(20) After the completion of this work, the latest revision of the X-ray data on subtilisin BPN showed that the two regions 175–177 and 195–199 are also part of β regions (J. Kraut, private communication). Thus, of the 14 extra regions that are predicted to be helical, *all* are experimen-

tally found to be part of β regions. This reinforces the conclusions of this paper.

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Polybenzazoles Containing 2-Benzimidazolyl Side Groups

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ABSTRACT: 1,2-Benzoylenebis(benzimidazoles) were allowed to react with tetrafunctional nucleophilic compounds [bis(o-phenylenediamines), bis(o-aminophenols), and bis(o-aminothiophenols)] in poly(phosphoric acid) (PPA) to prepare polybenzimidazoles (PBI), polybenzoxazoles (PBO), and polybenzthiazoles (PBT) containing 2-benzimidazolyl side groups. The introduction of 2-benzimidazolyl side groups leads to the formation of thermally stable polybenzazoles which are soluble in different organic solvents.

Introduction of thermally stable side groups in macromolecules is the most efficient route to improve solubility and, hence, tractability of rigid-chain polymers.¹ Thus, the introduction of phenyl substituents in polyphenylenes,² polyquinoxalines,^{3,4} and polybenzimidazoles⁵ considerably increases the solubility of these polymers; it should be noted that the introduction of nonpolar phenyl substituents decreases in most cases the softening temperatures of the polymers. Therefore, we have made an attempt to increase the solubility of the rigid-chain polymers by introduction of the polar 2-benzimidazolyl side groups in these macromolecules. Aromatic polybenzazoles (PBI, PBO, and PBT) containing 2-benzimidazolyl substituents have been studied for this purpose. These polymers were synthesized by the reaction of 1,2-benzoylenebis(benzimidazoles) with tetrafunctional nucleophilic compounds—bis(o-phenylenediamines), bis(o-aminophenols), and bis(o-aminothiophenols). The synthesis of polybenzazoles with 2-benzimidazolyl substituents was based on the ability of the CO-N< bond of the benzovlenebenzimidazole ring to cleave easily with o-phenylenediamine.6,7

Model Compounds

Prior to polymer synthesis model reactions and compounds were studied to determine the most favorable conditions for polymerization reactions and the structure of the resulting polymers. The model reactions were especially necessary, as the cleavage of 1,2-benzovlenebis-(benzimidazole) was previously carried out only by treatment with o-phenylenediamine in the melt⁶ while terephthaloylenebenzimidazole was cleaved with o-phenylenediamine in nitrobenzene.7 Performance of this process in PPA showed that under these conditions a purer end product, o-phenylenebis(benzimidazole), is formed in almost quantitative yield. Since the high yields in these reactions make possible the preparation of high molecular weight polymers and since the polycyclocondensation in PPA is one of the most suitable methods for polyheteroarylene synthesis,^{8,9} we have chosen PPA as the preferred reaction medium.

We extended the reaction of 1,2-benzoylenebis(benzimidazole) with *o*-phenylenediamines to other o-substituted anilines¹⁰—*o*-aminophenol and *o*-aminothiophenol—thus showing the general character of the reaction which may be represented by



More complex model compounds were prepared by the reaction of 1,2-benzoylenebis(benzimidazole) with bis(o-phenylenediamines), bis(o-aminophenols), and bis(o-aminophenols)



On the other hand, bis-model compounds were synthesized by the reaction of 1,2-benzoylenebis(benzimidazoles) with *o*-phenylenediamine, *o*-aminophenol, and *o*-aminothiophenol.

 Table I

 Model Compounds of General Formula



						Uv							
Com-		Formula of Model	Vield		·	Foun	d (%)			Calc	d (%)		Spectra ^a
pound	Х	Compound	(%)	$Mp \ (^{\circ}C)$	C	н	N	s	С	H	N	s	$\lambda_{\max}, m\mu$ (log ϵ)
V	NH	$C_{20}H_{14}N_4$	95	440 (dec)]	Literatu	ure data	6			$\begin{array}{c} 233 \ (4.44) \\ 282 \ (4.38) \end{array}$
VI	0	$C_{20}H_{13}N_{3}O$	90	240-241	77.25	4.36	13.85		77.15	4.21	13.50		$\begin{array}{c} 303 \ (4.35) \\ 229 \ (4.41) \\ 281 \ (4.32) \end{array}$
VII	S	$\mathbf{C}_{20}\mathbf{H}_{13}\mathbf{N}_{3}\mathbf{S}$	90	216–217	73.06	4.08	12.73	9.88	73.37	4.00	12.83	9 .80	318 (4.45) 243 (4.54) 298 (4.46) 322 (4.50)

^a Uv spectra are obtained in concentrated H_2SO_4 (c 10⁻⁵ M).



General properties of the resulting model compounds are given in Tables I-III.

All model compounds were prepared in high yields (85– 95%) and their structures were confirmed by the elemental and spectral analyses. The ir spectra of all model compounds contained an absorption band at 1630–1600 cm⁻¹ characteristic of C==N and C==C stretching of the benzazole ring and a broad band at 3600–2200 cm⁻¹ characteristic of NH stretching of the benzimidazole. The ir spectra of compounds containing benzoxazole units show clearly defined bands at 1060 cm⁻¹ assigned to the vibrations of this ring.¹¹ The uv spectra of the model compounds were nearly identical.

In spite of the fact that the model compounds melt in narrow ranges and at high temperatures, it is possible that some of them, and particularly compounds based on 1,2-benzoylenebis(benzimidazoles), are mixtures of gèometrical isomers. Isomer formation can be explained by the fact that the 1,2-benzoylenebis(benzimidazole) starting materials are not individual compounds. Thus, the product (I) of the reaction of pyromellitic dianhydride with o-phenylenediamine is a mixture of cis and trans isomers,¹² likewise the 1,2-benzoylenebis(benzimidazoles)



from other dianhydrides can also be considered as mixtures of isomers



The products of the reaction of 1,2-benzoylenebis(benzimidazoles) with o-substituted anilines are, therefore, also isomer mixtures



Figure 1. Isothermal weight loss curves of polybenzimidazoles at 425° in air.



Synthesis and Investigation of Polymers

Synthesis of polybenzazoles containing 2-benzimid-



Figure 2. Isothermal weight loss curves of polybenzazoles at 400° in air.

azolyl substituents in the ortho positions to the main chains was conducted by one-stage reaction of 1,2-benzoylenebis(benzimidazoles) with aromatic tetrafunctional nucleophilic compounds (bis(o-phenylenediamines), bis(oaminophenols), and bis(o-aminothiophenols)) in PPA¹³⁻¹⁸



Since the properties of the end products largely depend on reaction conditions which must ensure the highest possible molecular weight and extent of cyclization, some common tendencies of polybenzazole formation in PPA (effect of monomer concentration, reaction temperature, and duration) were studied on the reaction of 3,3',4,4'tetraamino(diphenyl ether) with 1,2-benzoylenebis(benzimidazole) (IV); optimum conditions were as follows: reaction temperature 200° for 3–6 hr followed by 220° for 1–2 hr; total concentration of the starting reagents was ~ 20 wt %. All polybenzazoles were synthesized under these conditions. The properties of the resulting polymers are given in Tables IV-VI.

The structure of the polymers was confirmed by the identity of uv and ir spectra of polybenzazoles and the corresponding model compounds. The absence of absorption bands at $1720-1700 \text{ cm}^{-1}$ assigned to -C(=O)— vibrations of the carboxyl groups and at $3500-3300 \text{ cm}^{-1}$

Table II Model Compounds of General Formula^a



						Anal.							Uv	
	Formula of				Found	d (%)	_	Calcd (%)				Spectra ^b		
No.	х	R	Compound	(%)	$Mp \ (^{\circ}C)$	С	Н	N	s	С	Н	Ν	s	$(\log \epsilon)$
VIII	NH		$C_{40}H_{26}N_8$	85	402-404	77.70	4.30	18.19		77.65	4.24	18.11		$\begin{array}{c} 233 \ (4.61) \\ 285 \ (4.47) \\ 316 \ (4.55) \end{array}$
IX	NH	0	$\mathbf{C}_{40}\mathbf{H}_{26}\mathbf{N}_{8}\mathbf{O}$	85	404-405	75.31	4.06	17.37		75.69	4.13	17.66		$\begin{array}{c} 243 \ (4.75) \\ 289 \ (4.61) \\ 320 \ (4.64) \end{array}$
x	NH	CH_2	$C_{41}H_{28}N_8$	95	382–384	78.09	4.41	17.71		77.83	4.46	17.71		243 (4.76) 293 (4.67) 325 (4.67)
XI	0	0	$C_{40}H_{24}N_6O_3$	95	279–281	75.72	3.91	13.42		75.46	3.80	13.20		226 (4.76) 278 (4.60) 326 (4.66)
XII	0	CH_2	$C_{41}H_{26}N_6O_2$	90	278-280.5	77.07	4.10	13.24		77.59	4.13	13.24		231 (4.59) 255 (4.34) 282 (4.49) 323 (4.61)
XIII	\mathbf{S}		$C_{40}H_{24}N_6S_2$	75	400402	73.55	3.45	12.92	9.59	73.59	3,71	12.88	9.82	216 (4,90) 272 (4.65) 355 (4.63)
XIV	S	0	$C_{40}H_{24}N_6S_2O$	9 0	378–380	71.44	3.41	12.49	9.57	71.83	3.63	12.57	9.59	225 (4.77) 280 (4.47) 298 (4.46) 337 (4.49)

^a In the syntheses of model benzoxazoles XI-XII and PBO, 3,3'-diamino-4,4'-dioxy compounds are used which gives rise to the formation of the 2,5-substituted benzoxazole ring. ^b Uv spectra are obtained in concentrated H₂SO₄ ($c \ 10^{-5} M$).

assigned to the vibration of free amino groups, which is characteristic for starting compounds, indicates complete conversion and cyclization.

Unfortunately, the elemental analyses data given in Tables IV-VI cannot be used to determine the structure of polymers, because even after thorough reprecipitation in all polymers there were found 2.5-3% of inorganic compounds—probably phosphoros salts. As a result only a limited number of elemental analyses data are given.

The introduction of 2-benzimidazolyl substituents in the ortho position to the main macromolecular chain has a varying influence on polymer solubility. While the solubility of polybenzoxazoles and polybenzthiazoles in polar solvents increases considerably, there are no marked changes in polybenzimidazoles solubility due to the presence of a 2-benzimidazolyl group.

All the polybenzoxazoles and polybenzthiazoles shown in Tables IV-VI are, as a rule, readily soluble at room temperature in sulfuric and trifluoroacetic acids, N, Ndimethylacetamide, N-methyl-2-pyrrolidone, tetrachloroethane-phenol (3:1), m-cresol, and hexamethylphosphoramide forming 20% solutions. This is in contrast to the behavior of ordinary polybenzoxazoles and polybenzthiazoles which are soluble in sulfuric acid.¹¹

The improved solubility of polybenzazoles can also be attributed to the amorphism of the polymers (X-ray analysis) and irregularity of polymer chains as a result of possible geometrical cis,trans isomerism in the starting 1,2benzoylenebis(benzimidazoles). In principle the resulting polymers can contain, therefore, the following structural units where pendant benzimidazolyl groups in the main chain are at p,p'-(A), m,m'-(C) or m,p'-(B) positions (see Scheme I).

It was of particular interest to determine the coefficient of packing of the resulting polybenzazoles, since the presence of bulky side substituents could possibly cause loose packing of the polymer chains. The coefficient of packing was calculated from the density of films according to the formula¹⁹

$$K = \frac{dN_{\rm a}\Sigma\Delta V_{\rm i}}{M}$$

where d is polymer density, N_a , Avogadro number, $\Sigma \Delta V_i$, the true volume of the resulting polymer repeat unit (The true volume of polymer was calculated by the method described in ref 20.) and M, molecular weight calculated for the polymer repeat unit. The results are given in Table VII.

The calculations showed that these polybenzazoles have approximately the same coefficient of packing ($K_{\rm av} = 0.7$) as all other polymeric materials in the amorphous state ($K_{\rm av} = 0.695$ ($K_{\rm av} = 0.695$ has been determined by G. L. Slonimskii and A. A. Askadsakii^{19,20} by analysis of the experimental data for many aromatic polymers.)). The bulky 2-benzimidazolyl groups pendent to the chain do not effectively change the nature of packing in the amorphous state.

Good solubility of polymers in organic solvents gave us an opportunity to determine molecular weights, to produce films, and to investigate their physicomechanical properties (Table VIII).



It is evident from these data that the films of polybenzimidazoles and polybenzoxazoles are very strong, but not too elastic. The low elongations apparently result from strong interchain interaction of the 2-benzimidazolyl substituents which cause great rigidity of polymeric chains.

Introduction of bulky substituents has a different influence on thermomechanical behavior of the polybenzazoles. Thus, the softening temperatures of these polybenzimidazoles decrease slightly as compared with ordinary polybenzimidazoles while those of the polybenzoxazoles and polybenzthiazoles increase. This can probably be explained by competitive influence of the following factors; on the one hand, increased interchain interaction and decreased kinetic mobility due to 2-benzimidazolyl substituent and, consequently, increased rigidity of macromolecules and on the other hand by the presence of m,m', m,p', and p,p' isomers in the polymer chains. The isomerism was confirmed by comparison of experimental T_{soft} (Tables IV-VI) with calculated $T_{\rm soft}$. It was concluded that the structural units of the main chains were at the m,m' or m,p' positions to each other.²¹

The influence of the structure on thermooxidative stability of polybenzazoles synthesized was studied under dynamic and isothermal conditions.²² DTGA in air for all polymers studied indicated similar thermal stability and a 10% weight loss at 450–500°. No marked difference in behavior of polymers containing various flexibilizing groups (-O-, $-SO_2-$, $-CH_2-$, -CO-) both in benzoylenebenzimidazole and amine components was observed. Nevertheless, the DTGA data indicate somewhat higher stability for polybenzthiazoles compared to the polybenzimidazoles and polybenzoxazoles which have approximately the same thermal stability.

Isothermal degradation at 425° for 5 hr of polybenzimidazoles containing various flexibilizing groups



(Figure 1) showed that introduction of electron-donating groups (-O-, $-CH_2-$) in the macromolecular chains caused a considerably greater decrease in thermooxidative stability than that for electron-accepting groups ($-SO_2-$, -CO-). The thermal stability of PBI containing these flexibilizing groups decreased according to

$$-CO - > -SO_2 - > -CH_2 - > -O - -$$

A comparative investigation of thermooxidative stability of polybenzazoles having similar structures



under isothermal conditions in air at 400° (Figure 2) indicated that the order of stability is as follows: PBI > PBT > PBO. This differs from that obtained under dynamic conditions. Degradation of the polybenzazoles *in vacuo* under isothermal conditions ($400^{\circ}C/5$ hr) gave the same general results.

Decomposition rates calculated for 400° in vacuo were 0.16/min for polybenzoxazoles, 0.065%/min for polybenz-thiazoles, and 0.002%/min for polybenzimidazoles.

A higher thermal stability of polybenzimidazoles (compared to polybenzoxazoles and polybenzthiazoles) is thought to be attributed either to formation of a denser (compared to other polybenzazoles) intermolecular lattice or to formation of condensed systems



Degradation of polybenzazoles *in vacuo* in a broad temperature range showed practically no weight loss on heat-

ing up to 400° . Analysis of decomposition products (up to 500°) indicated that these polymers decompose to yield water, hydrogen, traces of ammonia, and low molecular weight compounds, primarily benzimidazole. At higher temperatures benzimidazole, nitriles of aromatic acids, benzene, diphenyl, water, hydrogen, ammonia, HCN, CO, and CH₄ were found.

The occurrence of benzimidazole in the degradation products may apparently be connected with the presence of benzimidazolyl side groups, and CO formation may be attributed to profound transformations in polymer structure at 600°, in which the benzene rings and ether oxygen take part. During degradation of one polybenzimidazole (PBI-I) which did not contain ether oxygen, CO traces were not detected. The absence of CO_2 in the gaseous degradation products of all the polybenzazoles studied is of particular interest. It is indicative of an homolytic mechanism of polymer degradation and a high degree of cyclization in these polymers.²³

Experimental Section

Starting Materials. All starting tetrafunctional nucleophilic compounds were synthesized and purified by the known methods.²⁴ Synthesis and purification of 1,2-benzoylenebis(benzimid-azoles) were conducted by the methods described earlier.^{10,17}

Model Compounds. Stoichiometric amounts of starting material in a tenfold (by weight) quantity of PPA were thoroughly mixed under argon at room temperature to yield a homogeneous mass which was then heated at 140-200° for 5 hr. The warm solution was poured into ice water with stirring, brought up to neutral or slightly alkaline medium with a 5% solution of sodium carbonate, and allowed to stand overnight. The precipitate was filtered off, thoroughly washed with water, and reprecipitated from a dimethylformamide solution with water, then twice crystallized from a DMFA-water mixture. The resulting product was sublimed under reduced pressure of 10^{-2} - 10^{-3} mm at a temperature close to the melting point of the sample. The properties of the model compounds are given in Tables I-III.

Synthesis of Polybenzimidazoles with 2-Benzimidazolyl Substituents. Equimolar amounts (0.02 M) of bis (o-phenylenediamine) and a 1,2-benzoylenebis(benzimidazole) in 8-10-fold (by weight) quantity of 116% PPA were mixed under argon at room temperature to yield a homogeneous mass. The bath temperature was then increased up to 200° over a 3-hr period; heating and stirring were continued at 200° for 3 hr and at 220° for 2 hr. The solution revealed a strong fluorescence. The warm reaction mixtures were poured into ice water, the precipitated polymer was filtered off and washed many times with water, and then allowed to stand in a 5% solution of sodium bicarbonate overnight. The polymer was again thoroughly washed with water, acetone, and alcohol and dried in a vacuum oven at 100°. Polybenzimidazole was dissolved in 20-fold (by weight) quantity of N-methyl-2pyrrolidone and precipitated in a 100-fold (by weight) quantity of methanol. This procedure was repeated five times. Polybenzimidazole was collected and dried in a vacuum oven at 100°. The yield of polymer was quantitative. Properties of polybenzimidazoles are given in Table IV.

Synthesis of Polybenzoxazoles with 2-Benzimidazolyl Substituents. Equimolar amounts (0.02 M) of bis (o-aminophenol) and a 1,2 benzoylenebis(benzimidazole) in a tenfold (by weight) quantity of 116% PPA were mixed under argon at room temperature to yield a homogeneous mass. The bath temperature was then increased up to 200° over a 3-hr period; heating and stirring were continued at 200° for 3 hr and at 220° for 2 hr. The solution revealed a strong fluorescence. The warm reaction mixture was poured into ice water, the precipitated polymer was filtered off and washed many times with water and then allowed to stand in a 5% solution of sodium bicarbonate overnight. The polymer was again thoroughly washed with water, acetone, and alcohol and dried in a vacuum oven at 100°. Polybenzoxazole was dissolved in a 20-fold (by weight) quantity of N-methyl-2-pyrrolidone and precipitated in a 100-fold (by weight) quantity of methanol. This procedure was repeated five times. Polybenzoxazole was collected and dried in a vacuum oven at 100°. The yield of polymer was quantitative. Properties of polybenzoxazoles are given in Table V.

Synthesis of Polybenzthiazoles with 2-Benzimidazolyl Substituents. 3,3'-Dimercapto-4,4'-diamino(diphenyl ether) dihydro-



321 (4.50) 359 (4.56) 235 (4.62) 290 (4.72)	316 (4.63) 240 (4.30) 296 (4.42)	340 (4.47) 245 (4.65) 296 (4.79)	338 (4.82)					d (%)	N		80 16.37 16.52	69 15.95		rom dynamic
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		9.51		9.34				•	I	5 5 5	0) 23) 23)	2) 7		ves. [°] T
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4.20	3.82	3.70	4.18	3.63 3.27		teral F			ax (mμ)	325 (4 325 (4 321 (4 320 (4	298 (4 295 (4 295 (4	295 (4 322 (4 307 (4 319 (4		nermon
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⁷ L (37 75	2 2) 7(32 3		azoles			Jv Spec); 250); 246); 250); 250); 243 (); 238 (); 239 (); 241 (); 240 (); 243 (); 242 ()		tained
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O ^s N ³⁰	24N6O3	${}_{\rm s}^{\rm A}{\rm N}_{\rm s}{ m S}_{20}$	SN ₈ O	4N ₆ O3 4N ₆ S2O	0 ⁻⁵ M).	ss of P		4. L	$(^{\circ}C)$	q	350 320 320 340	340 335 335 335 335	360 380	ted H ₂ S
$C_{40}H_{2}$	C40H	C40H	$C_{4}H_{2}$	C ₄ H ₅ C ₄ H ₅	04 (c 10	operti		5	$(dl/g)^a$	$\begin{array}{c} 0.71 \\ 0.56 \\ 0.97 \\ 0.29 \\ 1.95 \end{array}$	$\begin{array}{c} 0.92 \\ 1.90 \\ 2.12 \\ 0.55 \end{array}$	$\begin{array}{c} 2.70\\ 2.35\\ 1.82\\ 0.58\end{array}$	$0.60\\0.91$	ncentra do not
HN	0	ß	ΗN	S	ted H ₂ S	me Pr				- ⁶			.	as in col
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					ra are (<u>بر</u>	*	\succ	\succ	\succ	\succ	determ es (air.
XVIII	XIX	XX	IXX		^a Spect.				N0.	PBI-I PBI-II PBI-IV PBI-IV PBI-V	PBI-VI PBI-VII PBI-VIII PBI-IX	PBI-X PBI-XI PBI-XII PBI-XII	PBI-XIV PBI-XV	$^{a}\eta_{\mathrm{red}}$ is (TGA curv





Table VII	
Coefficient of Packing of Polybenzazoles Containing Benzi	imidazolyl Side Substituents

Str	uctural Formula of Polymer Unit	R	$\Sigma \Delta V_i$	Mol Wt	Polymer Density (g/cm ³)	Coef of Packing (K)
PBI-VI PBI-VII PBI-VIII	$ \begin{array}{c} \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	O CH2	557.4 556.0 574.0	632 648 646	1.301 1.336 1.331	0.691 0.703 0.712
PBO-IV	$ \begin{array}{c} - & & \\ - & & \\ $		560.7	651	1.340	0.696
PBT-II	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $		580.0	682	1.364	0.700

Table VIII Physicomechanical Properties of Films

Polymer	Structural Formula of Polymer Unit	R	Film Strength, σ (kg/cm ²)	Elonga- tion, ϵ (%)	Mol Wt of Polymer
PBI-VI PBI-VII PBI-VIII	$ \begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	O CH₂	1770 1720 1480	11 8 11	296 ,000ª
PBO-IV	$ \begin{array}{c} - & & \\ & $		1240	13	$250,000^{b}$
PBT-II			763	9	50,000

^a By light scattering. ^b By the Archibald method.

chloride (0.02 M) was heated under argon in 20-fold (by weight) of 116% PPA at 100-140° for 1 hr. After the hydrogen chloride evolution was completed, the transparent solution was cooled to room temperature. To the solution there was added 0.02 ${\cal M}$ of a 1,2-benzoylenebis(benzimidazole) and the mixture was stirred at room temperature to yield a homogeneous mass. The bath temperature was then increased to 200° over a 3 hr period; heating and stirring were continued at 200° for 3 hr and at 220° for 2 hr. The solution revealed strong fluorescence. The warm reaction mixture was poured into ice water, the precipitated polymer was filtered off and washed many times with water, then allowed to stand in a 5% solution of sodium bicarbonate overnight. The polymer was again thoroughly washed with water, acetone, and alcohol and dried in a vacuum oven at 100° . Polybenzthiazole was dissolved in 20-fold (by weight) of N-methyl-2-pyrolidone and precipitated in 100-fold (by weight) of methanol. This procedure was repeated five times. Polybenzthiazole was collected and dried in a vacuum oven at 100°. Properties of polybenzthiazoles are given in Table VI.

Investigations of Polymers. The curves of the dynamic ther-

mogravimetric, differential thermal, and differential thermogravimetric analyses were obtained on a derivatograph of the "Paulik, Paulik, and Erdel" type in air. The temperature increase rate was 4.5°/min.

The ir spectra of polymers and model compounds were taken with the UR-10 and UR-20 spectrophotometers by using powders pressed with KBr.

The uv spectra of polymers and model compounds were taken with a Hitachi spectrophotometer.

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Polydepsipeptides. III. Theoretical Conformational Analysis of Randomly Coiling and Ordered Depsipeptide Chains

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ABSTRACT: A theoretical conformational analysis of polydepsipeptides comprised either of alternating glycine and glycolic acid units or of alternating alanine and lactic acid units is described. Conformational energy maps of depsipeptide structural units are presented and compared to similar maps for peptide and lactic acid units. Asymptotic characteristic ratios $C_x = \langle r^2 \rangle_0 / x l^2$ of 2.27 and 3.80 were calculated for randomly coiling poly(glycine-glycolic acid) and poly(L-alanine-L-lactic acid), respectively. Conformational analysis of ordered poly(L-alanine-L-lactic acid) revealed a low energy helical form very similar to the standard right-handed polypeptide α helix. The polydepsipeptide helix is of low energy in spite of the fact that it is stabilized by one-half the number of hydrogen bonds of the polypeptide α helix. Statistical mechanical aspects of the helix-to-random coil transitions of polypeptides and polydepsipeptides are compared.

High molecular weight polydepsipeptides comprised of alternating L-valine and L-lactic acid residues have recently been synthesized in our laboratory.¹ A preliminary experimental and theoretical conformational analysis of these polymers has been described.¹

The conformational properties of polydepsipeptides are of particular interest because of the close analogy between such molecules and polypeptides. Since both the amide and ester groups strongly favor the planar trans conformation, the skeletal geometry of the two types of chains is very similar. The steric and dipolar factors that determine the conformational energy of peptides and depsipeptides are also closely related because of the close similarity of their structural units. There are differences between important features of these structural units, however. Comparison of the conformational properties of polypeptides and polydepsipeptides will allow assessment of the importance of these features in determining polymer chain conformation. In particular, hydrogen bonding characteristics of polypeptides and polydepsipeptides will differ since every second amide NH group of the former chains is replaced by an ester O atom of the latter. This replacement will primarily affect the nature of ordered polydepsipeptide structures stabilized by hydrogen bonds. Random chain dimensions will also be affected by elimination of certain steric interactions that involved the replaced amide hydrogen atom.

In this paper we describe our calculations of the conformational energies of the structural units of poly(glycineglycolic acid) and of poly(L-alanine-L-lactic acid). Theoretical values for the mean square end-to-end distance of unperturbed randomly coiling depsipeptide chains are reported. A theoretical analysis of ordered polydepsipeptide structures is also described.

Theoretical Methods

Structural Parameters. A polydepsipeptide chain segment is shown in Figure 1 with the repeating unit i, composed of an α -amino and an α -hydroxy acid residue, indicated. The amide and ester groups are assumed fixed in their planar trans conformation^{2,3} so that depsipeptide chain conformations are determined by the torsional angles ϕ_{ai}, ψ_{ai} and ϕ_{hi}, ψ_{hi} describing rotations about the N-C_i^{α} and $C_i^{\alpha}-C'$ skeletal bonds of the α -amino acid and about the O-C_i^{α} and C_i^{α}-C' skeletal bonds of the α -hydroxy acid, respectively, for each repeating unit i of the chain. Virtual bonds l_a and l_h of Figure 1 join consecutive C^{α} atoms.

For convenience of conformational energy calculations, the chain is divided into the structural units AA and HA that are also shown in Figure 1. Coordinate systems are fixed to amide and ester groups with their origins at C' and their x axes aligned along the C'-N or C'-O bonds. The y axes are directed in the plane of the amide or ester groups so that O = C' oxygen atoms have positive y coordinates. The z axes are chosen to complete right-handed orthogonal coordinate systems.

The bond angles and bond lengths used in the calculation are presented in Table I. They are essentially those derived by Flory and coworkers from analysis of the structure of model amides and esters.^{2,3}

The structure of the two units is quite similar, except for the skeletal bond angle at the ester oxygen atom of the α -