/DMAC	Air (200°C)	21	0.15
		Steam	30	0.23
		o-Dichlorobenzene (179°C)	20	0.15

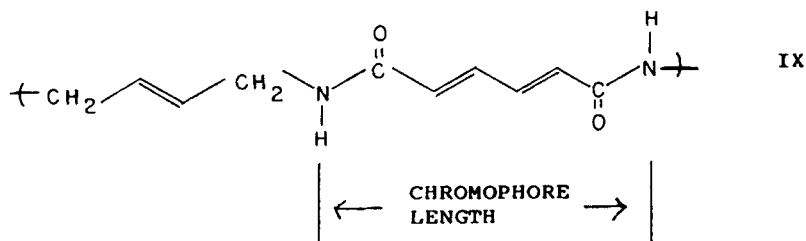
<sup>a</sup> Too low to measure.

choice of solvents for all of the muconic-acid-containing Polymers VI-IX and Polymer IV was limited to trifluoroethanol and strong acids, such as trifluoroacetic and sulfuric acid, which severely limited our ability to change processing conditions. Films of these polymers were too highly scattering to be characterized.

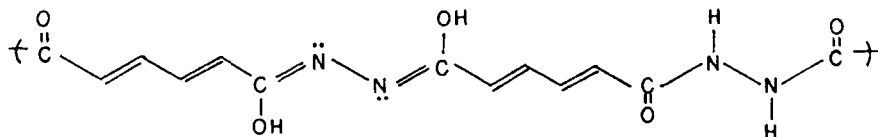
In regard to elongation, the best results of many attempts to stretch polymer films are shown in Table 3. The data clearly show that steam is the best stretching medium, consistently generating the highest elongation. The piperazine-containing polymers (I-III) were much easier to elongate than Polymer V; they could be stretched to more than 100% while the elongation of the latter did not exceed 30%. This behavior is difficult to rationalize since both types of polymers have approximately equal rigidity.

The birefringence data of the four polymers are also difficult to explain. For example, the birefringence of Polymer I increased only slightly up to 170% elongation ( $\Delta\eta = 0.05$ ). A similar result was obtained for Polymer III when stretched to approximately 150% in either DMAc or *o*-dichlorobenzene ( $\Delta\eta = 0.09$ ). However, when the latter was stretched in steam to 170% elongation, it exhibited a birefringence of 0.18. Polymer II seemed to behave normally in all stretching media; its birefringence increased linearly with elongation up to a maximum value of 0.17. Polymer V shows the highest birefringence of all ( $\Delta\eta = 0.23$ ) even though it exhibits the lowest elongation.

The fact that polydimethylmuconic hydrazide (V) exhibits higher birefringence than any of the aliphatic polyamides investigated was anticipated for several reasons, the first of which is absorptivity. Polyamides containing piperazine and homologs (I-III and VI-VIII) and 1,4-butenediamine (IV and IX) are colorless because the lowest-energy chromophore of each of them has two double bonds in conjugation with two amide groups. The tetrahedral carbon(s) bonded to the amide-nitrogen prevents extended conjugation; Polymer IX, shown below, illustrates the point.



In the polyhydrazides, however, multirepeat unit conjugation is clearly possible due to bis-keto-iminol structures [12, 13].



#### CHROMOPHORE LENGTH UNDETERMINED

The absorption band of the resulting polymer tails beyond 400 nm, thus imparting a yellow color. Since refractive index and birefringence are affected by the proximity of the absorption bands of the material to the wavelength at which the measurements are made, i.e., there is index dispersion, we used a 589-nm light source for the measurement in an attempt to circumvent this problem. However, we believe that the higher birefringence of Polymer V is due at least in part to its absorptivity.

A second equally important reason for the higher birefringence of Polymer V is also related to its extended conjugation. Specifically, the  $\pi$ -electrons, which lie along the polymer backbone, contribute significantly to the longitudinal polarizability but make very little contribution to the transverse polarizability. Conversely, the polyamides contain these highly polarizable electrons only in the muconic acid residue, and, in addition, the piperazine residues make significant contributions to the transverse polarizability.

The refractive index and polarizability of Polymer V are listed in Table 4 and compared to several related polymers. Polymer X, poly-muconic hydrazide, which we were unable to prepare in high molecular weight, has a higher polarizability than Polymer V because the  $\alpha, \alpha'$ -dimethyl groups of the latter contribute to the transverse polarizability. Polymers XI and XII, which contain biphenyl diamines with limited conjugation but high electron density, have polarizabilities which are nearly twice that of Polymer V. Concomitantly, much higher refractive index values were also exhibited by these polymers [3]. It must be concluded that the highly polarizable, extended  $\pi$ -electron system of Polymer V cannot exceed the polarizability of the electron-rich aromatic rings of Polymers XI and XII.

#### CONCLUSIONS

Methyl substitution, particularly on the acid residue, significantly enhances the solubility of muconic acid-containing aliphatic polyamides and hydrazides. The high molecular weight and wide range of processing conditions are directly attributable to this property.



TABLE 4. Comparison of Refractive Index and Polarizability Data<sup>a</sup> of Muconic Acid-Containing Polymers

Structure	$\Delta\alpha^b$	$n_{\text{iso}}^c$
<p style="text-align: center;">V</p>	0.775	1.68 <sup>d</sup>
<p style="text-align: center;">X</p>	0.853	-
<p style="text-align: center;">XI</p>	1.434	1.91 <sup>d</sup>
<p style="text-align: center;">XII</p>	1.488	1.77 <sup>e</sup>

<sup>a</sup>The procedure for determining polarizability is given in Ref. 3.

<sup>b</sup> $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$  = repeat unit polarizability. Units are  $10^{-23}$  cm<sup>3</sup>.

<sup>c</sup> $n_{\text{iso}}$  = isotropic refractive index.

<sup>d</sup>Becke line analysis at 589 nm.

<sup>e</sup>Brewster angle at 633 nm.

The polyamides are colorless due to limited conjugation, and the polyhydrazides are yellow because of extended conjugation. Extended conjugation contributes to the longitudinal polarizability which, on the macroscopic scale, enhances the refractive index and birefringence. The polarizability of polymuconic hydrazides does not, however, exceed that of the aromatic polyamides.

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