For the both isotactic and the syndiotactic polymerization, the coordinated anionic mechanism might be most probable. In the isotactic polymerization by the ethyldivinyleniminomagnesium, bis(divinylenimino)magnesium, and bromopentamethyleniminomagnesium, the polymers formed were 100% isotactic independent of the polymerization conditions. This indicates that steric control in the propagating chain is extremely intense, which suggests the coordination of the monomer to the catalyst. On the other hand, in the syndiotactic polymerization, the syndiotacticity increased as the polymerization temperature decreased. This phenomenon can be explained by the theory of the free anion propagating chain end. However, the experimental results that the polymer obtained in toluene has comparable or higher syndiotactic units compared with that obtained in tetrahydrofuran or diethyl ether are not fully consistent with the theory of free anion propagating species. Accordingly, the steric control in the syndiotactic polymerization is probably ascribed to the special mode of the coordination of the monomer to the catalyst, which permits the explanation for the extremely high rate of the polymerization with high syndiotacticity.

As shown in Figures 5 and 6, in the polymerization of methyl methacrylate the final conversion decreased as the polymerization temperature increased in spite of the higher initial rate of polymerization. This can be reasonably explained as the result of the deactivation of the catalysts by the reaction between the carbonyl in the monomer and the catalyst.

The Chemical Synthesis and Properties of Stereoregular Poly-α-(1→6′)-anhydro-D-galactopyranose

T. Uryu, H. Libert, J. Zachoval, and C. Schuerch

Chemistry Department, State University College of Forestry at Syracuse University, Syracuse, New York 13210. *Received December 23, 1969*

ABSTRACT: A third highly stereoregular α-(1→6′)-linked polysaccharide has been prepared by phosphorus pentafluoride-catalyzed polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose. For optimum results a higher temperature (−60°) and higher concentration of monomer is necessary than has been used to polymerize the corresponding glucose and mannose derivatives. The resulting polymer, $[\alpha]^{25}\text{D}$ 103–105° (*c* 1, chloroform) has been debenzylated to give a parent polysaccharide $[\alpha]^{25}\text{D}$ 219° (corrected to theoretical carbon content: *c* 1, 10% LiOH–0.5% borate). The polysaccharide is insoluble in all solvents tested except aqueous lithium hydroxide and borate mixtures and dimethylformamide–N_2O_4 solutions. Periodate oxidation demonstrates that this polymer is as stereoregular as the previously synthesized glucan and mannan and is, therefore, of essentially pure α configuration.

Until recently linear polysaccharides of high anomeric purity have only been available from a few natural sources. It has not been possible to synthesize regular polysaccharides of controlled structure or to relate physical properties to structure in any systematic way. With the discovery that cationic polymerization of 1,6-anhydro sugar derivatives could be controlled to produce poly-α-(1→6′)-anhydro-D-gluco- and -mannopyranose,[1–6] it has become possible to study systematically the chemical synthesis and physical properties of diastereomeric α-(1→6)-linked polysaccharides and also to investigate the immunological and other physiological properties of the individual polymers. We wish now to report the synthesis of poly-α-(1→6)-anhydro-D-galactopyranose, a proof of its structure and stereoregularity and some striking differences in its solubility from that of the two previously synthesized linear polymers.[4–6]

1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose can be prepared by modified conventional methods.[2,7,8] However, yields are generally poorer in most steps and somewhat more pains must be taken than with the corresponding anhydromannose and -glucose.

The polymerization of this monomer occurs with phosphorus pentafluoride at −78° in methylene chloride as was the case with the mannose and glucose derivatives. Typical experiments are listed in Table I.

The yield of poly-α-(1→6′)-anhydro-2,3,4-tri-*O*-benzyl-D-galactopyranose was 8–59% after 100 hr with 2.5–20.0 mol % PF_5 as catalyst at −78°. In contrast with the glucose and mannose derivatives which gave yields of polymer over 90%, the galactose derivative gave relatively high conversions only at high catalyst concentration. However, stereoregularity improved and molecular weight increased with decrease in catalyst concentration in the same manner as with the glucose and mannose derivatives.

Many attempts were made to improve the conversion at −78° with only limited success. Recently, studies

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TABLE I
POLYMERIZATIONS OF 1,6-ANHYDRO-2,3,4-TRI-*O*-BENZYL-β-D-GALACTOPYRANOSE[a]

No.	Mol % to monomer (PF_5)	Mol % to catalyst (H_2O)	Monomer-to-solvent ratio, g/100 ml	Temp, °C	Time, hr	Conversion, %	$[\alpha]_D$	φ	$[\eta]$[e]
1	2.5		33	−78	100	8.0	103.5[b]	448	0.59
2	5.0		33	−78	100	27.4	103.0[b]	446	0.45
3	7.5		33	−78	100	36.2	102.5[b]	443	0.43
4	10.0		33	−78	100	40.2	101.5[b]	439	0.39
5	10.0		33	−78	100	37.2	101.8[b]	441	0.39
6	20.0		33	−78	100	59.0	101.6[b]	439	0.35
7	20.0		33	−78	100	58.5	101.4[b]	439	0.36
8	40.0		33	−78	100	72.5	98.0[b]	424	0.23
9	20.0	15.0	33	−78	100	68.4	99.2[b]	429	0.27
10	20.0	8.0	33	−78	100	60.0	100.4[b]	434	0.24
11	20.0	30.0	33	−78	100	48.6	100.2[b]	433	0.19
12[d]			33	0	100	32.0	42.2[b]	183	0.05
13	5.0		33	−60	100	52.2	102.6[c]	444	0.26
14	7.5		33	−60	100	55.8	102.5[c]	443	0.25
15	10.0		33	−60	100	59.2	102.2[c]	442	0.27
16	20.0		33	−60	100	68.4	100.3[c]	433	0.22
17	5.0		33	−60	150	33.4	103.1[c]	446	0.25
18	5.0		33	−60	150	42.2	101.7[c]	440	0.33
19	2.5		63	−60	100	66.4	104.3[c]	451	0.46
20	5.0		63	−60	100	80.7	103.6[c]	448	0.43
21	7.5		63	−60	100	85.8	103.1[c]	446	0.48
22	0.9		100	−60	100	0			
23	1.3		100	−60	100	66.6	104.8[c]	453	0.53
24	2.5		100	−60	100	68.2	104.6[c]	452	0.46
25	5.0		100	−60	100	82.8	104.8[c]	453	0.45
26	7.5		100	−60	100	85.2	104.6[c]	452	0.35
27	5.0		120	−60	100	69.8	104.7[c]	453	0.39
28[f]	2.5		100	−60	100	78.8	105.1[c]	454	0.39
29[f]	5.0		100	−60	100	82.8	104.2[c]	450	0.39

[a] 0.5-g monomer scale. [b] $[\alpha]_D$ determined in chloroform, *c* 1 g/100 ml, at 20°. [c] $[\alpha]_D$ determined in chloroform, *c* 1 g/100 ml, at 25°. [d] 20 mol % catalyst $AgPF_6$–CH_3COCl, solvent CH_3NO_2. [e] Extrapolated from viscosity determinations in chloroform at 25°, *c* 0.5, 0.75, 1.0 g/100 ml. [f] Methylene chloride as solvent was purified by use of sodium mirror.

on other anhydro sugars,[9] notably anhydro disaccharides, revealed that a higher temperature of polymerization enhanced the rate of polymer formation and forcing conditions of high catalyst concentration were then not necessary. A higher temperature (−60°) was, therefore, tested and the results are shown in Table I. The conversion improved to 52–68% in reactions with 5.0–20.0 mol % catalyst in the monomer-to-solvent (weight to volume) ratio of 33%, but the molecular weight was considerably lower than that of the polymers obtained at −78°. As with the mannan derivative,[5] conversion was somewhat decreased with reaction times over 100 hr (Table I, *cf.* no. 13 and 18).

It eventually became clear that the rate of propagation of the galactose derivative was much less than that of levoglucosan tribenzyl ether for at least 95% of the latter was converted to polymer in less than 24 hr under conditions (Table I, no. 13 and 17) which gave only 33% of the galactan in 50 hr and 52% in 100 hr. Any impurity present in the medium which causes termination or chain transfer of propagating ions would thus be expected to limit the molecular weight of the galactan more severely. The monomer-to-solvent ratio was, therefore, increased and higher ratios (63 and 100% [grams of monomer/milliliter of solvent]) were found to give higher conversions, optical rotations, and molecular weights (Table I, no. 19–27). At these concentrations we were able for the first time to polymerize a 1,6-anhydro sugar derivative with as little as 1.3 mol % of PF_5 (no. 23).

The fact that the conversion and molecular weight increased with increase in monomer-to-solvent ratio might indicate that the termination reaction was caused to a large extent by the reaction between propagating polymer cations and methylene chloride. The further purification of methylene chloride was, therefore, attempted by means of a sodium mirror (no. 28). Although conversion was apparently about 10% larger than that of a similar experiment (no. 24) in which sodium mirror was not used, a slight decrease in molecular weight was observed.

Debenzylation of the stereoregular poly-α-(1→6′)-anhydro-2,3,4-tri-*O*-benzyl-D-galactopyranose proceeded normally with sodium in liquid ammonia under conditions described previously.[4] The product, however, had totally unexpected solubility characteristics. In contrast to poly-α-(1→6′)-anhydro-D-glucopyranose and poly-α-(1→6′)-anhydro-D-mannopyranose, this polymer was soluble in neither water nor dimethyl sulfoxide. Neither was it soluble in cuprammonium or urea solutions, nor sodium or potassium hydroxide

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TABLE II

DEBENZYLATION OF POLY-α-(1→6′)-ANHYDRO-2,3,4-TRI-*O*-BENZYL-β-D-GALACTOPYRANOSE

	Poly-α-(1→6′)-anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose			Poly-α-(1→6′)-anhydro-D-galactopyranose		
No.	No. shown in Table I	$[\alpha]^{25}_{\mathrm{D}}$, deg	$[\eta]^{25}$	Yield of water insolubles, %	$[\alpha]_{\mathrm{D}}$[a] obsd, deg	Periodate oxidation equilibrium $[\alpha]_{\mathrm{D}}$ (obsd), deg
DBGA-1	14, 15	$+102.5\sim102.6$	$0.25\sim0.27$	73.7[b]	+188.5[b]	
DBGA-2	13, 17, 19, 20	$+102\sim104$	$0.21\sim0.46$	94.4		+121.3
DBGA-3	16, 18[c]	$+100\sim102$	$0.22\sim0.33$	30.9[e]	+193.4	+126.4
DBGA-4	21, 23, 25	$+103\sim105$	$0.45\sim0.53$	85.8	+207.1	

[a] Determined in a 10% LiOH–0.5% borate solution, *c* 1 g/100 ml at 25°. [b] The corresponding values for water soluble product are 16.9% yield and $[\alpha]_{\mathrm{D}}$ 162.9°. [c] From 16 and 18 and two other similar preparations. The yield of debenzylated polymer was that recovered after reprecipitation from LiOH–borate solution.

solutions with or without added borate. Lithium hydroxide appeared to dissolve low molecular weight polymer and a combination of lithium hydroxide and borate was eventually found to dissolve the entire products. The greater degree of hydration of lithium ion in water makes this the most effective swelling and dispersing agent of the alkali metal ions. Unfortunately it is very difficult to regenerate an ashfree product from the borate solution.

A number of polar organic solvents in combination with N_2O_4 have been reported to be satisfactory cellulose solvents,[10] most recently dimethylformamide.[11] This latter combination also proved to be a solvent for the galactan, but on recovery the galactan contained 0.3% nitrogen.

It was also difficult to obtain an ashfree galactan following debenzylation. Successful results were obtained only when water was added to the ammonia solution after addition of ammonium chloride and prior to evaporation and the polymer suspension was dialyzed for 3 days with running distilled water. Elementary analyses were then very close to that calculated for a hemihydrate, as was the case with poly-α-(1→6′)-anhydro-D-gluco- and -mannopyranoses, but in our early experiments reproducibility was poorer than with the more soluble polymers.

The specific rotation of water-insoluble galactan in lithium hydroxide and borate was highly positive, $[\alpha]^{25}_{\mathrm{D}}$ $+189\sim-207$ (obsd), or $[\alpha]^{25}_{\mathrm{D}}$ $+199\sim219°$ when corrected to the theoretical carbon content 44.44% of polymer [*c* 1, 10% LiOH–0.5% borate]. These optical rotations appear to be quite sensitive to the optical rotation and molecular weight (viscosity) of the benzylated polymer from which they are derived. The highest optical rotation on the free polysaccharide was obtained from high molecular weight highly stereoregular benzyl ether (Table II). These high specific rotations indicate a great preponderance of α linkage, and the rotations are far in excess of that reported for α-(1→6′)-galactotriose, $[\alpha]_{5780}$ +144°,[12] or $[\alpha]_{5780}$ +147°[13] in water. As a further comparison, the rotation of the stereoregular mannan measured in lithium hydroxide–borate was $[\alpha]^{25}_{\mathrm{D}}$ +77° (corrected for 5.55% water content of polymer). The high stereoregularity could not be confirmed by analysis of nmr spectra measured in the same solvent, since the spectra were not sufficiently clear to give reliable data.

However, periodate oxidation of the glucan, mannan, and galactan can be used to correlate the stereoregularity of the three polymers since carbons 2 and 4 are oxidized to carbonyl functions. On periodate oxidation the specific rotation of a galactan solution became constant after 24 hr. The value for one galactan was $[\alpha]^{15}_{\mathrm{D}}$ +121.3° (obsd) and ±128.0° (corrected for theoretical carbon content of polymer). This polysaccharide was derived from benzyl ether of $[\alpha]^{25}_{\mathrm{D}}$ 102–104°. When the galactan reprecipitated (from LiOH–borate solution) was used (Table II) an $[\alpha]^{15}_{\mathrm{D}}$ +126.4° (obsd) or +133.4° (cor) was obtained. Under the same conditions the final value of a stereoregular mannan was +125.1° (obsd) and +132.5° (cor value based on 5.55% water content of polymer[5]). The final corrected value of the reprecipitated galactan was, therefore, identical with that of the stereoregular mannan within experimental error and it seems likely that the stereoregularity of this galactan is not less than 97% α.

It is to be expected that the polymerization of diastereomeric anhydro sugars will differ in rate, since the driving force of the polymerization probably derives from the unfavorable conformation and group interactions of the anhydro sugar, and the degree of strain in the molecule depends on the configurations of substituted carbons.[14] It is, however, surprising that three polysaccharides of identical anomeric form and linkage with configuration changed only on a single substituted carbon should all appear to form hemihydrates in the solid state and yet differ so widely in solubility.

In nature a number of α-(1→6′)-linked oligogalactosides are known.[15] Usually they are linked to sucrose through one of its primary hydroxyls.[16] They are often found as reserve foodstuffs in plant roots and it is reported that the higher homologs are found less frequently in nature.[16] It would be of interest to know whether the higher homologs have not been

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Table III

Typical Elementary Analysis Data of Galactan[a]

Sample	Obsd, % C	Obsd, % H	Obsd, % Ash	Remarks
DBGA-1	43.69	6.61	None or trace	Upper portion of freeze-dried polymer
DBGA-1	41.92	5.62	1.39	Lower portion of freeze-dried polymer
DBGA-2	41.55	5.95	None or trace	
DBGA-3	41.26	6.43	1.74	Purified by dissolving in LiOH–borate solution and reprecipitating
DBGA-4	42.17	5.95	None	
DBGA-4-P	41.18	6.04	None	Purified by dissolving in DMF–N_2O_4 and reprecipitating. Nitrogen 0.29%

[a] Calcd for $(C_6H_{10}O_5)_n$: C, 44.44; H, 6.22. Calcd for $[(C_6H_{10}O_5)_2 \cdot H_2O]_n$: C, 42.10; H, 6.48.

found because of their unexpected low solubility or whether the plants do not produce these linear highly insoluble galactans as reserve foodstuffs.

A few reports[12,13] of branched heteropolysaccharides from fungi and perhaps protozoa[17] speak of main chains of α-(1→6′)-linked galactopyranose residues. In these cases water solubility is imparted by the disorder introduced by branching, and the specific rotations are markedly lower than that of the synthetic polymer.

Experimental Section

Synthesis of Monomer. Penta-*O*-acetyl-β-D-galactopyranose was prepared *via* the sodium acetate, acetic anhydride procedure[18] and converted to phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside by a modification of Hudson's method for preparing phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside.[19] The product was crystallized twice to mp 116–119°, $[\alpha]^{25}_D$ +16.2° (lit.[20] $[\alpha]^{20}_D$ −0.7°). It was approximately 90% pure, contaminated with α anomer and was used in the synthesis without further purification.

Phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactoside, 58 g, was dissolved in 600 ml of anhydrous methanol and 12.0 ml of 0.1 *N* sodium methoxide solution was added to this solution with stirring, followed by heating at 98° for 2 min. The reaction mixture was then evaporated under reduced pressure to give syrup or crude crystals (34.5 g) of phenyl β-D-galactoside. Phenyl β-D-galactoside was cyclized to form 1,6-anhydro-β-D-galactopyranose (*cf.* Hudson's method[7]) as follows. The crude crystals (34.5 g) were dissolved in 850 ml of 2.6 *N* KOH solution and refluxed for 24 hr. After careful neutralization with 3 *N* sulfuric acid, the mixture was filtered to remove potassium sulfate that precipitated and evaporated to dryness. The residue was extracted by refluxing with absolute ethanol for 1 hr. The hot solution was filtered and evaporated to syrup or crude crystals (19.0 g).

The crude 1,6-anhydro-β-D-galactopyranose (19.0 g) was acetylated according to the method of Wolff,[21] by mixing with 50 ml of acetic anhydride and 75 ml of pyridine and the solution was kept at room temperature overnight. It was then concentrated *in vacuo* and the residue dissolved in chloroform. The chloroform solution was washed with water and dried over $MgSO_4$. After evaporation, most of the syrupy product was dissolved in a minimum quantity of ether and allowed to stand at room temperature. After unconverted insoluble phenyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside was separated, the supernatant was diluted with hexane and the product was crystallized. Recrystallization from isopropyl alcohol gave 1,6-anhydro-2,3,4-tri-*O*-acetyl-β-D-galactopyranose (12.0 g) of mp 73–74°, $[\alpha]^{25}_D$ −5.2° (*c* 1, chloroform); lit.[22] mp 74°, $[\alpha]^{21}_D$ −5.6° (*c* 1.4, chloroform). Crystallization from 1-chloropentane was later found to be more satisfactory. The yield of 1,6-anhydro-2,3,4-tri-*O*-acetyl-β-D-galactopyranoside based on phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactoside was 31%.

Benzylation of 1,6-anhydro-2,3,4-tri-*O*-acetyl-β-D-galactopyranose was carried out by previously reported[2] techniques at both 95 and 105°. The crude product was crystallized from isopropyl alcohol. White crystals formed from a yellow oil by keeping in a refrigerator for a few days. The crystals were collected by filtration. Crystallization of the remaining yellow oily product was repeated several times from isopropyl alcohol. Recrystallization was performed twice in absolute ethanol to give 35–45% yield.

The structure of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose was confirmed by infrared and nmr spectra. The product had mp 55–56°, $[\alpha]^{25}_D$ −46.1° (*c* 1, $CHCl_3$).

Polymerization and Recovery of Polymers. These procedures were carried out as described previously.[6]

Debenzylation of Polymer and Isolation of Polysaccharide. Polymer (Table I, no. 21, 23, and 25, 1.0 g) was dissolved in 20 ml of 1,2-dimethoxyethane and the solution was added to 100 ml of liquid ammonia containing 1.5 g of sodium at −78°. After 3 hr, ammonium chloride was added until the blue color completely disappeared and then about 30 ml of distilled water was added. After evaporation of ammonia under a stream of nitrogen, the debenzylated polymer suspension was washed several times with methylene chloride and the suspension was dialyzed for 3 days with running distilled water. The polymer was filtered and freeze-dried from doubly distilled water, yield 0.32 g (86%). A summary of similar debenzylations is given in Table II.

Purification of galactan was attempted by dissolving it into 10% lithium hydroxide–0.5% borate solution, filtering, and then precipitating from acetic acid–ethanol mixture. The polymer was washed successively with 70% ethanol and 100% ethanol several times each and freeze-dried from doubly distilled water (Table III).

Periodate Oxidation. Galactan (15 mg) and 2 ml of doubly distilled water were put in a 5-ml volumetric flask. A 3-ml sample of sodium periodate solution (30 g/l.) was

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introduced to the volumetric flask to form exactly 5 ml. After 4 hr, the solution was clear and 1 ml was put into a polarimetric cell. The solution was kept in a dark, cool (15–20°) place and optical rotations were determined at intervals thereafter for 96 hr. Periodate oxidation of stereoregular mannan was carried out under the same conditions as that of the galactan. The final observed optical rotation (constant from 24 to 96 hr) was α_D (obsd) +0.410 and the specific rotation (based on original galactan corrected to 44.44% C) was $[\alpha]^{20}{}_D$ +133°.

Acknowledgment. The present work has been supported by Research Grant GM06168 of the Division of General Medical Sciences, National Institutes of Health. The authors acknowledge the assistance of Mr. Ronald J. Eby.

Synthesis and Properties of Azoaromatic Polymers

F. Agolini and F. P. Gay

Film Department, E. I. du Pont de Nemours and Company, Inc., Experimental Station Laboratory, Wilmington, Delaware. *Received February 17, 1970*

ABSTRACT: Aromatic polyimides containing an azo link show reversible photo and thermal contractile behavior. The effect appears to be associated with *trans* $\rightleftarrows$ *cis* isomerization in the noncrystalline regions but the rate of the contraction or expansion is controlled by a process other than the isomerization.

Polymers containing the azoaromatic linkage were studied earlier.[1] The main objective at that time was the preparation of polymeric azo dyes that might have advantages over natural pigments and ordinary dyes. Azoaromatic polyesters were prepared[2] by condensation of 4,4′-dicarboxyazobenzene with phenols. The preparation of aromatic azopolymers by oxidation of diamines has been reported.[3] This work was improved and expanded by Bach.[4] The preparation of polyimides from azophthalic dianhydride and aromatic and aliphatic diamines was recently disclosed.[5]

Our interest in azoaromatic polymers came from the belief that such polymers could show good thermal stability, uv absorption, and *cis–trans* isomerism.

Experimental Section

Monomers. The azo monomers were prepared by standard paths.[6] Purification of monomers was by multiple recrystallization and vacuum sublimation to constant properties. Polymerization to give polymers of good inherent viscosity was the primary test of purity.

Solvent. Dimethylacetamide was purified by distillation from calcium hydride onto Linde Molecular Sieve 5A (fired at 500°) under dry nitrogen. It was stored over the desiccant at least 24 hr prior to use.

Polymerizations. Typical examples of the polymerization methods used are as follows.

Solution Polymerization of 4,4′-Diaminoazobenzene and Pyromellitic Dianhydride. 4,4′-Diaminoazobenzene (2.245 g) was dissolved in 50 ml of anhydrous dimethylacetamide and pyromellitic dianhydride (2.30 g) was added in portions. When the polymerization was complete the polyamic acid solution was cast on a glass plate with a 25-mil doctor knife and converted to polyimide by immersion for 1 hr in a benzene–acetic anhydride–pyridine bath. The red film was stripped from the plate, clamped on a frame, and dried in air 30 min at 180°, then 30 min at 300°.

Results and Discussion

With monomers of adequate purity, the polymerizations proceeded well. The properties of two polymers are shown in Table I.

The ultraviolet spectra of thin films (~500 Å) on quartz plates show absorption characteristic of model azoaromatics. Figure 1 gives such a spectrum of 4,4′-diphenylazopyromellitimide polymer (PN_2P-PI) with the spectrum of the parent diamine in ethanol for comparison. The coalesced doublet of the polymer was resolved on the Du Pont curve analyzer to give maxima at 3440 and 3040 Å ($\Delta\nu$ = 2300 cm^{-1}). In the parent diamine, the short wavelength absorption dominates while in the polymer the longer wavelength absorption is dominant. We observe that the areas under the two curves in the polymer change from a ratio of 10:1 at room temperature to 8:1 at 200°.

The polymer is semicrystalline (Figure 2) and has a repeat unit of 18.3 Å which is that calculated for the imide unit in the *trans* configuration. This restricts the *cis* configuration to the disordered or amorphous regions.

In the process of preparing films for measurement, an unusual phenomenon was seen. Normally when one dries or heat treats a film it will expand in the heating stage (some shrinkage can occur) and contract on cooling to give taut films. With many of these polymers it was observed that the films became taut when heated and slackened on cooling.

Two kinds of experiments were performed—at constant length and constant stress. In the constant-length experiments, a strain gauge measured the stress imposed on a film sample when exposed to heat or light. Figure 3 shows the curve obtained on exposure of a PN_2 P-PI film to an infrared lamp. Temperatures measured at the film surface were ~200°. A curve for

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