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#### **References and Notes**

- (1) F. C. De Schryver, Verh. Kon. Vlaam. Acad. Wetensch., Lett. Schone Kunsten Belg., Kl. Wetensch., No. 120 (1971).
- (2) F. C. De Schryver and G. Smets in "Polymer Chemistry," J. Jenkins and A. Ledwith, Ed., Academic Press, New York, N. Y., in press,
- (3) F. C. De Schryver, J. Feast, and G. Smets, J. Polym. Sci., Part A-1, 8, 1939 (1970).
- (4) F. C. De Schryver, N. Boens, and G. Smets, J. Polym. Sci., Part A-1, 10, 1687 (1972).
- (5) F. C. De Schryver, Pure Appl. Chem., 34, 213 (1973).
- (6) F. C. De Schryver, N. Boens, and G. Smets, J. Amer. Chem. Soc., in press.
- (7) One referee suggested that the propagation step via the triplet excited state could proceed via an intermediate

$$A^{3} + A^{0} \xrightarrow{k_{r}^{-1}} *A - A^{*} \text{ formation of an intermediate}$$
$$*A - A^{*} \xrightarrow{k_{r}^{-T}} 2A^{0} \qquad \text{dissociation of the intermediate}$$
$$*A - A^{*} \xrightarrow{k_{c}^{-T}} P' \qquad \text{product formation}$$

product formation

In this case the right-hand side of eq 1 and 3 should be multiplied by  $\Phi_D = k_c T / (k_c T + k_{-r} T)$ . Equation 5 rearranges to

$$1/\Phi_{\rm r}^0 = (1/2\Phi_{\rm ISC}\Phi_{\rm p}) + (k_{\rm d}^{\rm T}/2k_{\rm r}^{\rm T}\Phi_{\rm ISC}\Phi_{\rm p}[{\rm A}^0])$$

This would mean that the determined quantum yields for intersystem crossing (Figures 11 and 12) are in fact a product of  $\Phi_p \Phi_{1SC}$ . Since the value of  $\Phi_{1SC}$  could not be determined by an independent route no distinction can be made between the two mechanisms. However, in the photodimerization of N-butylmaleimide it has been shown that  $\Phi_{12}$  is close to unity.<sup>11</sup>

- (8) The degree of conversion p is calculated from the change in absorbance as a function of the irradiation time and equals 1 -- (OD)//  $(OD)_0$ , where  $(OD)_0$  is the absorbance at time  $t_0$  and  $(OD)_t$  is the absorbance at time t.
- (9) P. J. Wagner and I. Kochevar, J. Amer. Chem. Soc., 90, 2232 (1968).
- (10) P. J. Wagner and D. J. Bucheck, J. Amer. Chem. Soc., 92, 181 (1970).
- (11) J. Put and F. C. De Schryver, J. Amer. Chem. Soc., 95, 137 (1973).
- (12) E. L. Martin, C. L. Dickinson, and J. R. Rolands, J. Org. Chem., 26, 2032 (1961).
- (13) E. F. Ullman and P. Singh, J. Amer. Chem. Soc., 94, 5077 (1972).

# Polymerization of $\gamma$ -Benzyl L-Glutamate N-Carboxyanhydride with Metal Acetate-Tri-n-butylphosphine Catalyst System

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ABSTRACT: A novel type of catalyst, tri-n-butylphosphine-metal carboxylate (metal: Ni, Co, Cr, Cd, or Mg) catalyst system, was found for the polymerization of  $\gamma$ -benzyl L-glutamate N-carboxyanhydride. Molecular weights of polymers obtained with this type of catalyst depend on the nature of metal component of the catalysts and follow the order of Ni > Co > Cd > Mg > Cr. The polymers obtained with the nickel acetate-tri-nbutylphosphine catalyst system in higher than 90% yield have molecular weights larger than  $2 \times 10^5$  and relatively sharp molecular weight distributions: *i.e.*,  $\bar{M}_w/\bar{M}_n = 1.4-2.1$ .

Although a large number of papers had been published on the polymerizations of  $\alpha$ -amino acid N-carboxyanhydrides (NCA) using various kinds of catalyst such as water,<sup>2</sup> alcohols,<sup>3</sup> amines,<sup>4</sup> and alkali metal compounds,<sup>5-9</sup> only a few works had been published on the intended stereospecific and/or stereoelective polymerization.<sup>10-13</sup>

To realize the stereospecific and/or stereoelective polymerization of NCAs, it is necessary to search for the catalyst which is able to control effectively, in each step of the propagation reaction, the stereochemistry of addition of the monomer to the growing polymer end. During our explorative experiments, we found a novel type of catalyst, metal carboxylate-trialkylphosphine catalyst system. In these works,  $\gamma$ -benzyl glutamate NCA (BG-NCA) was selected as a monomer for testing most suitably the stereoregulating capacity of the catalyst, because  $poly(\gamma$ -benzyl glutamate) (P-BG) is known to dissolve easily in many kinds of solvents and is characterized by various types of physical methods.

### **Experimental Section**

Materials.  $\gamma$ -Benzyl L-glutamate N-carboxyanhydride (L-BG-NCA)<sup>14</sup> was prepared from  $\gamma$ -benzyl L-glutamate<sup>15</sup> (mp 170.5°). Since the NCA is unstable at high temperatures and to a contaminating moisture, both preparation and recrystallization (three times from chloroform-n-hexane and then four times from ethyl acetate-n-hexane) were carried out in a specially designed apparatus (Figure 1). In these operations, the supernatant liquid was transferred through a connecting glass tube equipped with a glass filter F with compressed nitrogen or argon from a cooled recrystallization vessel A (from -78 to  $-20^{\circ}$ ) to a vessel B. A suitable amount of solvent was poured into vessel A containing the crystalline NCA under a nitrogen or an argon atmosphere at room temperature to dissolve the NCA, while the glass filter in vessel A was set in the state of (b). The solution of the NCA in vessel A was cooled at -78° to crystallize the NCA. By repeating the recrystallization process, the NCA was purified until the Beilstein test became negative. In the case of L-BG-NCA, the yield was 80.0%, mp 92-93°,  $[\alpha]^{20}D = -17.1^{\circ}$  (c 3.32, ethyl acetate). Anal. Calcd for C13H13NO5: C, 59.31; H, 5.05; N, 5.44. Found: C, 59.49; H, 5.05; N, 5.28.

Tri-n-butylphosphine (n-Bu<sub>3</sub>P) was prepared by the method of Davies and Jones:<sup>16</sup> bp 144° (47 mm), nD 1.4549. Anal. Calcd for C12H27P: C, 71.21; H, 13.26. Found: C, 69.78; H, 13.26.

Triphenylphosphine (Ph<sub>3</sub>P) was recrystallized from benzene-diethyl ether (mp 80-81°).

 $Commercial \ reagent \ of \ Ni(OAc)_2 \cdot 4H_2O, \ Co(OAc)_2 \cdot 2H_2O,$  $Cd(OAc)_2 \cdot H_2O$ ,  $Cr(OAc)_2 \cdot H_2O$ , or  $Mg(OAc)_2 \cdot 4H_2O$  was used without further purification because of the recrystallization from usual solvents being difficult. Anal. Calcd for C4H14NiO8: C, 19.67; H, 5.62. Found: C, 19.64; H, 5.72. Calcd for C<sub>4</sub>H<sub>10</sub>CoO6: C, 22.55: H, 4.73. Found: C, 22.30; H, 4.73. Calcd for C<sub>4</sub>H<sub>8</sub>CdO<sub>5</sub>: C, 19.36; H, 3.22. Found: C, 19.76; H, 3.35. Calcd for C<sub>4</sub>H<sub>14</sub>MgO<sub>8</sub>: C, 22.40; H, 6.58. Found: C, 22.43; H, 6.59.

The complex,  $NiCl_2 \cdot 2(n-Bu_3P)$ ,<sup>17</sup> was recrystallized four times from ethanol: scarlet crystalline pellets, mp 46-47°. Anal. Calcd for C24H54Cl2NiP2: C, 59.3; H, 10.1. Found: C, 58.2; H, 10.3.

Purification of Solvents. All solvents were purified under a dry nitrogen or an argon atmosphere. Tetrahydrofuran was refluxed with metallic sodium for 48 hr and distilled, bp 66°.

Dioxane was refluxed with 10 vol % of 1 N HCl for 24 hr, allowed to stand over pellets of NaOH for 48 hr, and separated from aqueous layer. The acetate-free dioxane was refluxed with







Figure 2. A polymerization tube.



Figure 3. Relation observed between wave number of the band assigned to carboxyl group of  $M(OAc)_2 \cdot xH_2O$  and  $\tilde{M}_w$  for P-L-BG.

NaOH for 12 hr, with calcium hydride for 12 hr, and with metallic sodium for 12 hr. It was distilled from metallic sodium, bp  $101^{\circ}$ .

Chloroform was washed twice with concentrated  $H_2SO_4$ , washed three times with water, dried over  $Na_2CO_3$ , and then dried over  $P_2O_5$ . It was distilled from calcium hydride, bp 61°.

Ethyl acetate was washed three times with water and then dried over  $P_2O_5$ . It was distilled from calcium hydride, bp 77°.

*n*-Hexane was washed three times with concentrated  $H_2SO_4$ , washed with water, dried over CaCl<sub>2</sub>, refluxed with calcium hydride for 10 hr, and then distilled from metallic sodium, bp 67-68°.

Dichloroacetic acid was distilled under reduced pressure in the presence of one-third weight of concentrated  $H_2SO_4$ : bp 96.3° (20 mm),  $n_D 1.4654$ .

**Polymerization of L-BG-NCA.** All experiments were carried out under a nitrogen or an argon atmosphere. In procedure A the monomer (ca. 0.5 g) and the metal acetate were charged into a special polymerization tube (Figure 2), and the atmospheric air was replaced three times with dry argon. Dioxane (10 ml) was added to the tube using a syringe under an argon atmosphere, and the monomer was dissolved in the solvent with stirring at room temperature. After the solution was cooled to  $-78^{\circ}$ , n-Bu<sub>3</sub>P was added to the solution using a syringe. In procedure B Ni-(OAc)<sub>2</sub>·4H<sub>2</sub>O was allowed to react with n-Bu<sub>3</sub>P [Ni-P (atom-

Table I Specific Rotation of P-L-BG

Catalyst	$\mathbf{Solvent}^a$	$( imes 10^{-4})$	[α] <sup>20</sup> D (deg)
$\overline{\mathrm{Ni}(\mathrm{OAc})_2\cdot 4\mathrm{H}_2\mathrm{O}-n-\mathrm{Bu}_3\mathrm{P}}$	HCCl <sub>2</sub> COOH	14.7	-17.0
	$CHCl_3$	14.7	+15.3
$PhCH_2NH_2$	HCCl <sub>2</sub> COOH	3.34	- 16. <b>9</b>
-	$CHCl_3$	3.34	+16.0

<sup>a</sup> Concentration, 3.0 g/100 ml.

Table II Fractionation of P-L-BG

Fraction	Polymer (g)	$[\eta]^a$	${ar M}_{ m w}~( imes~10^{-5})$
1	0.466	13.5	6.1
2	4.1	9.86	5.3
3	1.23	4.7	3.5
4	0.008	3.2	2.9

<sup>a</sup> Measured in dimethylformamide at 20°.

Table III Polymerization of L-BG-NCA by M(OAc)<sub>2</sub>.xH<sub>2</sub>O*n*-Bu<sub>4</sub>P Catalyst System with Procedure A<sup>a</sup>

					_
${f M}({f OAc})_2\cdot xH_2{f O}\ (mmol)$	Yield (%)	$[\eta]^b$	$(\times 10^{-5})$	k' d	
$Ni(OAc)_2 \cdot 4H_2O$					
$(3.2 \times 10^{-2})$	92.0	2.80	5.64	0.375	
$Co(OAc)_2 \cdot 2H_2O$					
$(3.5  imes 10^{-2})$	94.8	2.16	5.28	0.430	
$Cd(OAc)_2 \cdot 2H_2O$					
$(4.2 \times 10^{-2})$	95.5	1.80	3,31	0.413	
$Cr(OAc)_2 \cdot H_2O$					
$(4.2 \times 10^{-2})$	74.0	1.00	1.71	0.413	
$Mg(OAc)_2 \cdot 4H_2O$					
$(3.6  imes 10^{-2})$	78.4	1.08	1.80	0.400	

<sup>a</sup> Polymerization condition:  $nBu_3P$ , 0.05 ml (0.21 mmol); L-BG-NCA, 0.50 g (1.91 mmol); solvent, dioxane 10 ml; temperature, 30°; time, 24 hr. <sup>b</sup> Measured in HCCl<sub>2</sub>COOH at 25.0  $\pm$  0.1°. <sup>c</sup> Calculated by equation  $[\eta] = 2.78 \times 10^{-5}$  $\overline{M}_{w^{0.57}}$  proposed by Doty *et al.*<sup>18</sup> <sup>d</sup> Calculated by equation  $\eta_{sp'c} = [\eta] + h'[\eta]^2c$ .

atom), 1:43] at 30° for 24 hr under a nitrogen atmosphere, and the brownish reaction mixture was added to the 10 wt % solution of the monomer in dioxane at 30° with stirring. In both procedures, the polymer solution obtained by polymerizing at a specified temperature and for a specified time was poured into 75% ethanol (200 ml) with vigorous stirring. The polymer obtained in either fibrous or colloidal state was separated from the supernatant liquid by filtering through a glass filter or by centrifuging. The polymer Was dried *in vacuo* at 50-60° for 12-24 hr. Anal. Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>3</sub>: C, 65.75; H, 5.93; N, 6.39. Found: C, 65.70; H, 5.90; N, 6.33.

**Physical Property of Polymer.** Intrinsic viscosity of polymer was measured in dichloroacetic acid solution at  $25.0 \pm 0.1^{\circ}$ , and molecular weight was calculated using an equation proposed by Doty et al.<sup>18</sup>  $[\eta] = 2.78 \times 10^{-5} M_w^{0.87}$ .

Ir spectrum was recorded using Jasco Model DS-402 spectrometer for thin film prepared by casting from chloroform solution of polymer on KBr plate. Ir spectrum of polymer obtained with metal acetate-n-Bu<sub>3</sub>P catalyst system agreed well with that with n-hexylamine.<sup>19</sup>

Specific rotations ( $[\alpha]^{20}D$ ) of L-BG-NCA and its polymer were measured using Yanagimoto Model ORD-185 and Jasco Model DIP-SL automatic polarimeter at 20° in 20-mm cells. Two different 20-mm cells were used for each sample in order to check the reproducibility. Optical rotatory dispersion (ORD) of polymer in dichloroacetic acid or CHCl<sub>3</sub> solution was measured using Yanagimoto Model ORD-185 or Jasco Model J-10 polarimeter at 20° in two different 20-mm cells. The results are shown in Table I. The  $b_0$  values of polymers calculated using an equation of Moffitt-Yang were -600 in both cases.

Molecular weight distribution was estimated in  $H_4$  furan solution using Simazu Model GPC 1-A type under the flow rate of 1



Figure 4. Polymerization with Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O-*n*-Bu<sub>3</sub>P catalyst with procedure A: ( $\bullet$ ) total yield; (O) [ $\eta$ ]. Polymerization condition: NCA, 1.91 mmol; *n*-Bu<sub>3</sub>P, 0.324 mmol; dioxane, 10 ml; 30°; 24 hr.



Figure 5. Polymerization with Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O-*n*-Bu<sub>3</sub>P catalyst with procedure A: (●) total yield; (O) [η]. Polymerization condition: NCA, 1.91 mmol; Ni salt, 2.20 × 10<sup>-3</sup> mmol; dioxane, 10 ml; 30°; 24 hr.

ml/min. The polymer was fractionated at  $25^{\circ}$  using CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH solvent system.<sup>20</sup> An example is shown in Table II.

### **Results and Discussion**

Polymerization of L-BG-NCA with  $M(OAc)_2 \cdot xH_2O$ *n*-Bu<sub>3</sub>P Catalyst System. Preliminary experiments showed that *n*-Bu<sub>3</sub>P has only a weak catalytic activity in contrast to the well-known catalytic activity of tri-*n*-butylamine. But the addition of a small amount of a metal salt, especially of a metal carboxylate, was found to increase, more than an order of magnitude, molecular weight of polymer (Table III).

The molecular weight of polymer obtained with metal acetate-*n*-Bu<sub>3</sub>P catalyst systems decreased in the order: Ni > Co > Cd > Mg > Cr. This dependence of polymer molecular weight on the nature of metal atom parallels with the polarity of CH<sub>3</sub>COO-M bond estimated by ir absorption frequency (Figure 3), relative rate constant of decarboxylation of acetone dicarboxylic acid catalyzed by a metal acetate,<sup>21</sup> and relative stability constant of the metal salt of an  $\alpha$ -amino acid.<sup>22</sup> The existence of these striking parallelisms suggests that the metal acetate plays a key role in this type of catalyst system.

Polymerization of L-BG-NCA with Ni  $(OAc)_2 \cdot 4H_2O$ *n*-Bu<sub>3</sub>P Catalyst System. Following these results, the polymerization of L-BG-NCA with Ni $(OAc)_2 \cdot 4H_2O$ -*n*-Bu<sub>3</sub>P catalyst system was studied using two different procedures. In procedure A, *n*-Bu<sub>3</sub>P was added with stirring to the suspension of Ni $(OAc)_2 \cdot 4H_2O$  and L-BG-NCA in dioxane. In procedure B, the reaction mixture prepared by reacting Ni $(OAc)_2 \cdot 4H_2O$  with *n*-Bu<sub>3</sub>P at 30° for 24 hr



Figure 6. Polymerization with Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O-*n*-Bu<sub>3</sub>P catalyst with procedure B: ( $\bullet$ ) total yield; (O) [ $\eta$ ]. Polymerization conditon: NCA, 1.91 mmol; Ni-*n*-Bu<sub>3</sub>P, 1:43 (mol/mol); dioxane, 10 ml; 30°; 24 hr.



Figure 7. Effect of monomer concentration on polymer molecular weight: ( $\bullet$ ) yield; (O) [ $\eta$ ]. Polymerization condition: NCA, 1.91 mmol; 30°; 24 hr.

under a nitrogen atmosphere in the absence of any added solvent was added to the dioxane solution of L-BG-NCA.

The effect of molar ratio L-BG-NCA:n-Bu<sub>3</sub>P:Ni(OAc)<sub>2</sub> on polymer molecular weight was studied by procedure A. When the molar ratio of L-BG-NCA to n-Bu<sub>3</sub>P was kept at 6, a maximum molecular weight was obtained at a molar ratio of n-Bu<sub>3</sub>P to nickel acetate of about 10 (Figure 4). When the molar ratio of L-BG-NCA to nickel acetate was kept at 87, a maximum molecular weight was obtained at a molar ratio of n-Bu<sub>3</sub>P to nickel acetate of about 11 (Figure 5). These experimental results indicate that the optimum molar ratio of L-BG-NCA:n-Bu<sub>3</sub>P:Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O for obtaining a high molecular weight polymer is about 80:10:1.

In contrast, polymerizations carried out using procedure B gave the following results (Figure 6). When the molar ratio of n-Bu<sub>3</sub>P to nickel acetate was kept at 43, in which nickel acetate dissolved completely in n-Bu<sub>3</sub>P, the molecular weight of polymer increased in the molar ratio of NCA to Ni salt up to about 600 and then decreased sharply.

Thus, the amount of nickel acetate required for forming the active catalyst species is definitely smaller in procedure B than in procedure A. This fact seems to indicate that only a small fraction of the nickel acetate used for polymerization acts effectively as a catalyst component due to its low solubility in the polymerizing medium and to suggest that the active catalyst species relates intimately to a nickel atom.

More detailed studies were carried out using procedure



Figure 8. Effect of temperature on yield and molecular weight of polymer: ( $\bullet$ ) yield; ( $\circ$ ) [ $\eta$ ]. Polymerization condition: NCA, 1.91 mmol; dioxane, 10 ml; 24 hr.



Figure 9. Gel permeation chromatography curve of polymer.  $\bar{M}_{w}$  = 2.8 × 10<sup>5</sup>; solvent, H<sub>4</sub>furan.

B for a most favorable monomer:catalyst ratio (L-BG-NCA:*n*-Bu<sub>3</sub>P:nickel acetate, 640:43:1). Molecular weight of polymer was almost constant over a rather wide range of monomer concentration (5-20%) and decreased sharply at lower concentrations (Figure 7). Also, it was nearly independent of polymerization temperatures up to 40° and decreased at higher temperatures (Figure 8). In these respects, this catalyst system contrasts with a typical anion-ic catalyst NaOCH<sub>3</sub>.<sup>14</sup> These differences observed in catalytic behavior are considered to indicate the characteristic property of nickel acetate-tri-*n*-butylphosphine catalyst system and probably reflect the difference in the polymerization mechanism and/or the effectiveness for suppressing any undesirable side reaction.

Some preliminary experimetal results showed that  $Ni(OAc)_2 \cdot 4H_2O-n$ -Bu<sub>3</sub>P system was a unique one among nickel salt-electron donor systems. NiCl<sub>2</sub> and nickel acetonate could not be replaced by  $Ni(OAc)_2 \cdot 4H_2O$ , and  $Ph_3P$ ,  $(EtO)_3P$ , and pyridine could not be replaced by n-Bu<sub>3</sub>P. These results combined with an important role played by the nature of metal-acetoxy bonding referred to above suggest that coordination of n-Bu<sub>3</sub>P to nickel atom activates metal-acetoxy bonding to some polarized state through which the reaction leading to the active catalyst species starts. According to this sense, the nature of an electron donor suitable for a component of this type of catalyst system seems to be considered to be limited to a rather narrow range.

Characteristics of the Polymer Obtained with Nickel

Table IV  $M_w/M_n$  of P-L-BG Prepared by Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O-*n*-Bu<sub>3</sub>P Catalyst System<sup>a</sup>

Sample	NCA:n- Bu <sub>3</sub> P:Ni	$(\times 10^{-4})$	$ar{M}_{ extsf{w}}/ar{M}_{ extsf{n}}{}^{ extsf{b}}$	
I	90:43:1	23.8	1.4	
II	190:43:1	25.8	2.1	

<sup>a</sup> Prepared by procedure B: L-BG-NCA, 0.50 g (1.91 mmol); temperature, 30°; solvent, 10 ml of dioxane; time, 24 hr. <sup>b</sup>  $M_w$  and  $\overline{M}_n$  were measured by viscosity and osmotic pressure, respectively.

Acetate-Tri-*n*-butylphosphine Catalyst System. The polymer obtained by polymerizing L-BG-NCA with  $Ni(OAc)_2 \cdot 4H_2O-n$ -Bu<sub>3</sub>P catalyst system was characterized by elemental analyses, in spectroscopy, optical rotation, ORD, and the monolayer method.<sup>23</sup> These results agreed well with those obtained by other catalysts.

A most characteristic property of the raw polymer is reflected in the sharp distribution of its molecular weight, in addition to its high molecular weight. This characteristic was observed for the asymmetrical narrow peak observed in the GPC curve (Figure 9) and in the fractionation result obtained with CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH solvent system (Table II), and for a low value of  $\overline{M}_w/\overline{M}_n$  (1.4-2.1) (Table IV). These properties of L polymer obtained with the catalyst system, particularly the active participation of the metal atom, should promise further investigations on the corresponding DL monomer, especially concerning its stereoregulating power.

## **References and Notes**

- Faculty of Pharmaceutical Sciences, Tokushima University, Tokushima 770, Japan.
- (2) R. B. Woodward and C. H. Schramm, J. Amer. Chem. Soc., 69, 1551 (1947).
- (3) T. A. Moore, J. H. Dice, E. D. Nicolaides, R. D. Westland, and E. L. Wittle, J. Amer. Chem. Soc., 76, 2884 (1954).
  (4) D. G. H. Ballard and C. H. Bamford, Proc. Roy. Soc., Ser. A, 223, 495
- (4) D. G. H. Ballard and C. H. Bamiord, Proc. Roy. Soc., Ser. A, 223, 495 (1954).
- (5) M. Idelson and E. R. Blout, J. Amer. Chem. Soc., 79, 3948 (1957).
- (6) E. R. Blout, R. H. Karlson, P. Doty, and B. Hargitay, J. Amer. Chem. Soc., 76, 4492 (1954).
- (7) E. R. Blout and R. H. Karlson, J. Amer. Chem. Soc., 79, 3961 (1957).
- (8) M. Idelson and E. R. Blout, J. Amer. Chem. Soc., 80, 2387 (1958).
   (9) M. Goodman and U. Arnon, J. Amer. Chem. Soc., 86 3384 (1964).
- (10) T. Tsuruta, K. Matsuura, and S. Inoue, Makromol. Chem., 80, 149 (1964).
- (11) J. Takeda, Abstracts, International Symposium of Macromolecular Chemistry, Tokyo and Kyoto, 1966, No. 1, p 167.
- (12) F. D. Williams, M. Eshaque, and R. D. Brown, *Biopolymers*, 10, 753 (1971).
- (13) H. Bührer and H. G. Elias, Makromol. Chem., 169, 145 (1973).
- (14) E. R. Blout and R. H. Karlson, J. Amer. Chem. Soc., 78, 941 (1956).
  (15) T. Hayakawa, J. Noguchi, K. Ikeda, T. Yamashita, and T. Isemura,
- Nippon Kagaku Zasshi, 82, 601 (1961).
- (16) W. C. Davies and W. J. Jones, J. Chem. Soc., 2109 (1931).
- (17) K.A. Jensen, Z. Anorg. Allg. Chem., 221 (1936).
- (18) P. Doty, J. H. Bradbury, and A. M. Holtzer, J. Amer. Chem. Soc., 78, 947 (1956).
- (19) E. R. Blout and A. Asadorian, J. Amer. Chem. Soc., 78, 955 (1956).
- (20) A. Cosani, E. Peggion, E. Scoffone, and A. S. Verdini, Makromol. Chem., 97, 113 (1966).
- (21) J. E. Prue, J. Chem. Soc., 2331 (1952).
- (22) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Wiley, New York, N. Y., 1961, Vol. 1, p 569.
- (23) T. Yamashita and S. Yamashita, Bull. Chem. Soc. Jap., 43, 3969 (1970).