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Characterization of poly-b-alanine (nylon 3)

Thomas O. Odozi

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CHARACTERIZATION OF POLY-\(\beta\)-ALANINE (Nylon 3)

A THESIS
SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

BY

THOMAS ONYISI ODOZI

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA

May 1979
ABSTRACT
CHEMISTRY

CHARACTERIZATION OF POLY-β-ALANINE (Nylon 3)

ODOZI, THOMAS O. B.S. SOUTHERN UNIVERSITY, 1976
Advisor: Professor Malcolm B. Polk
Thesis dated May 1979

A low molecular weight poly-β-alanine (350 mw) was prepared by thermal polycondensation of β-alanine ethyl ester. In thermal analysis, six transitions occurred in the initial polymer in approximate order of increasing temperature: glass transition temperature (Tg), crystal-crystal transition, cold crystallization, melt crystallization, crystalline disorientation, and melting.

Isothermal annealing of this polymer at 200° followed by quenching provided structures which exhibited multiple melting peaks in thermal analysis. In this work reasons are proposed for the dual endotherm. By prolonged annealing only, before analysis, part of the recrystallization exotherm can be observed in the differential scanning calorimetry (DSC) scan. DSC thermograms obtained at varying heating rates on samples showing poly-β-alanine endotherms supported the assignment of superheating as the cause of the shift to higher peak temperatures with increasing heating rate.

To further support the structural assignment, the infrared absorption showed typical polyamide bands, and the nuclear magnetic resonance spectrum gave two methylene peaks of equal intensity.
ACKNOWLEDGEMENTS

The author wishes to express his deepest gratitude to Professor M. B. Polk for his enduring patience, his keen interest in the composition of this thesis, and his thorough and precise instructions on the application of the thermal analysis techniques. Any merit that this thesis may have is due to his guidance. Finally, for his true and abiding friendship over the years, which will always be treasured, the author is extremely fortunate.

Appreciation is expressed to V. Lewis for the nmr run; to Professor T. W. Cole for advice in overcoming the solubility problems of the polymer; and to Professor K. Bota for his suggestions on the thermal behavior of materials. The author also wishes to thank the faculty and staff, Chemistry Department, Atlanta University for their financial support without which this work would not have been possible; and to the students for their strengthening encouragement throughout the course of his scientific education.
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INTRODUCTION

Poly-β-alanine of higher molecular weight with fiber forming properties was relatively unknown a few years ago. These polyamides, in which the repeating unit is the β-amino acid skeleton, differ from polyamides of the Nylon series in that the amide linkages are much more closely spaced, so that the polymers are therefore similar to the polypeptides and silk fibroin in particular. We have not adopted the term poly-β-peptides, which is also found in the literature, since the name polypeptides should be used only for polymeric α amino acids.

The polycondensation of β-alanine and its derivatives always led to low molecular weight poly-β-alanine.¹,² With the synthesis of β-lactams having no substituents on the nitrogen, it became possible to prepare high molecular weight poly-β-alanine.³ The ring strain in the β-lactams facilitated the opening of the ring at the amide linkage leading to open chain products having good fiber properties.

An unconventional method was successfully used by Breslow, Hulse, and Matlack⁴ for the synthesis of poly-β-amides. These authors converted acrylamide into poly-β-alanine by alkali catalyzed polyaddition and isolated a small yield of a higher molecular weight substance; the molecular weight of this substance as calculated from light scattering measurements was 76000. The relatively low specific viscosity of 0.639 (measured in formic acid) indicates that the molecular weight of this polymer is too low for production of fibers.

In our work we were interested in determining the thermal
properties, morphology, and structure of poly-β-alanine\(^5\) prepared by base catalyzed thermal polycondensation of β-alanine ester. In doing so we have made extensive use of thermal analysis techniques and to a lesser extent the nmr and ir spectroscopy.

To explain the course of the reaction it may be assumed that the addition of ammonia initially led to the formation of β-lactam intermediates occurring through intramolecular cyclization of the carbonyl group and the NH nitrogen atom. A summary of the possible reaction course of β-alanine ester leading to the formation of poly-β-alanine (1) is shown here.

\[
\begin{align*}
\text{H}_2\text{NCH}_2\text{CH}_2\text{COCH}_2\text{CH}_3 & \xrightarrow{\text{NH}_3} \text{H}_2\text{N-CH}-\text{CH}_2-\text{C-NH}_2 \xrightarrow{-\text{NH}_3} \text{HN-CH}_2 \\
& + \\
\text{H}_2\text{NCH}_2\text{CH}-\text{C-OCH}_2\text{CH}_3 & \xrightarrow{} \text{HNCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3
\end{align*}
\]

(1)

The polymerization is believed to proceed by the protonation of the nitrogen atom followed by the cleavage of the amide linkage of the lactam. Further reaction with unreacted β-alanine ester leads to the stepwise formation of the oligomeric β-alanine products. High molecular weight polymers could not be obtained by this method because the stepwise growth of the polymer molecule by addition of lactam intermediate is a slow reaction. Raising the temperature to increase reaction rate leads to side reactions, presumably ring opening between N and C\(_\beta\), which stop the growth of the polymer chain.
We have no evidence that the reaction process involves a cyclic intermediate. Repeated attempts to isolate it failed owing to the instability of the four member ring. But the occurrence of a strong amide II band of the polymer indicates that the amide group changes from the cis to the trans configuration on opening of the ring and subsequent attachment to the macromolecule. On account of this we are led to believe that the intermediate may involve a cyclic transition.

Structure (1) was assigned on the basis of elemental analysis, infrared (ir) and nuclear magnetic resonance (nmr) spectroscopy. Evidence in support of the structure will be discussed in full detail.

The ability of materials to change in temperature is a fundamental property which may be used in the analysis of their characteristics. The term thermal methods of analysis will be defined in this paper to include only those techniques in which some physical parameter of the polymer is measured as a function of temperature. Within the scope of the above definition, the principal techniques which will be discussed are: differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

Differential thermal analysis (DTA), or thermal spectrometry, measures the heat energy change occurring in a substance as a function of temperature. The essential difference between differential thermal analysis and differential scanning calorimetry are found in the degree of control of the sample temperature and in the methods used to detect and measure the energy transitions within the sample. DTA uses the differential thermocouple arrangement. In this technique the temperature of the sample under study is compared with that of a thermally
inert reference material. The sample and reference material are subjected to programmed temperature changes. When the sample undergoes a transition a signal proportional to the temperature difference, \( dT \), is sensed by the differential thermocouple, amplified, and recorded.

As reported earlier,\(^6\) there are a number of factors which will produce errors in the differential thermal analysis results. The major sources of error include the dependence of heat transfer to the sample thermocouple on sample geometry, particle size, particle size distribution, and packing density. These errors are not constant but tend to change as the sample is subjected to heating, and thus, are difficult to correct. Another source of error arises from the inability to control reproducibly the temperature of the sample under study. This limitation is due to a relatively massive heating block and furnace which produce a large thermal lag during operation.

The differential scanning calorimeter was designed to sense and measure the same type of thermal events as are studied by differential thermal analysis techniques. The ways in which sample temperatures are controlled and thermal transitions measured are different from those employed in DTA. The sample and reference holders are small stainless steel containers, each having a heater built into its base. The DSC compares the average temperature of the sample and reference holders, and proportionately adjusts the heating current so as to correct any deviation from the selected thermal program. During a transition such as melting, the differential temperature amplifier senses heat absorbed by the sample and alters the distribution of heat energy between the
sample holder and reference holder so as to instantly regain thermal balance.

In DSC, the distance moved by the recorder pen from the base line is directly equivalent to the rate of energy absorption or release, in calories per second, and the area under the thermogram peak measures the heat of transition directly in calories. Thus, for these reasons a DuPont 900 Thermoanalyzer with a DSC plug in module cell was used to evaluate physical transitions occurring in poly-β-alanine.

The melting behavior and other physical changes associated with it are among the most important properties of polyamides. They are directly related to the chemical structure and influence the fabrication and end uses of polyamide fibers.

The thermal behavior of polyamides has been investigated by cooling curves\(^7\) and by specific heat measurements by the "calibrated" heat conductivity method.\(^8\) Specific heat measurements have given quantitative results for polyhexamethyleneadipamide and sebacamide.\(^9\) The effect of copolymer composition on the melting behavior has also been investigated. However, the structure and physical properties of polyamides of poly-β-alanine type prepared by thermal polycondensation have been little investigated or not at all.

Differential thermal analysis has been found useful in characterizing various polyolefins.\(^10\) The melting points, heats of fusion, and crystallization can be determined by this technique. Inasmuch as poly-β-alanine is crystalline and has defined transition temperatures, it should be amenable to study by this method.
Differential scanning calorimetry has therefore been used to study melting, glass transition ($T_g$), and other physical transitions in poly-$\beta$-alanine.

In the approximate order of increasing temperature, six transitions may take place in linear poly-$\beta$-alanine: glass transition which involves motion of short chain segments in the amorphous region and is related to the brittleness of the polymer; crystal-crystal transition; cold crystallization which occurs when segments of neighboring chains in the amorphous portion crystallize above the glass transition temperature but far below the melting point; melt crystallization; crystalline disorientation; and melting which as the transition from the crystalline to amorphous state has been studied extensively.

Generally, both the crystallization and the polycondensation processes affect the morphology of the final polymer. In this paper, we will discuss such effects for poly-$\beta$-alanine.

The melting point of any crystalline or semicrystalline polymer is one of its important characteristics. Two categories of melting points should be distinguished: (1) first cycle melting point, in which the thermal and crystallization history of the sample influences its melting behavior; and (2) second melting point, in which the history of the sample is erased by melting, and a new controlled crystallization is carried out prior to determining the melting point. Determinations in the first category provide information about the crystalline nature and thermal history of the sample. Determinations in the second category provide information about effects of chemical composition on the melting
behavior of the polymer. Only the first cycle melting points are discussed in this paper.

Several workers have reported general changes in the differential thermal analysis (DTA) or differential scanning calorimeter (DSC) melting thermograms of crystalline polymers when the polymers were annealed at temperatures below the melting point. This phenomenon has been characterized for polystyrene,\textsuperscript{11} Nylon 66,\textsuperscript{11,12} and polyethylene terephthalate.\textsuperscript{13,14,15} The change in the thermogram during annealing is the appearance at a lower temperature of a new peak which enlarges and shifts to a higher temperature.

Kanetsuna,\textsuperscript{14} and Bell and Dumbleton\textsuperscript{11,12} postulated that two distinct morphological forms are responsible for the two endotherms. These latter two authors labelled the form responsible for the initial high temperature endotherm as form I and the form represented by the endotherm developed by annealing as form II. The same changes were observed in the melting thermograms of Nylon 66. Bell summarized these observations by assigning the folded chain crystal structure to form I and a partially extended chain or bundle crystal structure to form II.

Ikeda,\textsuperscript{13} on the basis of his results from DSC studies of the melting behavior of polyethylene terephthalate, proposed an alternative interpretation. He postulated that the melting endotherm assigned to form I represents the melting of a structure not present initially in the sample but formed through annealing or recrystallization of the crystallites during the programmed heating in the instrument, while the form II corresponds to melting of the folded chain structure initially present in the sample.
Most of the experimental observations reported here result from the following sequence of operations: (I) crystallization of low molecular weight polymers at a range of temperatures, (II) polycondensation and annealing of the crystalline polymers, and (III) measurement of the DSC or DTA melting curve.

Poly-β-alanine (Nylon 3) exhibits two crystalline phases by DTA techniques; here, we are interested in determining the reason(s) for the difference.
EXPERIMENTAL

Thermal Polymerization of $\beta$-Alanine Ethyl Ester

Poly-$\beta$-alanine $^5$ was prepared by thermal polycondensation of $\beta$-alanine ethyl ester in the presence of a base catalyst by heating $\beta$-alanine ethyl ester at 50° in bulk. As the polymerization proceeded, fine particles of colorless material were deposited on the inner wall of the flask. The product was washed several times with ether and water, filtered, and dried under reduced pressure.

Structural characterization of the polymer was based on infrared (ir) and nuclear magnetic resonance (nmr) spectroscopy and on analytical data. Nuclear magnetic resonance spectra were determined on a Varian HA-100 spectrometer. Sweep widths were calibrated using the known separation between tetramethysilsilane and chloroform.

Infrared spectra were obtained with a Beckman 4240 IR spectrophotometer in KBr. Carbon, hydrogen, and nitrogen assay values were provided by the Galbraith Laboratory (Knoxville, Tennessee).

Poly-$\beta$-alanine (352 mw): nmr (TFA) 8.20 (S, 3, HNCO), 7.20 (S, 1, NHCH$_2$), 4.25 (m, 2, OCH$_2$CH$_3$), 3.75 (S, 8, CH$_3$NH), 2.85 (S, 8, CH$_2$CO), 1.35 ppm (t, 3, CH$_3$CH$_2$O).

Anal. Calcd. for $C_{14}H_{26}N_4O_5 \cdot \frac{1}{2}H_2O$ (352): C, 49.56; H, 7.96; N, 16.52

Found: C, 49.37; H, 7.60; N, 16.20
Thermal Analysis

The polymer was dried overnight in a vacuum oven at 77° before the determination of the thermogram. The equipment and the experimental procedures used in the thermal analysis have been described. In this work a Dupont 900 differential thermal analyzer with differential scanning calorimeter cell was used—at a heating rate of 20°/min. The glass transition temperature (Tg) and melting point were determined by taking the midpoint in the thermogram as measured from the extensions of the pre- and post-transition baselines.

Short term annealing.

Annealed samples were obtained by heating the polymer material directly in the cell 4–8° before the melting point and allowing the sample to cool naturally at 10°/min. The thermogram for the annealed poly-β-alanine was then obtained simply by reheating through a second cycle.

Quenched sample.

The quenched sample was obtained by annealing isothermally at 200° and quenching in a Dry Ice/acetone bath to interrupt the crystallization at various stages, before the determination of the thermogram.

Melting points.

The melting points of the polymer were obtained with a Dupont 900 differential thermal analyzer (DTA) at a heating rate of 20°/min.
unless otherwise specified. The samples used weighed on the average about 15 mg. The instrument was calibrated daily; indium, tin, and zinc being used as standard samples; and also calibrated whenever the heating rate was changed. All scanning as well as annealing in the instrument was conducted in air.
RESULTS AND DISCUSSION

Glass Transition

Poly-β-alanine, like many other crystalline polyamides, may undergo second order transitions in which enthalpy undergoes a sudden change at the transition temperature. The transition point is marked by the onset of motion of chain segments in the amorphous region of the polymer. This motion is caused by the sudden abrupt shift in the free volume which permits segmental motion. Glass transition temperatures have been reported for the common polyamides.17,18,19

The poly-β-alanine polymer shows a glass transition temperature of 110° and this is shown in Fig. 1. The transition may be seen as an abrupt shift in the baseline of the thermogram; and this change in specific heat is proportional to the amount of amorphous material present.

Crystallization

Polymer crystallization is usually accompanied by evolution of latent heat. The heat evolved during crystallization yields exothermic peaks.

Crystal-crystal transition.

The most well-known crystal-crystal transition is probably that occurring in some higher members of paraffin hydrocarbons.20 In one
Fig. 1. Thermogram of the initial polymer dried overnight at 77°.
such transition occurring in dotriacontane, the thermogram consists of two closely situated peaks, the first due to a chain-rotational transition a few degrees below melting. The premelting peak has been attributed to a crystal-crystal transition from the monoclinic form in which chain rotation is restricted to the hexagonal form. In dotriacontane the heat of rotational transition is about half that of normal melting.

In Fig. 1, poly-β-alanine displays a unique first order transition (crystal-crystal transition) at 190° followed by a subsidiary transition at about 215°. Evaluation of the peak areas showed that the heat of the 190° transition is much greater than the heat of the 215° transition.

Similar physical transitions have been reported for polytetrafluoroethylene (teflon), where it is observed to display a first order transition near 20° followed by a subsidiary transition at 30°; and the heat of the 20° transition is known to be tenfold that of the 30° transition.

X-ray studies have indicated that these transitions occurring far below the true melting point (327°) of teflon actually involve partial disordering of the crystalline region, and it is known as a crystal-crystal transition. The disordering has been attributed to either longitudinal translation along or angular displacement about the chain axis. Cold crystallization.

Some polymers can crystallize at temperatures far below the melting point but above the glass transition temperature (Tg). This type of crystallization has been called cold crystallization and is assumed to
involve nearest neighboring chain units in the amorphous regions leading to the formation of small crystallites.

Cold crystallization has been observed in some polymers like quenched polyethylene terephlate;\textsuperscript{23} at low temperatures in polydimethylsiloxanes;\textsuperscript{24} and in polyurethane crosslinked with isocyanate called "I-rubber."\textsuperscript{25}

In poly-\(\beta\)-alanine, cold crystallization occurs at about 245\(^\circ\).

\textbf{Melt crystallization.}

Melt crystallization in polymers is not only of theoretical interest for understanding polymer morphology, but also of basic importance in such practical operations in plastics fabrication as extrusion and spinning of molten polymers. Melt crystallization has been observed in thermograms of Marlex,\textsuperscript{26} a mixture of isotatic polypropylene and high density polyethylene.

In Fig. 1 poly-\(\beta\)-alanine showed a remarkable high melt crystallization at 310\(^\circ\), the onset of crystallization and the maximum at 335\(^\circ\). The difference was approximately 25\(^\circ\).

\textbf{Crystalline disorientation.}

If crystallites in the polyamides are oriented, they should become disoriented before melting. Oriented Nylon 66\textsuperscript{27} has been observed to display a double peak; the first endothermic peak has been attributed to disorientation, which is followed by normal melting. The doublet in oriented yarn has been observed previously.\textsuperscript{28}
In Fig. 1, the poly-β-alanine thermograms exhibit a doublet peak; the first endothermic peak is attributed to crystallite disorientation and the second to normal melting.

**Melting point.**

Melting of poly-β-alanine begins at $345^\circ$ and ends at about $425^\circ$. The melting point (Fig. 1) was not sharp but somewhat broad because of the presence of different crystalline forms. Evidence for the crystalline forms was based on the observation of identical (ir, nmr) spectra of the polymer crystals. Repeated differential thermal analysis on crystallized melts showed random shifting from one melting endotherm to another, further confirming the existence of different crystallite forms. A detailed discussion and results of poly-β-alanine morphology will be presented in this paper.

**Annealed sample.**

If a polymer has a low crystallization rate compared with the cooling rate used, an exothermic peak may not result. Such a case has been reported for isotactic polystyrene and linear polyester.

In the thermogram (Fig. 2) for the annealed poly-β-alanine, the glass transition near $110^\circ$ is barely perceptible; and both crystallization peaks are virtually missing. Instead, diffuse dual exothermic effects occurred over a small temperature range, indicating partial recovery of crystallinity. The flattening of the glass transition deflection is expected because the crystalline portion would impose
Fig. 2. Thermogram of the polymer annealed 4-8° before the melting point.
strain on the amorphous segments. The annealed polymer material displays a sharper melting peak.

**Morphological Studies**

**Long term annealing.**

From the thermogram (Fig. 3) we have observed that long term annealing of poly-β-alanine conforms closely to the observations of previous investigators.

This long term annealing of poly-β-alanine at 200° followed by quenching has produced a highly perfected crystalline structure, which is indicated by the broad melting temperature. In the same thermogram it can be seen that the poly-β-alanine recrystallizes after it melts. The recrystallization of this material may be attributed to the retention of order from the highly annealed sample and is accompanied by an exotherm. We rationalize the exothermic behavior in this manner. If the heat of fusion appears as the low endotherm and again as part of the high temperature endotherm, there must be an exotherm counter-balancing the latter. Since the recrystallization process in this special case proceeds beyond the initial heat of fusion, an exotherm appears in the observed DTA thermogram of poly-β-alanine (Fig. 3). The higher endotherm temperature found in the quenched sample thermogram actually represents the melting of a structure not present initially in the sample but formed through annealing or recrystallization of the crystallites during programmed heating in the instrument. This is in agreement with the observations\textsuperscript{30,31} that under rapid crystallization
Fig. 3. Thermogram of the quenched polymer.
conditions, in which the sample is quenched, spherulitic crystallization occurs. The nature of such a change is not clear, but the result cited seems to require it.

**Effect of heating rate on the endotherm of poly-β-alanine.**

Both Bell\textsuperscript{11} and Ikeda\textsuperscript{13} observed that the peak temperature of low molecular weight polymeric material endotherms increases significantly with increasing heating rate. Bell attributed this result to superheating of the bundle crystals. Ikeda rationalized the phenomenon as the effect of heating rate on the kinetic balance between melting (endothermic) and recrystallization (exothermic) of partially melted regions.

To test these interpretations, the effect of DTA heating rate on the peak temperature of poly-β-alanine was determined using multiple heating rates of 10, 20, 40, and 80°/min. The results of this experiment are given in Tables 1, 2, Figs. 4 and 5. These results show that the peak temperature (endotherm) increases with increased heating rate. However, our results do not support Ikeda's hypothesis because the recrystallization peak (exotherm) remained virtually identical with heating rate. The results do support the assignment of superheating as the cause of this phenomenon. Wunderlich and coworkers\textsuperscript{32} have shown that extended chain crystals of several polymers superheat, whereas folded chain crystals do not. Chain extension can be judged as an end result of the thickening process; the lowest free energy with the folds removed. We can visualize it in a manner in which as a crystal grows it is found to thicken; that is while chains are folding against a growth face, those already folded are still able to and do readjust their
Table 1. Effect of heating rate on peak temperature of DTA endotherms.

<table>
<thead>
<tr>
<th>Heating Rate °C/Min.</th>
<th>Peak Temperature °C</th>
<th>Log of Heating Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>370</td>
<td>1</td>
</tr>
<tr>
<td>20</td>
<td>390</td>
<td>1.3</td>
</tr>
<tr>
<td>40</td>
<td>412</td>
<td>1.6</td>
</tr>
<tr>
<td>80</td>
<td>435</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 2. Effect of heating rate on the crystallization peak temperatures.

<table>
<thead>
<tr>
<th>Heating Rate °C/Min</th>
<th>Peak Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>340</td>
</tr>
<tr>
<td>20</td>
<td>340</td>
</tr>
<tr>
<td>40</td>
<td>338</td>
</tr>
<tr>
<td>80</td>
<td>338</td>
</tr>
</tbody>
</table>
Fig. 4. Thermograms of the endothermal peak temperatures of the polymer annealed at 200°C at heating rates of 10(A), 20(B), 40(C), 80(D)°/min.
Fig. 5. A plot of endotherm peak temperatures vs. the logarithm of heating rates for the thermograms of Fig. 4.
positions within the lattice removing defects and increasing the fold period.

From the foregoing data and discussion we conclude that the behavior of the peaks may be of practical value such as in rationalizing different mechanical properties. For example, during crystallization, density increases leading to weak points at the spherulite boundaries; thus, one method of toughening a sample is to add a foreign particle to reduce the spherulite size. However, one cannot draw conclusions as to the morphology of poly-β-alanine from the behavior of the peaks alone. The ability of the samples to recrystallize after melting depends on the degree of supercooling and the nuclei present.

Other causes of superheating are not yet available. Whether or not annealing described in earlier work produced crystals containing extended chains, resulting in superheating, remains in question. But available data favor eventual production of extended chains; the time required is not known.

In general, the following possible facts can be postulated to account for the double peaked fusion patterns:

I. Thermal degradation of poly-β-alanine takes place on heating.

II. The melting temperature of the initial polymer differs from that of the quenched crystalline state.

III. Different crystal forms, of different thickness, co-exist in the original polymer.

IV. Extended chain polymers are the most thermodynamically stable form and, also, are associated with low molecular weight polymers. This is in accord with the low molecular weight range of poly-β-alanine.
Structure Characterization

The structure of compound (1) is supported by elemental analysis and spectral data. The infrared spectrum (Fig. 6) showed strong hydrogen bonded NH stretching vibrations at 3300 cm$^{-1}$ and a weaker component peak at 3060 cm$^{-1}$ and a still weaker one at about 2920 cm$^{-1}$. The infrared spectrum (ir) of the polymer indicates the presence of C=O groups at identical frequencies (1738 cm$^{-1}$) with those of $\text{OC}_2\text{H}_5$. The nmr spectrum of the polymer shows finely split triplet and quartet signals at the same chemical shift values as $\text{OCH}_2\text{CH}_3$.

When estimated from analytical values, the 49.37% carbon content corresponds to one molecule of $\text{OC}_2\text{H}_5$ per 4.1 monomer units. The observations imply that the ethyl group in the polymer is included as a form of ethyl ester ($\text{OC}_2\text{H}_5$).

The characterization of the structure of poly-$\beta$-alanine type (1) was concluded from the following: 1) ir bands at 1650, 1550, 1200, 700, and 600 cm$^{-1}$ correspond to amide-I, -II, -III, -V, and -IV frequencies respectively. The intensity of the amide-II band (Fig. 6) is about half the intensity of amide-I indicative of a hydrogen bonded form of amide-II band. 2) The methylene signals in the nmr spectrum (Fig. 7) constitute a broad singlet; the $\text{NCH}_2$ group peak is centered at 3.75 ppm and that of $\text{CH}_2$ at 2.80 ppm. The NH protons were found to be chemically nonequivalent giving rise to two separate broad peaks at 7.20 ppm ($\text{CH}_2\text{NH}$) and 8.25 ppm ($\text{NH}$). The broadening of the absorption is due to the magnetic and electric properties of $^{14}$N. It has been reported$^{33,34}$ that the rotation about C-N bond is slow due to the partial double bond
Fig. 6. The ir spectrum of the polymer.
Fig. 7. The nmr spectrum of the polymer.
character of the amide structure. As a result the environment of the NH protons are not averaged. Hence, they can usually be observed separately by nmr. 3) The relative intensity of $\text{NCH}_2\text{CH}_2\text{C} = 0 \text{NHCH}_2\text{O}$ observed was 8.2:8.2:1:1:3:1.8, in contrast to the theoretical value of 8:8:1:1:3:2.

These results are consistent with the postulated structure of poly-$\beta$-alanine type (1) where the ethyl group attributes solely to the end groups of the polymer of average degree of polymerization (DP) of 4.
SUMMARY

The transitions which occur in polymers are determined by the composition and structure of the polymers and include glass transition temperature (Tg), crystal melting (Tm), and crystalline transitions (Tc). Nearly all the mechanical properties are determined by these transitions and by the temperatures at which they occur. High Tg is widely accepted as a critical macromolecular property in many applications because it reflects the resistance of the polymer to deformation, to creep, to craze, and to permeants.

Poly-ß-alanine was found to be insoluble in some common organic solvents; it is slightly soluble in CF₃COOH, and CCl₃COOH, but readily soluble in HCOOH, and H₂SO₄. The poor solubility of the polymer in organic solvents might be attributed to the highly crystalline nature.

The preparation of fibers and films of poly-ß-alanine is encumbered by its insolubilities, high melting point, and low molecular weight. It should, therefore, be emphasized here that though preliminary data obtained from the thermal analysis shows features of a typical fiber forming polymer, its low molecular weight discourages any attempt towards such a direction.

Since poly-ß-alanine undergoes yellowing at higher temperatures it may possess a good affinity for dyestuffs and should be able to impart thioxotrophic properties to coloring materials. It has been shown that crystalline Nylons of low molecular weight have a demonstrated
potential for use in paints and pigment dispersions. They permit a reduction in the titanium dioxide content of some latex type paints such as those based on polyvinyl acetate emulsions.

We have made limited review of the possible end uses of the low molecular weight poly-β-alanine and the following are suggested:

(a) From the Tg value, poly-β-alanine has low flexibility and high rigidity, therefore it should display some acoustic properties in applications such as loud speakers where it is desirable to reflect sound completely and precisely.

(b) Poly-β-alanine blended with melamine-formaldehyde resin could be used for abrasion-resistant coatings.

(c) Poly-β-alanine of sufficiently low molecular weight could be used as a substitute for gelatin in the manufacture of photographic emulsions and carriers for coloring materials in inks.

(d) The hydrophilic properties of poly-β-alanine can be achieved by formaldehyde treatment or making its copolymer by simultaneous polycondensation of two or more polyamide forming monomers which could be used as adhesives in leather finishing and for the impregnation of paper.

The case of crystal-crystal transitions, a true first order transition occurring in poly-β-alanine type (1), may be due to the motion of the end groups which are sufficiently different from the rest of the polymer molecule. They could create serious imperfections in the crystal structure and subsequent reduction in crystallinity. The ends of the polymer (H-, -OC₂H₅) are fairly mobile and flexible to create looser packing, lower crystallinity and subsequently lower melting points. This is one case that merits further studies.
REFERENCES
