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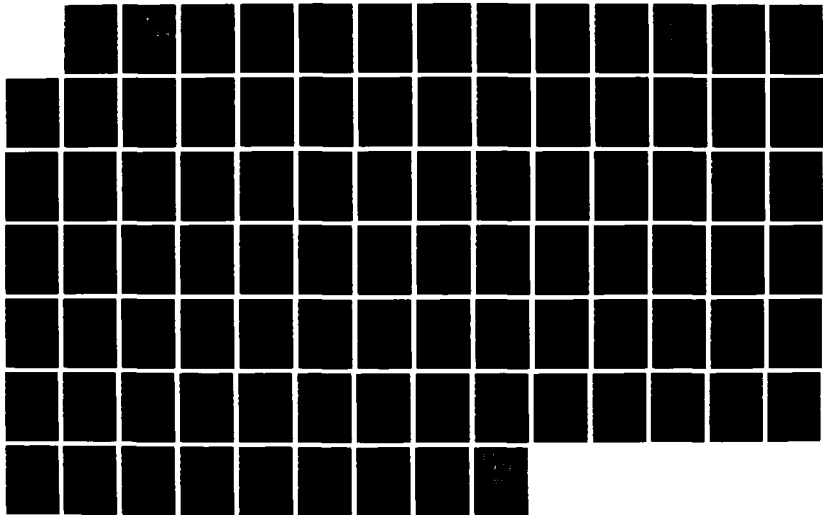
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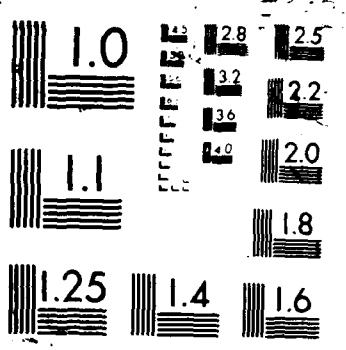
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DEVELOPMENT OF POLYMERIC FILMS WITH PIEZOELECTRICAL PROPERTIES FROM POLYPETIDES; LOW, ODD NYLONS; OR POLYUREAS

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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) A 33-month project was undertaken to study piezoelectricity in low, odd nylons; odd, odd nylons; polyureas; and polypeptides. The commercially available polypeptides oly(L-alanine), poly(L-valine), and poly(L-asparagine) were apparently not of sufficiently high molecular weight to provide usable films for piezoelectric testing. Likewise, the polyureas we synthesized — poly(trimethyleneurea), poly(pentamethyleneurea), and poly(1,2-propylene diisocyanate) — were also poor film-forming materials. Consequently, we devoted most of our efforts to synthesizing film-forming nylons. High-molecular-weight nylon 5 was prepared via anionic ring-opening polymerization of α -piperidone. Films of high quality were solvent cast from trifluoroethanol, and these films were poled in the presence and absence of a plasticizer (2-ethyl-1,3-hexanediol). The highest values of the piezoelectric strain (d_{31}) and stress (e_{31}) constants obtained were for plasticized nylon 5 — 1.3 pC/N and 2.8 mC/m ² , respectively. <i>key...</i> | | | | | |
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Nylon 3 was prepared via hydrogen-transfer polymerization of acrylamide. As such, only low-molecular-weight polymer was obtained. The nylon 3 films could be handled and poled only in plasticized form, and the highest values of d_{31} and e_{31} observed were 0.8 pC/N and 1.1 mC/m².

The synthesis of the odd, odd nylons 3,5, 3,7, 5,5, 5,7, and 7,7 was also explored. Only nylons 5,7 and 7,7 could be made into good films; however, insufficient time remained in the project to evaluate the piezoelectric response of these nylons.

The piezoelectric constants obtained for nylons 3 and 5 are not high compared with those for poly(vinylidene fluoride). Nevertheless, these values are higher than the constants reported for many other polymers. Given the high dipole densities of nylon 3 and nylon 5 and our early position on a learning curve, we believe that these results show great promise. Additional studies with these materials would undoubtedly result in films with higher piezoelectric constants. Values of d_{31} on the order of 8 to 15 pC/N should be attainable.

As a result of our inability to produce useful films from commercially available polypeptides, a literature survey was undertaken to identify piezoelectric attributes of polypeptides so that this information might aid future research. Based on this survey, we believe additional studies in this area are warranted.



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DEVELOPMENT OF POLYMERIC FILMS WITH PIEZOELECTRICAL PROPERTIES
FROM POLYPEPTIDES; LOW, ODD NYLONS; OR POLYUREAS

I. INTRODUCTION

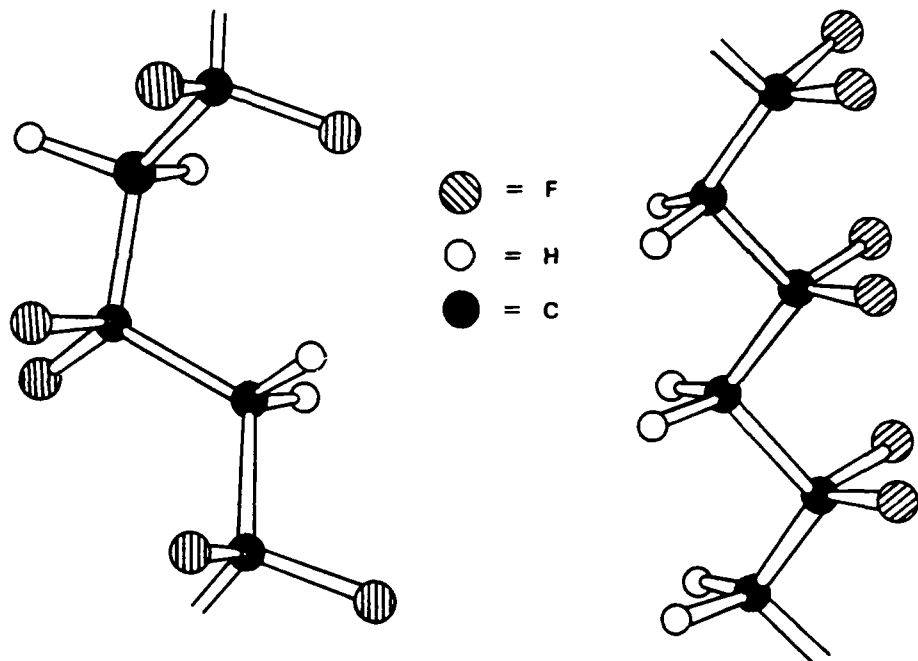
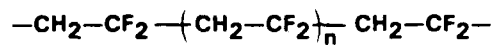
A piezoelectric material is one that transforms mechanical force into an electrical response and, conversely, transforms an electrical signal into mechanical motion. Traditional examples of piezoelectric materials include quartz crystals and some ceramics. As such, these materials are dense, brittle, stiff, and difficult to fabricate into useful shapes. In recent years, polymeric piezoelectric films have been developed and studied.¹⁻⁴ These films are lightweight, flexible, rough, and easily fabricated into intricate configurations. Of all polymers tested to date, films made from poly(vinylidene fluoride) (PVF₂) show the highest piezoelectric and pyroelectric activities. (Pyroelectricity is electric polarization induced by a thermal stimulus.) PVF₂ films are commercially available and have found use as transducers for acoustic and sonar applications, pressure switches, electro-motional devices, temperature monitors, and fire alarms.^{5,6}

Because of its flexibility, PVF₂ is a better transformer of mechanical to electrical energy than is quartz and ceramic materials. Conversely, the rigidity of quartz and ceramics is an advantage when converting electrical energy to mechanical vibration. Consequently, the properties of the two types of materials complement each other.

Although PVF₂ is the best currently available piezoelectric polymer, the piezoelectricity of this material is still far below that of certain inorganic crystalline materials. Consequently, a need exists for better polymeric materials. Anticipated applications of improved piezoelectric films by the Navy include their use as acoustic transducers, infrared detectors, and impact sensors.

Although the piezoelectric effect in polymers (particularly PVF₂) has been extensively studied,⁷⁻¹⁴ a complete understanding of the origin of the phenomenon is lacking. It is known that certain requirements must be met by polymers before they can be piezoelectric. According to most theories, the most important criterion is that a polymer be highly crystalline with a large net dipole in the unit cell of the crystalline phase. The unit cell must also be noncentrosymmetric so that a net dipole moment is possible. The polymer must be relatively high melting so that the oriented dipoles are not destabilized at working temperatures.

The precise origin of the piezoelectric effect in polymers is obscure, but the case of PVF₂ is perhaps the best-understood example.⁵ PVF₂ as melt extruded or solution cast is a semicrystalline, high-molecular-weight polymer with a predominantly head-to-tail arrangement of monomer units as shown in Figure 1. The principal crystalline forms are a nonpolar α form and a polar β form (Figure 1). These regions of crystallinity (crystallites) are embedded in



α OR PHASE II FORM,
ANTIPARALLEL CHAIN PACKING

β OR PHASE I FORM,
PARALLEL CHAIN PACKING

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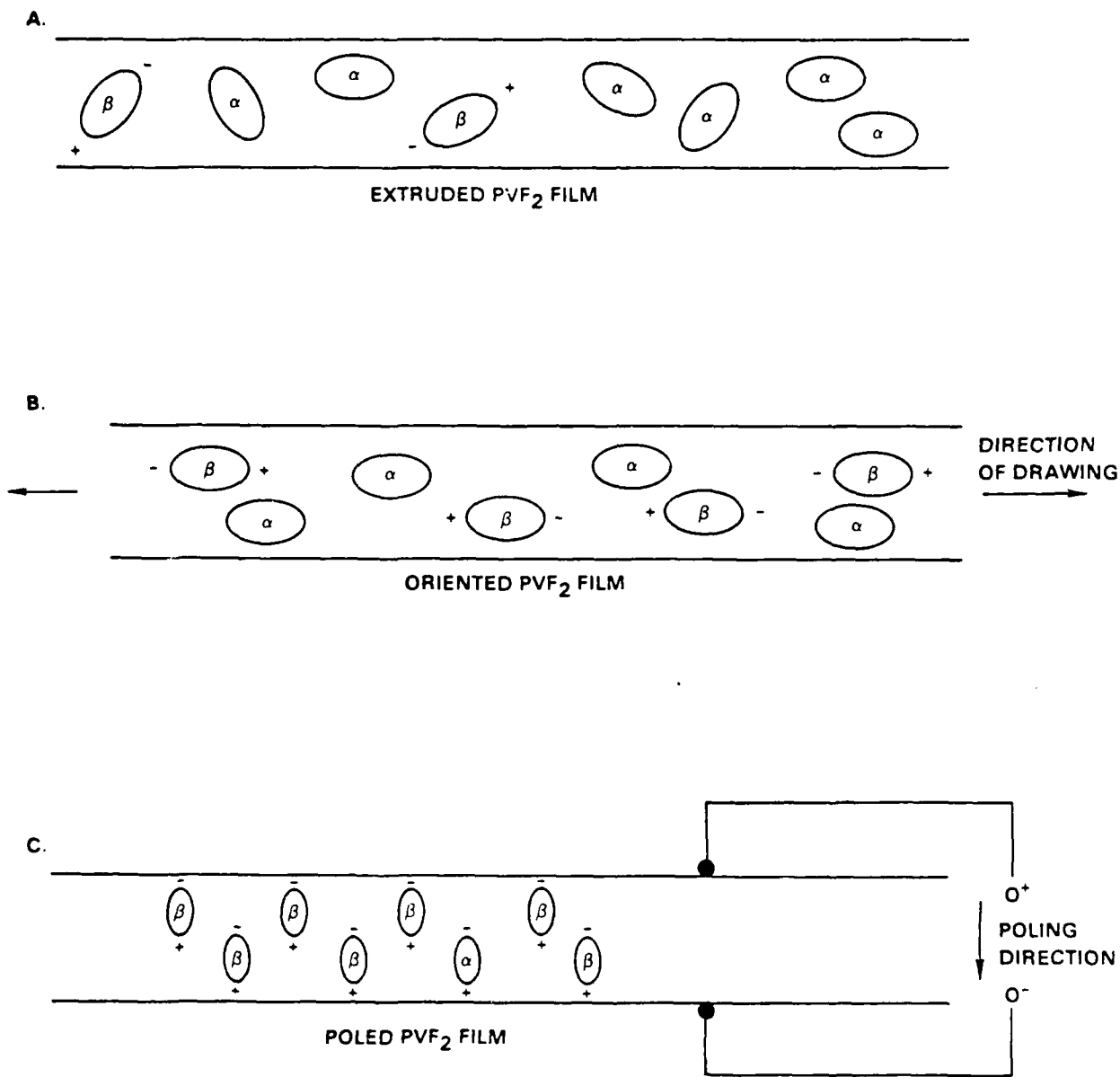
Figure 1. Chemical and crystal structures of poly(vinylidene fluoride) (PVF₂).

an amorphous matrix. The piezoelectric response is associated with the polar β crystallites in which the fluorine atoms are arranged to give the highest dipole moment per unit cell.

As extruded, a PVF_2 film consists of predominantly α -phase crystallites embedded in an amorphous region, as shown pictorially in Figure 2. The film is then uniaxially or biaxially mechanically drawn at elevated temperatures. Drawing has two functions: it orients the polymer chains in the direction of drawing, and it increases the amount of polar β -phase crystallites. It is probable that β -phase crystallites are formed at the expense of α -phase crystallites in addition to their creation from ordering of the amorphous regions. Polarization (poling) of the oriented film at elevated temperature also accomplishes two objectives: conversion of nonpolar α -crystallites to polar α - or polar β -crystallites (field-induced phase transitions) and orientation of the polar crystallites along the axis of the applied electric field. After poling, the films are piezoelectric. In the case of PVF_2 , then, piezoelectric and pyroelectric activities are believed to result from the aggregate properties of polar crystallites with preferred alignment dispersed in an amorphous matrix. Indeed, the piezoelectric strain and stress constants d_{31} and e_{31} have been found to be proportional to the volume fraction of polar crystallites.¹³

The odd nylons have been studied extensively in recent years as piezoelectric polymers, particularly nylon 11.¹⁵⁻²⁴ The prediction that the odd nylons should be piezoelectric is based on their semicrystalline nature and their ability to crystallize into polar, noncentrosymmetric unit cells. The amide group has a much larger dipole moment (3.7 D) than does PVF_2 (1.52 D), and the odd nylons can crystallize in an all-trans conformation (stabilized by hydrogen bonding) giving rise to large dipole moments perpendicular to the chain axis (Figure 3).¹⁵ From knowledge of the unit-cell dimensions of the various odd nylons,²⁵ the theoretical dipole concentration per unit volume can be calculated. For example, nylons 11 and 7 were reported to have values of 1.4 D/100 \AA^3 and 2.1 D/100 \AA^3 as compared to 2.9 D/100 \AA^3 for PVF_2 .¹⁵ Nylons 3 and 5 would be expected to have dipole densities greater than that for PVF_2 . Similar dipole density arguments can be made for a similar class of polymers, the polyureas.

Nylon 11 can assume a variety of crystal structures depending on chemical and thermal history. One early result indicated that the polar α phase of nylon 11 was less active than the nonpolar γ phase after poling. This behavior was attributed to a lower energy barrier for rotation of dipoles in the less ordered γ phase.¹⁶ Later work indicated that the polarization mechanism of γ phase nylon 11 was not a field-induced phase transition from γ to α forms. Thus, the existence of a polar γ form was postulated.¹⁷ Other workers reported the orientation of nylon 11 crystallites under the influence of a poling field. A correlation between crystal orientation and piezoelectric activity was observed.¹⁸ Similar behavior was also seen in the plasticized α' phase of nylon 11.¹⁹ Furthermore, oriented films gave higher values of the piezoelectric constants d_{31} and e_{31} than did unoriented films poled under the same conditions. Also, static-switching experiments demonstrated that nylon 11 films show a reversible polarization with hysteresis behavior of d_{31} and e_{31} .



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Figure 2. Schematic representation of the preparation of piezoelectric PVF₂ film. Ovals represent crystallites of the type indicated.

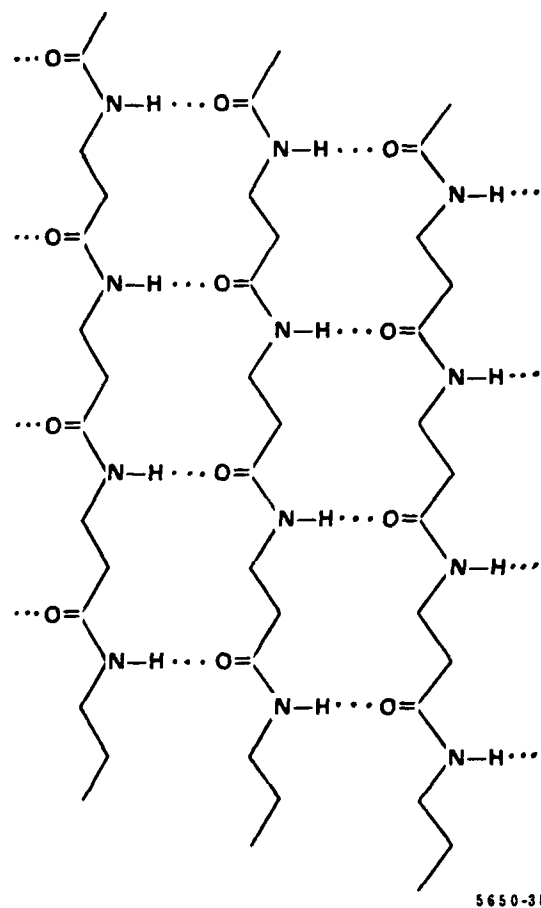


Figure 3. All-trans configuration of an odd nylon (Nylon 3) showing polar hydrogen-bonded sheet structure and parallel alignment of chains.

These observations were all consistent with film polarization caused by ferroelectric dipole switching as seen with PVF₂. However, no evidence for a field-induced phase transition was found in nylon 11 films.¹⁹

Their understanding of the origin of piezoelectricity in odd nylons was considerably complicated by new data concerning plasticized nylon 11 films. The authors concluded that the origin of the piezoelectric response for nylon 11 probably lies primarily in the amorphous regions rather than in the crystalline regions of the film.²³ This revolutionary conclusion was based on the following observations. The piezoelectric response of nylon 11 was observed to increase with increasing amounts of amorphous phase originally present in the films. The piezoelectric response was also highest for films containing the most plasticizer (2-ethyl-1,3-hexanediol) during poling. The poling field did not appear to favor the formation of a preferred crystalline phase in highly plasticized films, although a significant amount of crystallization occurred upon evaporation of plasticizer. Furthermore, there was no crystallographic evidence for a preferred alignment of crystallites.

From the above discussion, it is apparent that the origin of the piezoelectric effect in odd nylons and related materials is not well understood.

Many biological polymers, polypeptides in particular, exhibit intrinsic piezoelectricity attributed to an internal strain of naturally ordered crystallites. Although the piezoelectric constants for these materials are about an order of magnitude lower than those of PVF₂, considerable interest has arisen in these materials. A more complete discussion of piezoelectricity in polypeptides is given in Section III.D.

Another class of high-melting crystalline polymers that could have significant piezoelectric properties is the polyureas. To our knowledge, no data have been published concerning piezoelectricity in these materials. The prediction that these materials have promise is based upon their inherent crystallinity and the high dipole moment (4.6D) of the urea group.

It was the original purpose of this investigation to evaluate the piezoelectric properties of low, odd nylons (nylon 3 and nylon 5), polypeptides, and polyureas. A further objective was to investigate the use of biomolecular self-assembly to maximize the piezoelectric properties of selected polypeptides.

Our inability to produce useful films from the polypeptides and polyureas necessitated a change in the scope of the project. Consequently, we examined the piezoelectric properties of nylons 3 and 5 only. A literature search was conducted to identify promising attributes of polypeptide materials with respect to piezoelectricity.

II. SUMMARY

A 33-month project was undertaken to study piezoelectricity in low, odd nylons; odd, odd nylons; polyureas; and polypeptides. The commercially available polypeptides poly(L-alanine), poly(L-valine), and poly(L-asparagine) were apparently not of sufficiently high molecular weight to provide usable films for piezoelectric testing. Likewise, the polyureas we synthesized-- poly(trimethyleneurea), poly(pentamethyleneurea), and poly(1,2-propylene diisocyanate)--were also poor film-forming materials. Consequently, we devoted most of our efforts to synthesizing film-forming nylons.

High-molecular-weight nylon 5 was prepared via anionic ring-opening polymerization of α -piperidone. Films of high quality were solvent cast from trifluoroethanol, and these films were poled in the presence and absence of a plasticizer (2-ethyl-1,3-hexanediol). The highest values of the piezoelectric strain (d_{31}) and stress (e_{31}) constants obtained were for plasticized nylon 5--1.3 pC/N and 2.8 mC/m² respectively.

Nylon 3 was prepared via hydrogen-transfer polymerization of acrylamide. As such, only low-molecular-weight polymer was obtained. The nylon 3 films could be handled and poled only in plasticized form, and the highest values of d_{31} and e_{31} observed were 0.8 pC/N and 1.1 mC/m².

The synthesis of the odd, odd nylons 3,5, 3,7, 5,5, 5,7, and 7,7 was also explored. Only nylons 5,7 and 7,7 could be made into good films; however, insufficient time remained in the project to evaluate the piezoelectric response of these nylons.

The piezoelectric constants obtained for nylons 3 and 5 are not high compared with those for poly(vinylidene fluoride). Nevertheless, these values are higher than the constants reported for many other polymers. Given the high dipole densities of nylon 3 and nylon 5 and our early position on a learning curve, we believe that these results show great promise. Additional studies with these materials would undoubtedly result in films with higher piezoelectric constants. Values of d_{31} on the order of 8 to 15 pC/N should be attainable.

As a result of our inability to produce useful films from commercially available polypeptides, a literature survey was undertaken to identify piezoelectric attributes of polypeptides so that this information might aid future research. Based on this survey, we believe additional studies in this area are warranted.

III. RESULTS AND DISCUSSION

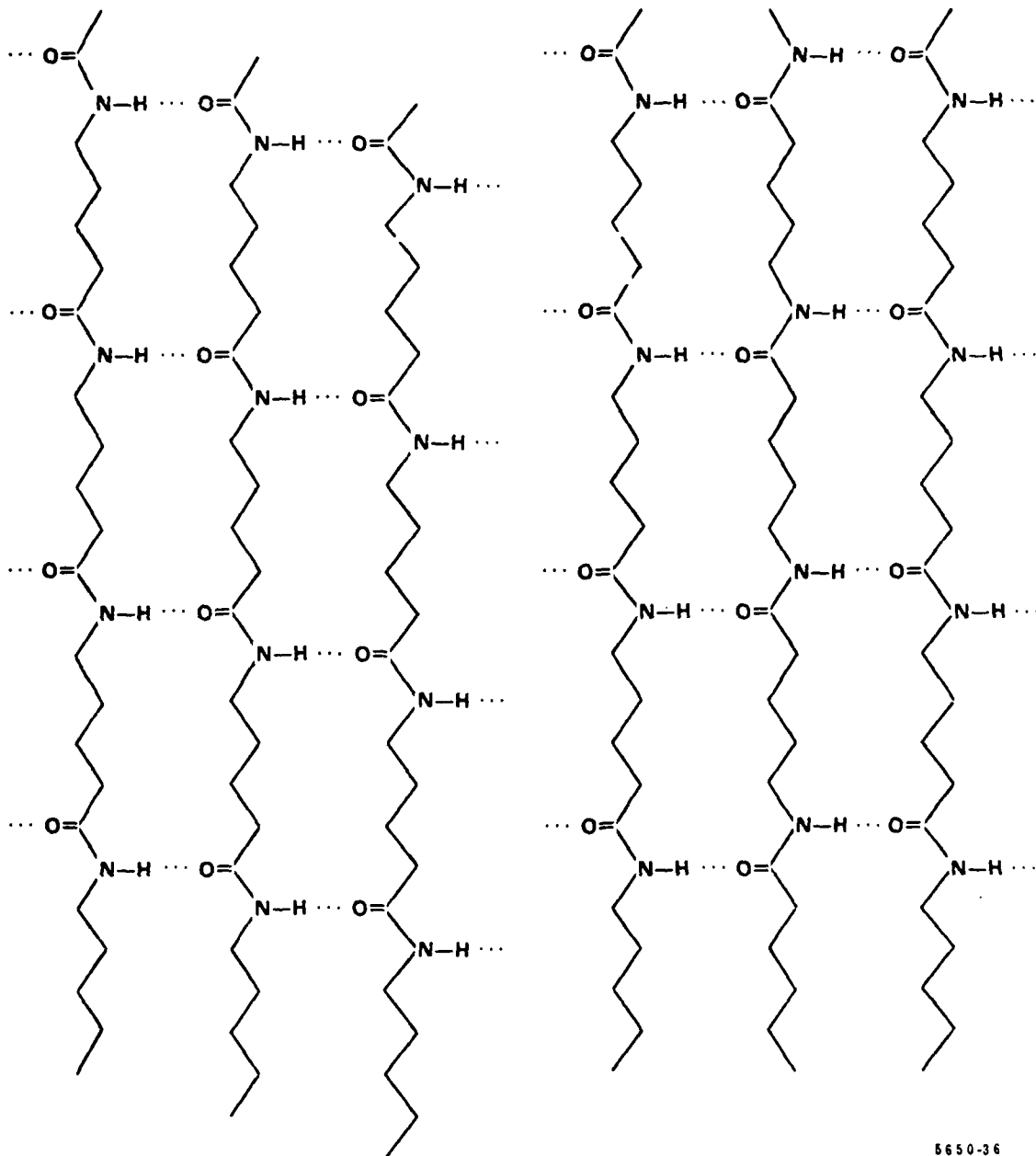
A. Synthesis of Monomers and Polymers1. Polyamides

As discussed in the Introduction, polyamides have shown considerable potential as piezoelectric materials. For example, a value of d_{31} of 7.1 pC/N has been reported for nylon 11.²³ This compares favorably with that reported for PVF₂ ($d_{31} = 23$ pC/N).⁵ The piezoelectric properties of polymers may be dependent on dipole concentration. Masamoto and co-workers²⁶ have reported that the unit cell of nylon 3 is monoclinic and contains four monomeric units. From this information, a dipole concentration of 4.4 D/100 Å³ was calculated. Because this value is larger than the dipole concentration of PVF₂ (2.9 D/100 Å³), nylon 3 was expected to be highly piezoelectric. To obtain information about the effect of chain length and dipole density on piezoelectric activity, nylon 5 was also synthesized and studied.

The synthesis of odd,odd polyamides from diamines and dicarboxylic acids was also investigated. There are at least two potential advantages of odd,odd nylons over the odd nylons (derived from ω-aminocarboxylic acids or lactams). First, the chains of odd,odd nylons are symmetrical, so only a parallel packing of chains can exist.²⁵ In the odd nylons, both parallel and antiparallel packing of chains can occur (Figure 4). Second, the odd,odd nylons offer only half of the hydrogen bonding possible in the corresponding odd nylons (Figure 5). For example, nylon 5,5 can have only two hydrogen bonds per 24 chain atoms, while nylon 5 can have up to four hydrogen bonds per 24 chain atoms. Each structure has an equal number of polar amide groups. Therefore, nylon 5,5 should be easier to draw orient than nylon 5 because of its diminished intermolecular hydrogen bonding. Lin and co-workers²⁷ have established the crystal structure of nylon 5,7 and have shown that the material was easily poled to a medium degree of pyroelectric activity. We are not aware of any extensive piezoelectric evaluations with the odd,odd nylons. Unfortunately, we were unable to evaluate the prospect of piezoelectricity in the odd,odd nylons. Nylons 3,5, 3,7, and 5,5 were not prepared in sufficiently high molecular weights to provide usable films. Although high-molecular-weight samples of nylons 5,7 and 7,7 were prepared, insufficient time remained in the contract for their evaluation. The chemical structures of the polyamides prepared in this program are given in Figure 6.

a. Synthesis of nylon 3

The preparation of nylon 3 (poly-β-alanine) has been reported by various methods in the literature. The most commonly reported route is the hydrogen-transfer (transition) polymerization of acrylamide as shown below.

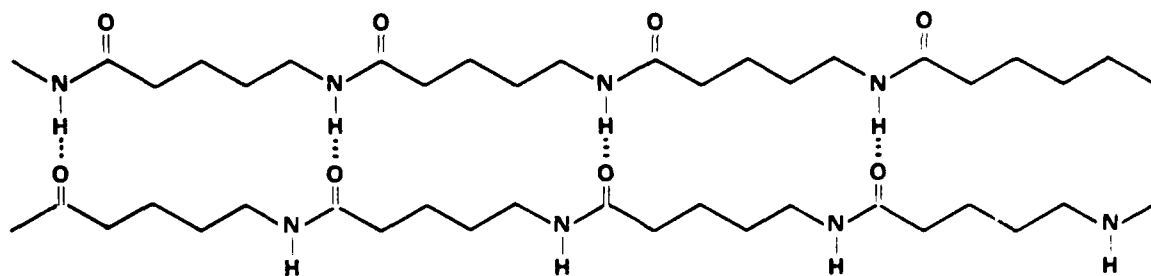


NYLON 5, PARALLEL CHAINS

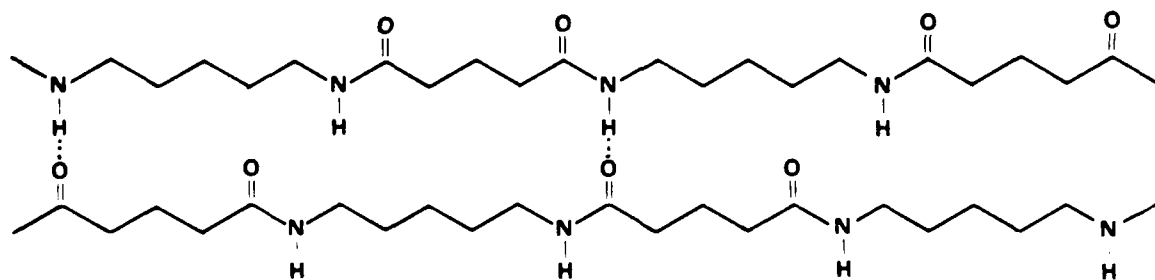
NYLON 5, ANTIPARALLEL CHAINS

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Figure 4. Parallel and antiparallel chain packing in odd nylons.



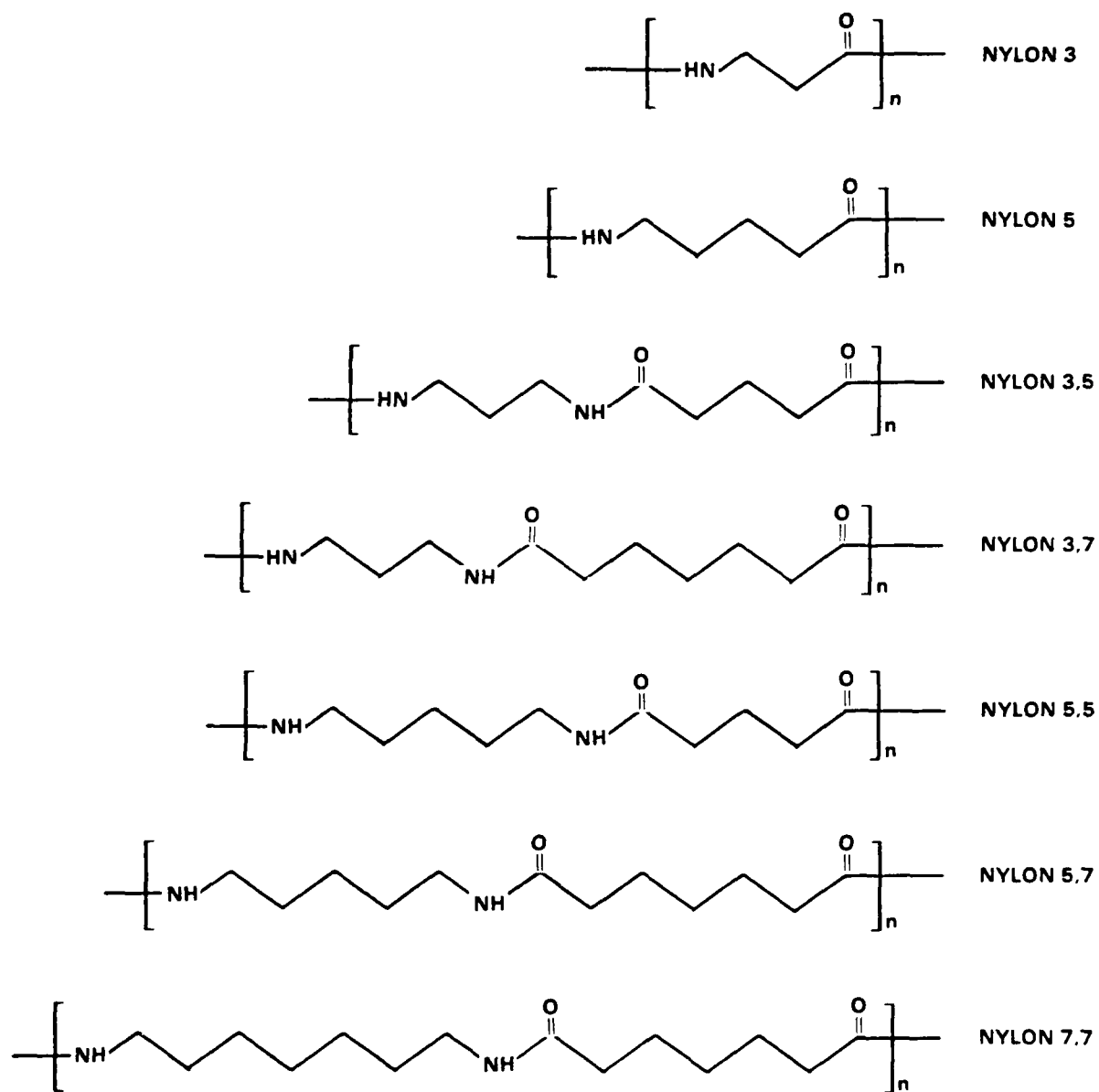
NYLON 5 4 HYDROGEN BONDS PER 24 ATOMS



NYLON 5.5 2 HYDROGEN BONDS PER 24 ATOMS

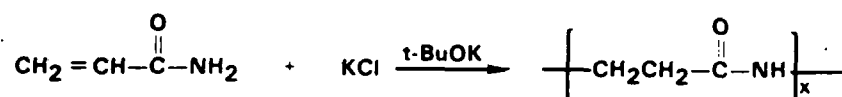
5650-31

Figure 5. Hydrogen bonding in Nylon 5 and Nylon 5.5.



5660-37

Figure 6. Chemical structures of odd and odd,odd nylons synthesized.



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This reaction was first reported by Breslow et al.^{28,29} and has been studied and modified by others.³⁰⁻³⁵ Weight-average molecular weights (\bar{M}_w 's) of nylon 3 up to 80,000 have been reported by this method.²⁹ Consequently, we relied heavily upon this route to prepare nylon 3. Nylon 3 and derivatives of nylon 3 have also been reported via anionic ring-opening polymerization of β -propiolactam and substituted β -propiolactams.^{36,37} Nylon 3 with an \bar{M}_w of 500,000 has been reported by this route,³⁶ although no experimental details were given. This method is severely limited in that the preparation of β -propiolactam is very difficult.³⁸ During this program we attempted to synthesize β -propiolactam, without success.

The ring-opening polymerization of the cyclic dimer of β -alanine (perhydro-1,5-diazocine-2,6-dione) has also been reported.³⁹ Unfortunately, the inherent viscosities (IVs) of nylon 3 prepared by this route were low (0.2 to 0.4 dL/g).

Finally, low-molecular-weight nylon 3 has been reported via polycondensation of β -alanine⁴⁰ and β -alanylchloride hydrochloride.⁴¹

(1) Nylon 3 by hydrogen-transfer polymerization

As stated above, the nylon 3 used in this program was prepared by hydrogen-transfer polymerization of acrylamide. The polymerizations were carried out under dry nitrogen between 95 and 150 °C (most commonly at 115 °C) in *o*-dichlorobenzene. Although the polymerizations were continued for 3 to 4 h, a solid polymer always precipitated from solution within 15 min after the initiator (potassium *t*-butoxide, *t*-BuOK) was added. The insolubility of the polymer in *o*-dichlorobenzene may have limited the molecular weight that was obtained in these polymerizations. This limitation was evident from the IVs of polymer, which ranged from 0.16 to 0.54 dL/g in 88% formic acid at 30 °C (≈ 0.5 g/dL). Breslow has reported that nylon 3 with an intrinsic viscosity in 90% formic acid of 0.42 dL/g corresponds to an \bar{M}_w of 58,000.²⁹ In an attempt to increase the degree of polymerization (DP) of these polymers, several modifications were made, such as changing the initiator level, using different monomer/KCl ratios, and using different polymerization times. None of these changes increased the polymer solubility in *o*-dichlorobenzene or gave a polymer with an IV greater than 0.54 dL/g. In other attempts to increase the DP of nylon 3, we used LiCl and CaCl₂ in place of KCl.⁴² When LiCl was used, the solvent was changed to hexamethylphosphoramide (HMPA), and the resultant polymer was soluble in this system. However, when either LiCl or CaCl₂ was

used, polyacrylamide and not nylon 3 was obtained. The structure of the products was confirmed by IR spectroscopy. Nylon 3 was easily distinguished from polyacrylamide by this analysis. The polymerization conditions and IVs of the nylon 3 samples are given in Table 1.

We obtained the most consistent results (IVs >0.40 dL/g) by polymerizing 97% acrylamide in the presence of undried KCl in a 1:2 acrylamide/KCl weight ratio (5 wt% t -BuOK). Conversions of acrylamide to nylon 3 were typically 75% under these conditions. Consequently, we employed these conditions to prepare nylon 3 for piezoelectric evaluations. Samples C840-137, -144, -145, and -146 (Table 1) were combined and twice reprecipitated from 96% formic acid. The resultant 100-g sample of nylon 3 (C840-147-1) had an IV of 0.45 dL/g and was utilized in piezoelectric evaluations.

Because the nylon 3 prepared for piezoelectric evaluations was found to be too brittle for adequate testing, we attempted to prepare higher-molecular-weight material in hopes of obtaining more flexible films. Additional experiments were conducted at various levels of initiator and KCl as well as at various temperatures (Table 1). None of these samples produced polymer with a sufficiently high IV to provide flexible films.

(2) Attempted syntheses of β -propiolactam

In an effort to produce a higher-molecular-weight nylon 3 than had previously been obtained from acrylamide, we attempted to synthesize β -propiolactam. According to the literature, nylon 3 with molecular weights up to 500,000 (IV = 4 to 5 dL/g) can be obtained via anionic ring-opening polymerization of this monomer.³⁶

Several syntheses of β -propiolactam have been reported, but we were unable to duplicate these results. This highly strained cyclic monomer was first synthesized by Holley and Holley in 0.76% yield by the reaction of ethyl β -aminopropionate and ethyl magnesium bromide.⁴³ Another procedure involves reaction of the β -aminoester with one equivalent of a hindered aryl Grignard reagent to form the lactam.⁴⁴ The reaction is said to result in 50 to 75% yields of pure β -propiolactam, but no experimental details were given. We were successful in obtaining ethyl β -aminopropionate by reaction of ethyl alcohol with β -alanine in the presence of dry HCl followed by neutralization with ammonia. However, only traces of β -propiolactam were detected spectroscopically from the reaction of ethyl β -aminopropionate and mesitylmagnesium bromide. We also attempted the synthesis of β -propiolactam by reaction of N -(trimethylsilyl)- β -alanine, trimethylsilyl ester and mesitylmagnesium bromide, without success.⁴⁵ Direct dehydration of β -alanine using DMSO⁴⁶ and dibutyltin oxide (n -Bu₂SnO)⁴⁷ also failed to produce β -propiolactam. The reactions described above are shown schematically in Figure 7. The yields obtained for the β -propiolactam precursors are given in the figure.

b. Synthesis of nylon 5

Nylon 5 was synthesized via anionic ring-opening polymerization of α -piperidone (δ -valerolactam) with two types of catalysts--potassium

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TABLE 1. SYNTHESIS OF NYLON 3 BY HYDROGEN-TRANSFER
POLYMERIZATION OF ACRYLAMIDE

| Sample No. | Amount of acrylamide, g | Acrylamide/KCl, w/w | t-BuOK, wt % | Reaction time, h | Reaction temp, °C | Inherent viscosity, ^a dL/g |
|---------------------|-------------------------|---------------------|--------------|------------------|-------------------|---------------------------------------|
| <u>C840</u> | | | | | | |
| -1-1 | 25 | 3/1 | 5.0 | 3 | 115 | 0.54 |
| -55-1 | 25 | 3/1 | 5.0 | 4 | 115 | 0.30 |
| -59-1 | 25 | 1.5/1 | 6.0 | 2.5 | 115 | 0.42 |
| -63-A | 25 | 1.5/1 | 3.0 | 4 | 130 | 0.39 |
| -75-1 | 25 | 3/1 ^b | 5.0 | 6 | 115 | 0.31 |
| -79-1 | 25 | 1/2 | 5.0 | 3 | 115 | 0.46 |
| -80-1 | 25 | 1/2 ^b | 5.0 | 3 | 115 | 0.37 |
| -84-1 | 25 | 3/1 ^c | 5.0 | 3 | 115 | 0.16 ^d |
| -86-1 | 25 | 3/1 ^e | 5.0 | 3 | 115 | 2.47 ^d |
| -97-1 | 25 | 1/2 | 5.0 | 3 | 115 | 0.48 |
| -137-1 | 25 | 1/2 | 5.0 | 3 | 115 | 0.44 |
| -138-1 | 25 | 1/2 | 5.0 | 3 | 115 | 0.37 |
| -144-1 | 50 | 1/2 | 5.0 | 3 | 115 | 0.43 |
| -145-1 | 50 | 1/2 | 5.0 | 3 | 115 | 0.41 |
| -146-1 | 50 | 1/2 | 5.0 | 3 | 115 | 0.43 |
| -147-1 ^f | | | | | | 0.45 |
| -149-1 | 25 | 1/2 | 2.5 | 3 | 150 | 0.32 |
| -153-1 | 25 | 1/2 | 1.2 | 3 | 150 | 0.17 |
| -155-1 | 25 | 1/2 | 0.6 | 3 | 150 | 0.22 |
| -157-1 | 25 | 1/2 | 0.3 | 3 | 150 | 0.19 |
| -159-1 | 25 | 1/2 | 5.0 | 3 | 95 | -- ^d |
| -160-1 | 25 | 1/2 | 7.5 | 3 | 150 | 0.17 |
| <u>E175</u> | | | | | | |
| -3-1 | 25 | 1/1 | 5.0 | 3 | 115 | 0.32 |
| -5-1 | 25 | 2/1 | 5.0 | 3 | 115 | 0.33 |
| -7-1 | 25 | 4/1 | 5.0 | 3 | 115 | 0.27 |
| -9-1 | 25 | 4/1 | 7.5 | 3 | 115 | 0.29 |

^aDetermined at 30 °C in 88% formic acid at a concentration of 0.5 g/dL.

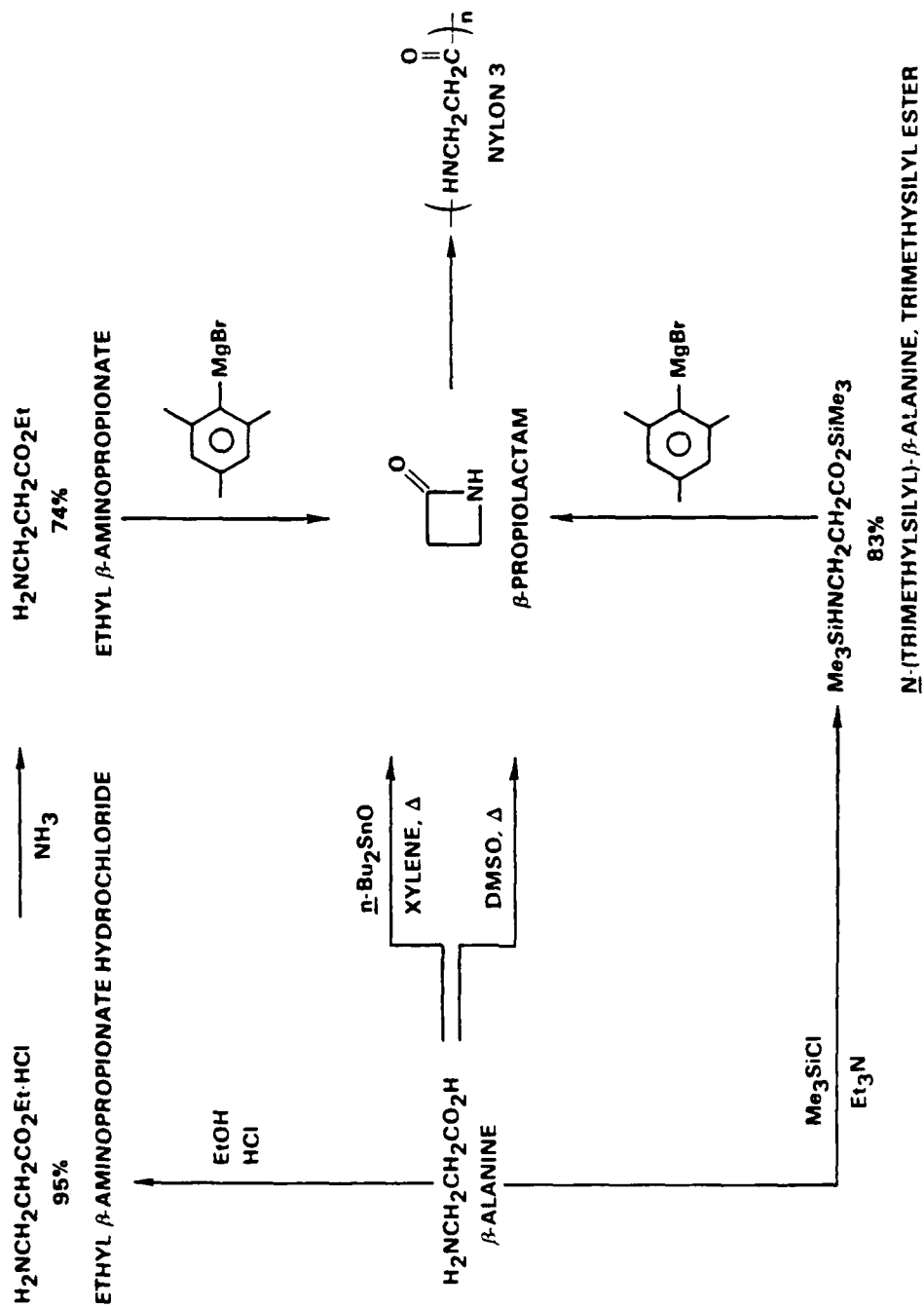
^bAcrylamide was sublimed before use. KCl was dried at 80 °C in vacuo.

^cLiCl used in place of KCl.

^dPolymer identified as polyacrylamide.

^eCaCl₂ used in place of KCl.

^fA 50 wt % solution of C840-137, -144, -145, and -146 in 96% formic acid was precipitated in 90:10 methanol/water.



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Figure 7. Attempted syntheses of β -propiolactam.

piperidonate/triethylaluminum and tetramethylammonium piperidonate (TMAP). N-Acetyl- α -piperidone was used as the polymerization initiator in conjunction with both catalyst systems. Use of the quaternary ammonium salt TMAP as catalyst gave the highest molecular weight of the polymer in the shortest length of time. A generalized mechanism for the anionic ring-opening polymerization of α -piperidone is shown in Figure 8.

(1) Potassium piperidonate/triethylaluminum catalysts

Nylon 5 was first prepared via anionic ring-opening polymerization of α -piperidone using metallic aluminum alkylates as catalysts. The polymerization of α -piperidone is extremely slow compared with the corresponding polymerizations of α -pyrrolidone (nylon 4) and ϵ -caprolactam (nylon 6), requiring approximately one month at 45 °C with this catalyst system. Nevertheless, high-molecular-weight nylon 5 has been reported in the literature using various forms of the alkali metal piperidonate/triethylaluminum catalyst.^{48,49} The polymerization requires an activator (catalyst) and an acylating agent (initiator) to proceed (Figure 8). We evaluated three forms of this catalyst system to effect polymerization: KAlEt_4 , KAlEt_3 (piperidone), and KAlEt_3 (in situ). N-Acetyl- α -piperidone was used as the polymerization initiator. The polymerization probably proceeds with all three catalysts by the mechanism indicated in Figure 8.

Triethylaluminum (AlEt_3) is reported to have two roles in the polymerization sequence.⁴⁸ First, AlEt_3 protects the N-acyllactam group in both the initiator and the propagating polymer chains from side reactions by stabilizing the amide-metal salt via complexation. Second, AlEt_3 increases the solubility of the metal salt in the polymerization medium.

The polymerizations were carried out in the solid state at 45 °C. It was necessary to exclude water and remove all traces of solvent from the polymerization vessel to obtain polymer with a high IV, and typically, 20 to 30 days were required for the polymerization. Thus, considerable care was taken at each step to prevent the extremely hygroscopic α -piperidone from sorbing moisture. Experimental details are given in Section IV.A.2.a.

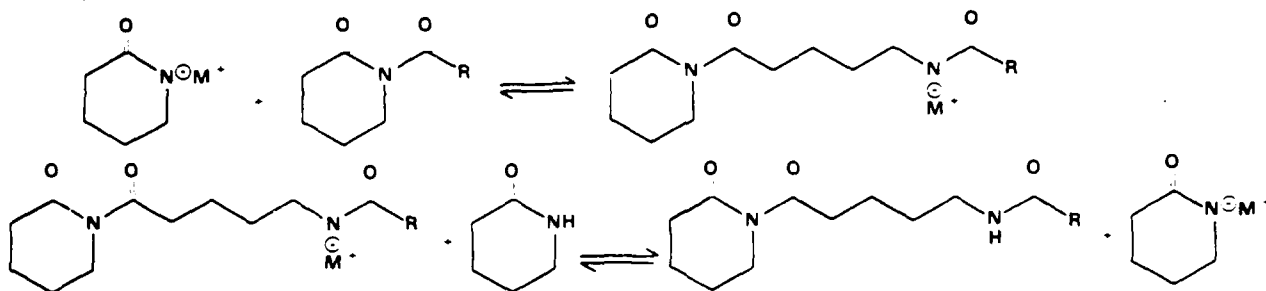
(a) KAlEt_4 catalyst system

The polymerization trials shown in Table 2 were conducted using KAlEt_4 as the catalyst. Although reduced viscosities (η_{red}) of nylon 5 as high as 0.9 dL/g have been reported with this catalyst,⁴⁹ we obtained polymer with reduced viscosities no higher than 0.38 dL/g (IV = 0.35 dL/g) in m-cresol at 30 °C. We were not able to cast coherent films with this low-viscosity material, and no further studies using this catalyst were made.

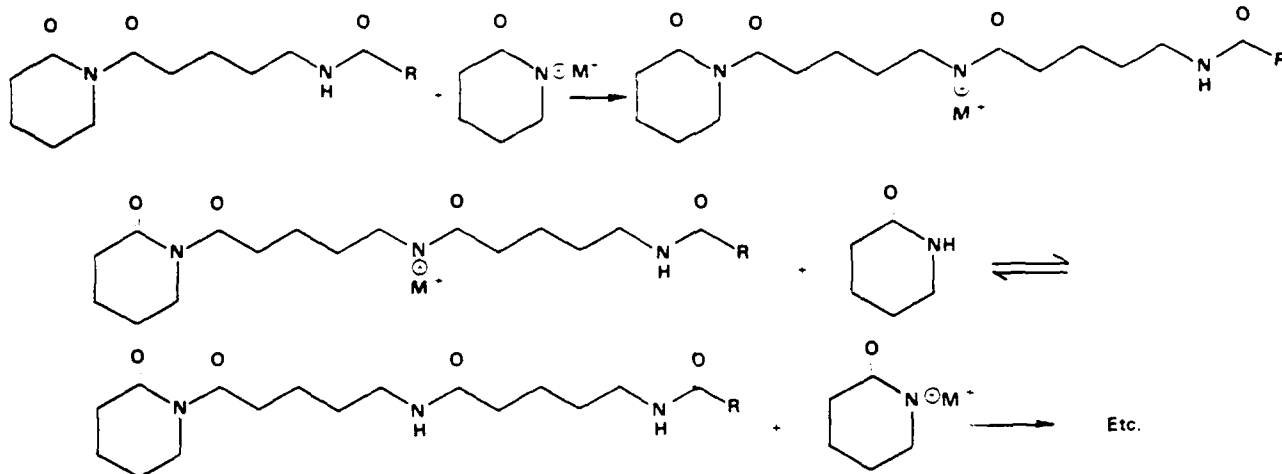
(b) KAlEt_3 (piperidone) catalyst system

Much better results were obtained using KAlEt_3 (piperidone) as catalyst, as shown in Table 3. Reduced viscosities of nylon 5 as high as 1.1 dL/g have been reported in the literature⁴⁹ with this catalyst system, and we obtained nylon 5 with η_{red} of 0.84 dL/g (IV = 0.70 dL/g) after purification of

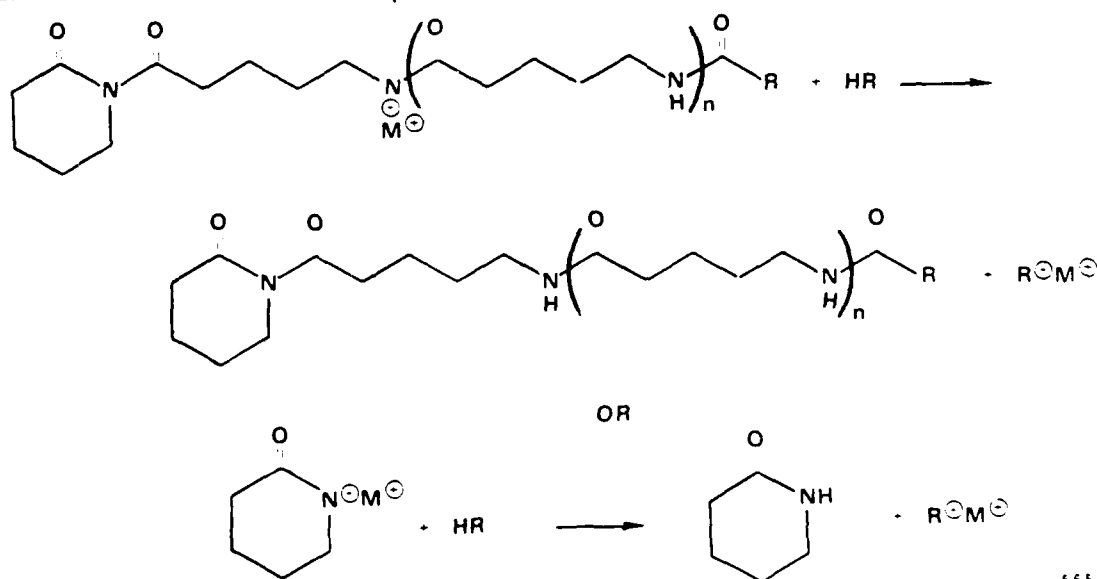
INITIATION:



PROPAGATION:



TERMINATION:



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Figure 8. Possible mechanism for the anionic ring-opening polymerization of α -piperidone.

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TABLE 2. POLYMERIZATION OF α -PIPERIDONE WITH KAlEt_4 AS CATALYST

| Sample No. | KAlEt_4 , mol % | <u>N</u> -Acetyl- α -piperi- done, mol % | Polymerization time, d | IV, ^a dL/g | Conversion, % |
|------------|-----------------------------|--|---------------------------|--------------------------|------------------|
| C840-25-1 | 2.8 | 2.8 | 2 | 0.15 ^b | -- ^c |
| C840-25-2 | | | 5 | 0.25 ^b | -- |
| C840-25-3 | | | 12 | 0.28 ^b | -- |
| C840-25-4 | | | 15 | 0.27 ^b | -- |
| C840-25-5 | | | 21 | 0.24 ^b | -- |
| C840-27-1 | 2.8 | 2.8 | 5 | 0.14 ^b | -- |
| C840-27-2 | | | 11 | 0.18 ^b | -- |
| C840-27-3 | | | 14 | 0.17 ^b | -- |
| C840-27-4 | | | 20 | 0.15 ^b | -- |
| C840-32-1 | 2.8 | 2.8 | 7 | 0.12 | -- |
| C840-33-1 | 5.6 | 5.6 | 7 | 0.12 | -- |
| C934-15-1 | 2.6 | 2.6 | 7 | 0.14 | 41 |
| C934-15-2 | | | 15 | 0.14 | 12 |
| C934-15-3 | | | 18 | 0.13 | 29 |
| C934-16-1 | 4.0 | 4.0 | 7 | 0.34 | 40 |
| C934-16-2 | | | 15 | 0.34 | 28 |
| C924-16-3 | | | 28 | 0.35 | 40 |
| C934-23-1 | 5.0 | 5.0 | 28 | 0.32 | 41 |

^aDetermined in *m*-cresol (0.5 g/dL, 30 °C) unless otherwise indicated.

^bDetermined in 88% formic acid (0.5 g/dL, 30 °C).

^cPercent conversion not calculated.

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TABLE 3. POLYMERIZATION OF α -PIPERIDONE WITH KAlEt_3 (PIPERIDONE) AS CATALYST

| Sample No. C934 | KAlEt_3 (piperi- done), mol % | <u>N</u> -Acetyl- α -piperi- done, mol % | Polymerization time, d | IV, ^a dL/g | Conversion, % |
|--------------------|---|--|---------------------------|--------------------------|------------------|
| -17-1 | 2.0 | 1.0 | 9 | 0.38 | 14 |
| -17-2 | | | 16 | 0.43 | 26 |
| -18-1 | 3.0 | 1.5 | 9 | 0.42 | 9 |
| -18-2 | | | 16 | 0.45 | 12 |
| -18-3 | | | 26 | 0.53 | 36 |
| -24-1 | 4.0 | 2.0 | 28 | 0.59 | 52 |
| -24-2 | | | | 0.62 ^b | 89 ^c |
| -24-3 | | | | 0.70 ^d | 80 ^c |
| -24-4 | | | | 0.57 ^e | 90 ^c |

^aDetermined in *m*-cresol (0.5 g/dL, 30 °C) unless otherwise indicated.

^bA 15 wt % solution of C934-24-1 in 88% formic acid was precipitated into 10 volumes of methanol.

^cPercent of polymer recovered from precipitation.

^dA 10 wt % solution of C934-24-1 in 88% formic acid was precipitated into 10 volumes of water.

^eA 10 wt % solution of C934-24-1 in trifluoroethanol was precipitated into 10 volumes of ethanol.

the polymer by reprecipitation. We were able to cast films of fair strength from this material.

(c) KAlEt_3 (in situ) catalyst system

Nylon 5 of moderately high molecular weight was also obtained when KAlEt_3 was generated in situ (Table 4). Reduced viscosities of nylon 5 as high as 0.8 dL/g after 10 days have been reported using this catalyst.⁴⁹ Similarly, we prepared nylon 5 with η_{red} of 0.86 dL/g (IV = 0.71 dL/g) after a 28-day polymerization.

(2) Tetramethylammonium piperidonate catalyst

A superior preparation of nylon 5 employing the quaternary ammonium salt TMAP was used to provide polymer for piezoelectric evaluations.^{50,51} By this method, we were able to prepare nylon 5 at comparable or higher IV in only four to five days at 45 °C. Indeed, the sample with the highest IV (1.15 dL/g in *m*-cresol at 30 °C, 0.5 g/dL) obtained was made via this procedure. On a small scale (23 g of monomer), we obtained nylon 5 with an IV of 0.63 dL/g after a polymerization time of only two days (Table 5). This viscosity was comparable to that obtained using the potassium piperidonate/triethylaluminum catalyst employed previously in polymerizations that required 25 to 30 days. Three scaled-up batches of nylon 5 employing ≈100 g of α -piperidone each were made using TMAP as catalyst under the same reaction conditions (Table 5). Two of the batches yielded polymer of nearly the same IV (0.60 dL/g, C934-80-1 and C934-89-1), while the third batch gave a sample with a much higher IV (1.15 dL/g, C934-83-1). Because the high-IV batch was synthesized during a period of low ambient humidity in the laboratory, we suspect that unavoidable contamination by traces of water limited the IVs of the other batches.

Because a minimum of 100 g of one lot of polymer was desired for piezoelectric testing, we combined the two lots (C934-80-1 and -89-1) with similar IVs by solvent blending and reprecipitation. The resultant lot, C934-90-1, had an IV of 0.62 dL/g. Unfortunately, the quality of the films cast from this lot was not good enough for routine manipulations during piezoelectric testing. Consequently, the high-IV lot, C934-83-1, was used for piezoelectric testing despite the fact that 100 g was not available. Experimental details of the synthesis of nylon 5 using TMAP as catalyst are given in Section IV.A.b.

c. Synthesis of odd,odd nylons

Odd,odd nylons of the AABB type were synthesized by three routes: melt polymerization, interfacial polymerization, and solution polymerization. High-IV nylon 5,7 and nylon 7,7 were easily prepared by melt polymerization of the corresponding nylon salts. Nylons 3,5, 3,7, and 5,5 could not be prepared with high IVs under any of the usual conditions for preparing the higher-chain-length nylons. More details concerning the preparation of these polymers are given below.

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TABLE 4. POLYMERIZATION OF α -PIPERIDONE WITH IN SITU FORMATION OF KAlEt_3

| Sample No. C934 | KAlEt_3 , mol % | AlEt_3 , mol % | <u>N</u> -Acetyl- α -piperi- done, mol % | Polymerization time, d | IV, ^a dL/g | Conversion % |
|--------------------|-----------------------------|----------------------------|--|---------------------------|--------------------------|-----------------|
| -25-1 | 3.9 | 1.3 | 2.0 | 28 | 0.47 | 37 |
| -26-1 | 3.9 | 1.3 | 2.0 | 28 | 0.65 | 53 |
| -26-2 | | | | | 0.71 ^b | 85 ^c |
| -29-1 | 3.9 | 1.3 | 2.0 | 28 | 0.60 | 35 |
| -29-2 | | | | | 0.64 ^b | 74 ^c |

^aDetermined in m-cresol (0.5 g/dL, 30 °C) unless otherwise indicated.

^bA 10 wt % solution of C934-26 in 88% formic acid was precipitated into 10 volumes of water.

^cPercent of polymer recovered from reprecipitation.

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TABLE 5. POLYMERIZATION OF α -PIPERIDONE WITH TETRAMETHYLAMMONIUM PIPERIDONATE (TMAP) AS CATALYST

| Sample No. C934 | TMAP, mol % | N-Acetyl- α -piperi- done, mol % | Amount of α -piperidone, g | Polymerization time, d | IV, ^a dL/g | Conversion, % |
|--------------------|----------------|--|---|---------------------------|--------------------------|------------------|
| -66-1 | 7.3 | 1.0 | 23 | 2 | 0.63 | 32 |
| -80-1 | 8.0 | 1.0 | 108 | 4 | 0.60 | 55 |
| -83-1 | 8.0 | 1.0 | 105 | 5 | 1.15 | 59 |
| -89-1 | 8.0 | 1.0 | 101 | 5 | 0.62 | 70 |
| -90-1 | | | | | 0.62 ^b | 95 ^c |

^aDetermined in *m*-cresol (0.5 g/dL, 30 °C) unless otherwise indicated.

^bA 20 wt % solution of C934-80-1 and -89-1 in 96% formic acid was precipitated into 10 volumes of ether.

^cPercent of polymer recovered from reprecipitation.

(1) Melt polymerization

Nylons of the AABB type are most commonly prepared by melt polymerization, which involves the direct amidation of dibasic acids and diamines (Figure 9). A diammonium salt (nylon salt) was first prepared by mixing equimolar alcoholic solutions of the diamine and diacid. The salts precipitated from solution and were isolated by filtration. The use of a nylon salt helps provide the proper stoichiometry for the subsequent polycondensation. Table 6 contains a list of the salts prepared in this program.

High-IV samples of nylons 5,7 (2.81 dL/g) and 7,7 (1.76 dL/g) were prepared from their corresponding salts (Table 7). The salts were first heated above their melting points under nitrogen pressure to form prepolymers. The prepolymers were subsequently heated above their melting temperatures under vacuum to remove the water formed during the polycondensation reaction. Similar treatment of nylon 3,5, 3,7, and 5,5 salts resulted in low-IV polymers (Table 7). The low IVs can probably be attributed to side reactions competing with polycondensation. Figure 10 shows two possible side reactions encountered when glutaric acid and 1,3-diaminopropane are used as components. A growing polymer chain capped with a glutaric acid unit can intramolecularly cyclize to give a six-membered cyclic imide. With 1,3-diaminopropane at the end of a chain, a tetrahydropyrimidine derivative can result. These side reactions would reduce the molecular weights of any polymer employing either monomer in its preparation. We were aware that these side reactions were possible; nevertheless, we tried to find those conditions that would produce the highest-IV polymers under these circumstances. Most of the data in Table 7 concerns the preparation of these difficult-to-obtain nylons. After considerable effort, we obtained a sample of nylon 5,5 with an IV of 0.64 dL/g, but much lower IVs were obtained for nylons 3,5 (0.25 dL/g) and 3,7 (0.15 dL/g).

(2) Interfacial polymerization

We attempted to prepare high-IV samples of the short-chain-length odd,odd nylons by interfacial polymerization. In the interfacial process, a diacid chloride is dissolved in a water-immiscible solvent and added to an aqueous solution of the diamine. Polycondensation takes place in the organic layer at the interface. The HCl produced is scavenged by an inorganic base added to the aqueous layer or by use of excess diamine. Because the reaction of an acid chloride and an amine is much faster than the reaction of a carboxylic acid and amine, the reactions were run at room temperature or below.

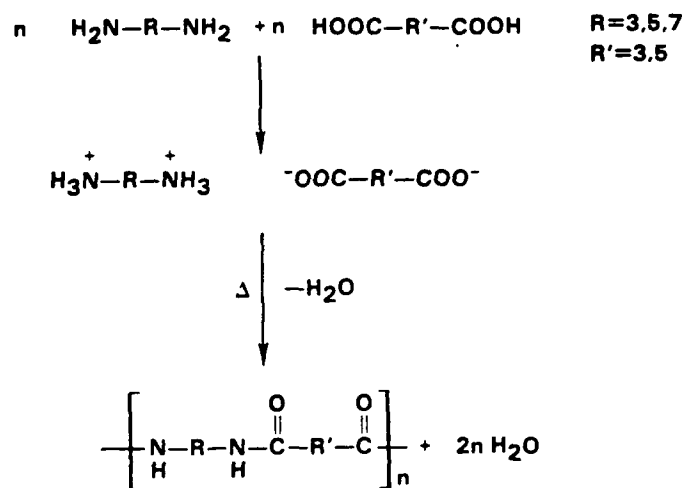
The experiments we conducted by interfacial polymerization are shown in Table 8. The highest-IV sample of nylon 5,5 prepared by this technique was 0.55 dL/g. These conditions were then used for the preparation of samples of nylon 3,5 (0.16 dL/g) and nylon 3,7 (0.46 dL/g).

(3) Solution polymerization

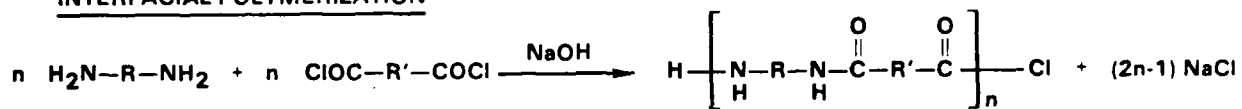
One sample of nylon 5,5 was prepared by the reaction of glutaryld chloride

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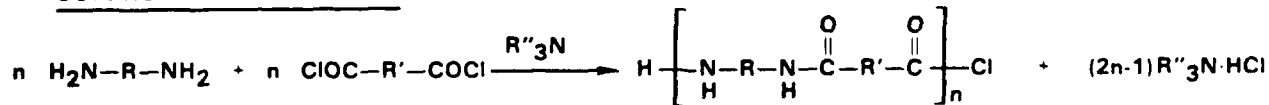
MELT POLYMERIZATION



INTERFACIAL POLYMERIZATION



SOLUTION POLYMERIZATION



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Figure 9. Synthetic routes to polyamides of the AAB type.

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TABLE 6. SYNTHESIS OF NYLON SALTS

| Sample No. | Nylon salt | Diamine | Diacid | Yield, % | Melting range, °C |
|------------|------------|---------------------|---------------|----------|-------------------|
| C934-110-1 | 3,5 | 1,3-diamino-propane | glutaric acid | 96 | 195-196 |
| C934-118-1 | 3,7 | 1,3-diamino-propane | pimelic acid | 92 | 131-134 |
| B209-135-1 | 5,5 | 1,5-diamino-pentane | glutaric acid | 99 | 180-181 |
| C934-119-1 | 5,7 | 1,5-diamino-pentane | pimelic acid | 95 | 194-196 |
| C934-107-1 | 7,7 | 1,7-diamino-heptane | pimelic acid | 86 | 191-194 |

TABLE 7. SYNTHESIS OF ODD, ODD NYLONS FROM NYLON SALTS

| Sample No. C934 | Nylon type | Pressure step | | Indicated polymerization conditions Sample No. C934 | Vacuum step | | N ₂ backpressure | | IV, ^a dL/g |
|--------------------|---------------|---------------|-------------------|--|-------------|---------------------|-----------------------------|-------------|--------------------------|
| | | Temp, °C | Pressure, psig | | Time, h | Temp, °C | Time, h | Temp, °C | |
| -114-1 | 3,5 | 216-218 | 105-220 | 2 | -114-1 | 262(m) ^b | 2 | 0.14 | |
| -114-2 | | | | | -114-1 | 240 | 5 | 0.21 | |
| -114-3 | | | | | -114-1 | 198-200 | 5 | 0.23 | |
| -114-4 | | | | | -114-1 | 198-200 | 16 | 0.20 | |
| -114-5 | | | | | -114-1 | 198-200 | 16 | 0.21 | |
| -117-1 | | | | | -114-1 | 262(m) | 2 | 0.18 | |
| -122-1 | 3,5 | 220 | 110-245 | 2 | -122-1 | 224 | 16 | 0.15 | |
| -122-2 | | | | | | | | 0.25 | |
| -120-1 | 3,7 | 148-150 | 110-145 | 2 | -120-1 | 162(m) | 2 | 0.10 | |
| -120-2 | | | | | -120-1 | 162(m) | 4 | 0.09 | |
| -120-3 | | | | | | | | 0.09 | |
| -123-1 | 3,7 | 198 | 105-190 | 2.5 | -123-1 | 228(m) | 2 | 0.12 | |
| -123-2 | | | | | -123-1 | 228(m) | 4 | 0.13 | |
| -123-3 | | | | | -123-1 | 224(m) | 16 | 0.14 | |
| -123-4 | | | | | | | | 0.15 | |
| -97-1 | 5,5 | 188-190 | 105-195 | 2 | -97-1 | 200 | 16 | 0.16 | |
| -97-2 | | | | | -97-1 | 220 | 16 | 0.64 | |
| -97-3 | | | | | -97-1 | 240 | 16 | 0.60 | |
| -97-4 | | | | | -97-1 | 180 | 16 | 0.64 | |
| -97-5 | | | | | -97-1 | 158(m) | 16 | 0.51 | |
| -97-6 | | | | | -97-1 | 258(m) | 2.5 | 0.44 | |
| -97-7 | | | | | -97-1 | 154 | 16 | 0.42 | |
| -97-8 | | | | | | | | 0.52 | |

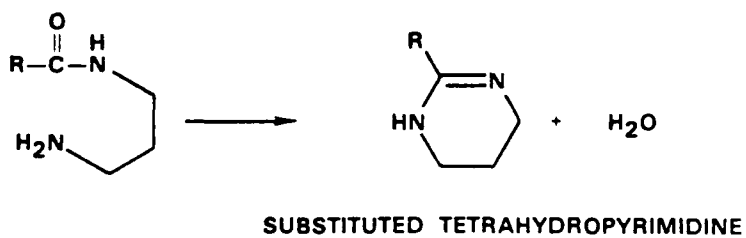
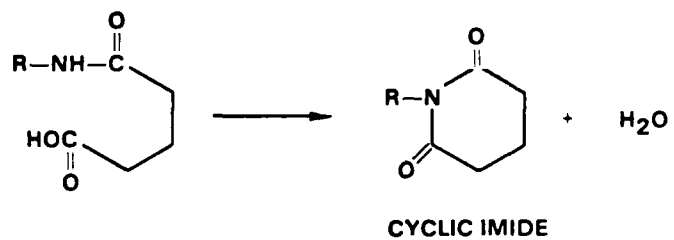
(continued)

TABLE 7 (continued)

| Sample No. C934 | Nylon type | Pressure step | | Indicated polymerization conditions Sample No. C934 | Vacuum step | | N ₂ backpressure | | IV, ^a dL/g |
|--------------------|---------------|---------------|-------------------|--|-------------|-------------|-----------------------------|-------------|--------------------------|
| | | Temp, °C | Pressure, psig | | Time, h | Temp, °C | Time, h | Temp, °C | |
| -111-1 | | | | -97-1 | | | 180-182 | 16 | 0.58 |
| -111-2 | | | | -97-1 | | | 180-182 | 16 | 0.50 |
| -111-3 | | | | -97-1 | | | 260-262(m) | 1.5 | 0.37 |
| -111-4 | | | | -97-1 | | | 260-262(m) | 1.5 | 0.46 |
| -113-1 | | | | -97-1 | | 200 | | 16 | 0.60 |
| -99-1 | 5,5 | 181-183 | 105-180 | -99-1 | | 181-183 | | 2 | 0.16 |
| -99-2 | | | | -99-1 | | 181-183 | | 21 | 0.44 |
| -99-3 | | | | -99-1 | | | | 16 | 0.56 |
| -98-1 | 5,5 | | | | | 170 | | 16 | 0.11 |
| -102-1 | 5,5 | | | -102-1 | | 183 | | 16 | 0.49 |
| -102-1V | | | | -102-1 | | | | 16 | 0.58 |
| -121-1 | 5,7 | 214 | 105-200 | -121-1 | | 244(m) | | 2 | 0.32 |
| -121-2 | | | | -121-1 | | 244(m) | | 4 | 2.09 |
| -121-3 | | | | -121-1 | | | | 4 | 2.81 |
| -112-1 | 7,7 | 212 | 105-195 | -112-1 | | 250-252(m) | | 2 | 0.35 |
| -112-3 | | | | -112-1 | | 250-252(m) | | 4 | 1.46 |
| -112-3 | | | | -112-1 | | 250-252(m) | | 4 | 1.76 |

^adetermined in trifluoroethanol at 30 °C at ≈0.5 g/dL.

^b(m) Indicates that polymer was in molten state at that temperature.



6650-40

Figure 10. Possible side reactions encountered in the synthesis of polyamides from glutaric acid and 1,3-diaminopropane.

TABLE 8. SYNTHESIS OF ODD, ODD NYLONS BY INTERFACIAL POLYMERIZATION

| Sample No. C-934 | Nylon type | Diamine | Diacidchloride | Diamine/ diacidchloride, (mol/mol) | Acid acceptor | Solvent | Temp, °C | IV, ^a dL/g |
|---------------------|---------------|-------------------------|----------------------|--|------------------|---|-------------|--------------------------|
| -130-1 | 3,5 | 1,3-diamino- propane | glutaryl chloride | 2:1 | NaOH | CH ₂ Cl ₂ | 0 | 0.16 |
| -131-1 | 3,7 | 1,3-diamino- propane | pimeloyl chloride | 2:1 | NaOH | CH ₂ Cl ₂ | 0 | 0.46 |
| -101-1 | 5,5 | 1-5-diamino- pentane | glutaryl chloride | 2.7:1 | -- ^b | C ₂ H ₂ Cl ₄ | 25 | 0.33 |
| -103-1 | 5,5 | 1-5-diamino- pentane | glutaryl chloride | 2.7:1 | -- | C ₂ H ₂ Cl ₄ | 25 | 0.30 |
| -132-1 | 5,5 | 1-5-diamino- pentane | glutaryl chloride | 2:1 | NaOH | CH ₂ Cl ₂ | 25 | 0.47 |
| -116-1 | 5,5 | 1-5-diamino- pentane | glutaryl chloride | 2:1 | NaOH | CH ₂ Cl ₂ | 0 | 0.55 |
| -124-1 | 5,5 | 1-5-diamino- pentane | glutaryl chloride | 4:1 | NaOH | CH ₂ Cl ₂ | 0 | 0.51 |

^aDetermine in trifluoroethanol at 30 °C at =0.5 g/dL.^b-- = Excess diamine.

and 1,5-diaminopentane in N-methylpyrrolidone at 0 °C (Figure 9). Triethylamine was used as the acid scavenger. The sample had an IV of 0.46 dL/g after reprecipitation from TFE.

The highest IVs that we obtained for the odd,odd nylons prepared by the three methods described above are given in Table 9.

2. Polyureas

As stated in the Introduction, polyureas have considerable potential as piezoelectric materials based on their high crystallinity and the high dipole moment of the urea group (4.6D). Three polyureas were synthesized in this program: poly(trimethyleneurea) (PTMU), poly(pentamethyleneurea) (PPMU), and poly(1,2-propylene diisocyanate) (PPDI). As can be seen in Figure 11, PTMU is an analog of nylon 5, while PPMU is an analog of nylon 7. PPDI can be thought of as a substituted nylon 1. Unfortunately, we were unable to prepare these polymers in molecular weights high enough to provide usable films for piezoelectric testing. More details concerning the synthesis of these materials are given below.

a. Synthesis of poly(trimethyleneurea)

We attempted to synthesize poly(trimethyleneurea) (PTMU) via two routes. The first route⁵² involved the reaction of equimolar quantities of trimethylene diisocyanate (TMDI) and trimethylenediamine (TMDA, 1,3-diaminopropane) in DMF as illustrated in Figure 12. TMDI was synthesized via glutaric dihydrazide, which in turn was prepared via the reaction of dimethyl glutarate and hydrazine hydrate (Figure 12).⁵³ The structure of TMDI was confirmed by IR and NMR analyses, and a GC analysis showed that the TMDI was greater than 99% pure. When a stoichiometric amount of TMDI was added dropwise to TMDA in dimethylformamide at 0 °C, a white solid precipitated during the addition. The temperature was increased to 100 °C and maintained at this temperature for 4.0 h, but the solid did not dissolve. The number-average molecular weight of this solid, determined by end-group analysis, was 4500. The IV was 0.20 dL/g in hexafluoroisopropanol (HFIP) at 30 °C. Several attempts to prepare PTMU by this method gave similar results.

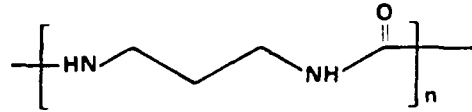
In the second approach to poly(trimethyleneurea), a 1:2 TMDI/TMDA adduct was prepared and reacted with urea (Figure 12). The major product obtained from the second reaction was N,N'-trimethyleneurea. This material was identified by its melting point (258 to 259 °C) and IR and NMR spectra.⁵⁴ N,N'-trimethyleneurea is probably formed by a depolymerization mechanism as shown below.

TABLE 9. HIGHEST INHERENT VISCOSITIES OF ODD,ODD
 NYLONS PREPARED BY VARIOUS METHODS

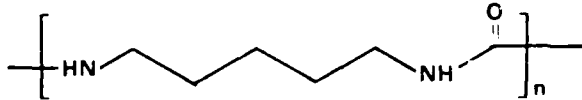
| Nylon type | IV, ^a dL/g, for each polycondensation method | | |
|---------------|--|-------------|-----------------|
| | Melt | Interfacial | Solution |
| 3,5 | 0.25 | 0.16 | -- ^b |
| 3,7 | 0.15 | 0.46 | -- |
| 5,5 | 0.64 | 0.55 | 0.46 |
| 5,7 | 2.81 | -- | -- |
| 7,7 | 1.76 | -- | -- |

^aDetermined in trifluoroethanol at 30 °C at 0.5 g/dL.

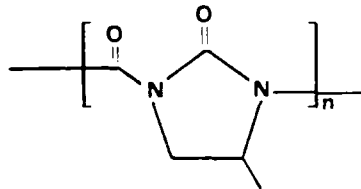
^bSynthesis of nylon not attempted by indicated method.



POLY(TRIMETHYLENEUREA)



POLY(PENTAMETHYLENEUREA)

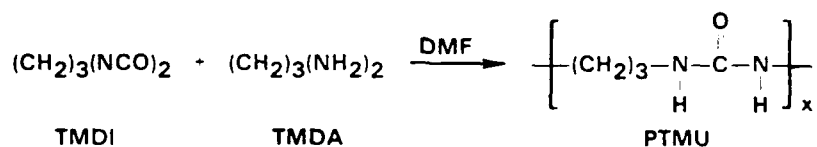
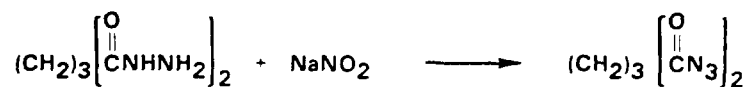
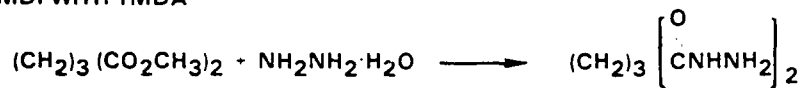


POLY (1,2-PROPYLENE DIISOCYANATE)

5650-41

Figure 11. Chemical structures of polyureas synthesized.

REACTION OF TMDI WITH TMDA



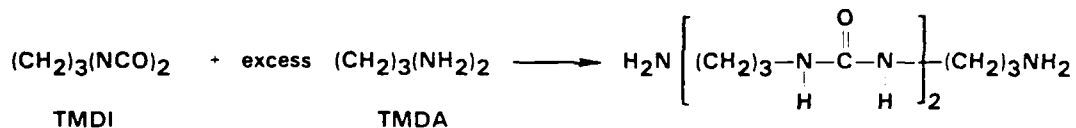
TMDI

TMDA

PTMU

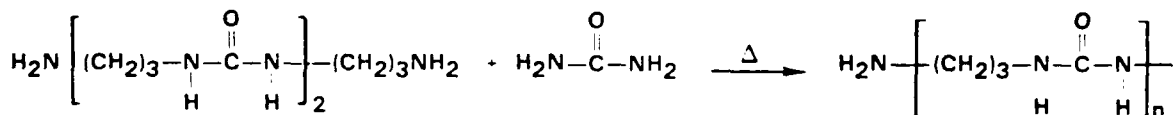
5650-14

REACTION OF 1:2 TMDI/TMDA WITH UREA



TMDI

TMDA



1:2 TMDI/TMDA

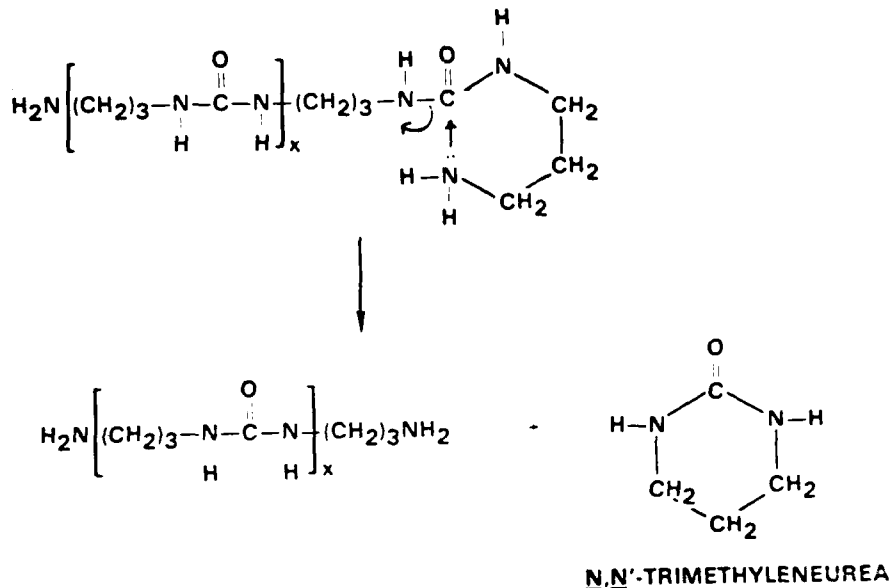
UREA

PTMU

5650-15

Figure 12. Synthetic routes to poly(trimethyleneurea) (PTMU).

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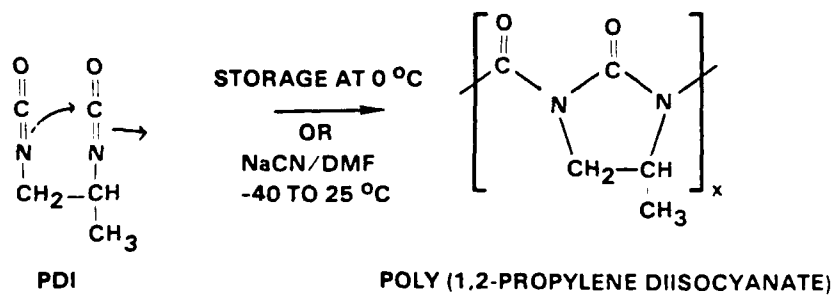
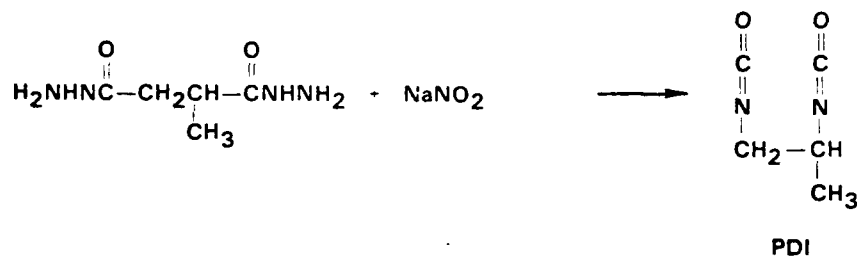
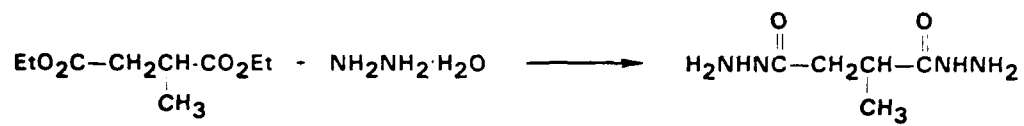
5650-16

b. Synthesis of poly(1,2-propylene diisocyanate)

Because we were unable to prepare PTMU that had film-forming properties, a second polyurea, poly(1,2-propylene diisocyanate) (PPDI), was prepared as illustrated in Figure 13.

PDI was synthesized by the method of King⁵³, purified by vacuum distillation, and stored at 0 °C. During storage, it polymerized by intramolecular cyclization (uncatalyzed) to PPDI. The IV of these polymers ranged from 0.32 to 0.52 dL/g in HFIP, and their IR spectrum was consistent with the expected structure of the polymer.

In an effort to obtain PPDI with an IV higher than 0.52 dL/g, we divided approximately 30 g of freshly distilled PDI into five 6-g samples under dry nitrogen and placed them in a freezer at 0 °C. After three weeks at this temperature, no apparent polymerization of this monomer had taken place. The monomer samples were then placed in a 5 °C chamber in an attempt to initiate polymerization. The monomer samples were maintained at this temperature for two to three weeks, allowed to warm to room temperature, and then maintained at this temperature for several days. Because this is a solid-state polymerization, the monomer must migrate to the reactive sites on the growing polymer chains. The room-temperature step of this polymerization should have increased the mobility of the residual monomer, which should have resulted in better contact of the monomer with the reactive sites on the polymer chains, thus giving a higher-molecular-weight product. However, the IVs of these polymers were in the same range as the previously prepared PPDI polymers (0.32 to 0.52 dL/g).



5650-17

Figure 13. Synthetic route to poly(1,2-propylene diisocyanate).

We also attempted to prepare PPDI by allowing the PDI to polymerize in DMF at -40 to 25 °C in the presence of NaCN catalyst.⁵³ However, the IVs of these polymers were only 0.05 and 0.07 dL/g.

c. Synthesis of poly(pentamethyleneurea)

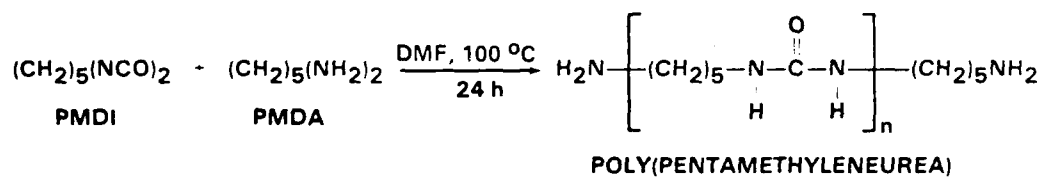
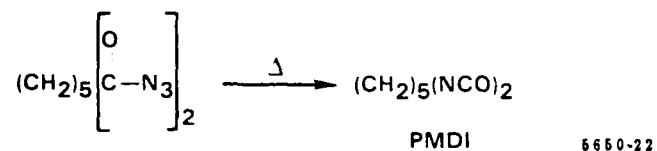
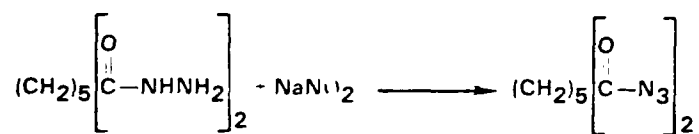
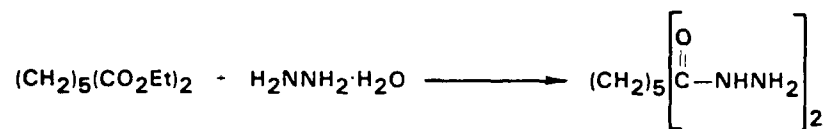
Poly(pentamethylene diisocyanate) (PPMU) was prepared via reaction of equimolar portions of pentamethylene diisocyanate (PMDI) and pentamethylenediamine (PMDA, 1,5-diaminopentane) in DMF at 100 °C as shown in Figure 14.⁵² PMDI was prepared by the same method used to prepare TMDI (Figure 12).⁵³ The PPMU thus obtained had an IV of 0.42 dL/g in HFIP at 30 °C and melted at 273 to 283 °C with decomposition.

3. Polypeptides

The three polypeptides initially selected for study in this program were poly(L-valine), poly(L-asparagine), and poly(L-alanine) (Figure 15). All three polymers were obtained from commercial suppliers as indicated in Table 10.

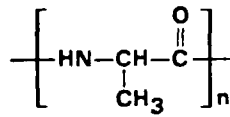
The effect of branching on the formation and distortion of the α -helix of a polypeptide could have an impact on the piezoelectric properties of the polymer. Additionally, a dipole moment in the polypeptide branch could augment or detract from the dipole moment of the polymer backbone, thereby altering the piezoelectric properties of the polymer. The three polypeptides were selected so that the effects of two types of branching could be studied. By comparing the properties of poly(L-alanine) with those of poly(L-valine), the effect of helix distortion might be ascertained. By comparing the properties of poly(L-valine) with those of poly(L-asparagine), we had hoped to observe the effect of a dipolar branch on piezoelectric properties. And from the results of this study, we planned to design experimental polypeptides using biomolecular self-assembly techniques.

Unfortunately, we were not able to cast usable films with these polypeptides, primarily because of low molecular weights. Consequently, no piezoelectric testing was carried out with these materials. Because the maximum molecular weights that could be expected by biomolecular self-assembly ($\approx 20,000$) are lower than most of these materials, it was decided that the chances of obtaining flexible polypeptide films having high piezoelectric properties using these techniques alone were poor. Instead, an extensive literature search was conducted to identify the desirable features of piezoelectric polypeptides (Section III.D.) for this phase of the program, and the remainder of the program was devoted to obtaining as good a piezoelectric response as possible from the low, odd nylons.

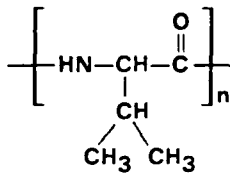


5650-43

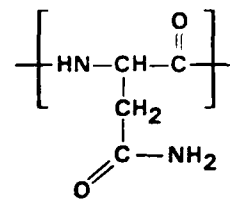
Figure 14. Synthetic route to poly(pentamethyleneurea).



POLY(L-ALANINE)



POLY(L-VALINE)



POLY(L-ASPARAGINE)

5650-42

Figure 15. Chemical structures of polypeptides evaluated.

TABLE 10. POLYPEPTIDES EVALUATED AS FILM-FORMING MATERIALS

| Polypeptide | Source | Lot No. | Molecular weight |
|--------------------|---------|-----------|------------------|
| Poly(L-valine) | Sigma | 104F-5026 | 8,000 |
| Poly(L-valine) | Chemlog | 117666 | 50,000-100,000 |
| Poly(L-asparagine) | Sigma | 92F-5040 | 9,000 |
| Poly(L-alanine) | Sigma | 53F-5076 | 25,000 |

B. Film Preparation, Orientation, and Properties

1. Preparation of films by solvent evaporation

Many thermoplastic polymers can be melt-extruded into films (e.g., PVF₂). Because the low, odd nylons, polyureas, and polypeptides decompose below their melting temperatures, we were not able to form films with these materials by melt extrusion. Therefore, films of these materials had to be cast from solution.

The nature of the solvent employed has a great bearing on the physical and mechanical properties of the resultant films. When a polymer is dissolved in a good solvent, the polymer becomes highly dispersed, and the individual polymer chains are highly extended. When a poorer solvent is used, the polymer chains are coiled more tightly and form supermolecular aggregates with their neighbors. As the solvent is removed from the nascent film by evaporation, a sol-to-gel transition occurs, essentially freezing any gross movements of the polymer chains. Therefore, the disposition of the polymer chains prior to gelation has an important bearing on the outcome of the dried film. Films cast from good solvents tend to be more amorphous, less dense, and less tough than films cast from poor solvents. The formation of crystallites in films is favored by use of poor solvents.

The properties of solvent-cast films are also influenced by the evaporation rate of the solvent and the atmospheric humidity. In general, maximum density and crystallinity are obtained with rapidly evaporating solvents. In cases where water is a nonsolvent for the polymer and is highly miscible with the casting solvent, the relative humidity above the nascent film has a great bearing on the properties of the resultant film. Sorption of atmospheric moisture by the drying film causes coagulation of the polymer with the formation of a porous internal structure. The distribution of pores can be symmetric or asymmetric, depending on the system.

In general, we were unable to solution cast films of nylon 3 that were sufficiently flexible for extensive piezoelectric testing. Nylon 3 (0.48 dL/g) films cast from mixtures of trifluoroethanol (TFE) (a nonsolvent) and formic acid (a solvent) gave translucent or transparent films depending on the solvent composition (Table 11). The films were somewhat flexible, while some residual solvent remained, but they became brittle with age. These films were reasonably flexible under conditions of high humidity but brittle under arid conditions. The films also had low tear and tensile strengths.

Films of nylon 5 (0.64 dL/g) cast from TFE had properties similar to those discussed above for nylon 3 (Table 11). The films were fairly flexible when moist or when recently cast, but they became brittle with age or when maintained in a dry atmosphere. The films also had low tear and tensile strengths. A film cast from the high-IV (1.15 g dL/g) lot of nylon 5 had excellent film properties. We were able to cold draw this film to at least 100% elongation. Consequently, this lot of nylon 5 was used for piezoelectric

TABLE 11. PROPERTIES OF SOLUTION-CAST FILMS

| Polymer | Lot or Sample No. | Supplier | MW | IV, dL/g | Casting solvent | Casting concentration, wt % solids | Appearance of films |
|-----------|-------------------|----------|-----------------|-------------------|-------------------------------|------------------------------------|--|
| Nylon 3 | C840-97-1 | SoRI | ND ^a | 0.48 ^b | 50:50 TFE/ 97% formic acid | 20 | Translucent, somewhat flexible in humid atmospheres; brittle in desiccated state; poor tear and tensile strength |
| | C840-97-1 | SoRI | ND | 0.48 ^b | 75:25 TFE/ 97% formic acid | 20 | Transparent, flexible wet; brittle dry; poor tear and tensile strength |
| Nylon 5 | C934-29-2 | SoRI | ND | 0.64 ^c | TFE | 13.3 | Translucent; flexible wet; brittle dry; poor tear and tensile strength |
| | C934-83-1 | SoRI | ND | 1.15 ^c | TPE | 10 | Translucent; flexible; able to cold draw; good tear and tensile strength |
| Nylon 3,7 | C934-131-1 | SoRI | ND | 0.46 ^d | TFE | 10 | Opaque; poor film quality; brittle, poor tear and tensile strength |
| Nylon 5,5 | C934-97-4 | SoRI | ND | 0.64 ^d | TFE | 10 | Translucent; brittle; poor tear and tensile strength |
| Nylon 5,7 | C934-121-3 | SoRI | ND | 2.81 ^d | TFE | 3 | Translucent; flexible; good tear and tensile strength |
| Nylon 7,7 | C934-112-3 | SoRI | ND | 1.76 ^d | TFE | 5 | Translucent; flexible; good tear and tensile strength |

(continued)

NADC 87184-60

TABLE II (continued)

| Polymer | Lot or Sample No. | Supplier | MW | IV, dL/g | Casting solvent | Casting solution concentration, wt % solids | Appearance of films |
|----------------------------------|-------------------|----------|----------------|-------------------|---------------------------------------|---|---|
| Poly(1,2-propylene diisocyanate) | C840-82-1 | SoRI | ND | 0.32 ^b | 97% formic acid | 20 | Film not handleable; extremely brittle; transparent |
| | C840-104-1 | SoRI | ND | 0.52 ^b | 97% formic acid | 20 | Film not handleable; extremely brittle; transparent |
| Poly(L-valine) | 117666 | Chemalog | 50,000-100,000 | | trifluoroacetic acid | 13 | Transparent; discolored; extremely brittle; not handleable; cracked on drying |
| | 104F-5026 | Sigma | 8,000 | | trifluoroacetic acid | 15 | Transparent; colorless; extremely brittle; not handleable; cracked on drying |
| Poly(L-asparagine) | 92F-5040 | Sigma | 9,000 | | water | 20 | Transparent; colorless; extremely brittle; not handleable; flexible in humid atmosphere |
| Poly(L-alanine) | 53F-5076 | Sigma | 25,000 | | trifluoroacetic acid | 14 | No coherent film |
| | | | | | 50:50 trifluoroacetic acid/chloroform | 10 | No coherent film |

(continued)

TABLE II (continued)

| Polymer | Lot or Sample No. | Supplier | MW | IV, dl./g | Casting solvent | Casting solution concentration, wt % solids | Appearance of films |
|----------------|-------------------|----------|----|-----------|----------------------|---|----------------------------|
| Poly(L-alanine | | | | | Methanesulfonic acid | 15 | Solvent does not evaporate |
| | | | | | Dichloroacetic acid | 8 | Solvent does not evaporate |

^aNot determined.

^bDetermined in 88% formic acid at 30 °C at ≈0.5 dl./g.

^cDetermined in m-cresol at 30 °C at ≈0.5 dl./g.

^dDetermined in TFE at 30 °C at ≈0.5 dl./g.

testing. The nylon 5 films cast from the lower-IV lots did not have sufficient strength to be drawn significantly under any circumstances.

Strong, flexible films of nylon 5,7 (2.81 dL/g) and nylon 7,7 (1.76 dL/g) were obtained from TFE solution. On the other hand, films of poor quality were obtained from nylons 3,7 (0.46 dL/g) and 5,5 (0.64 dL/g) (Table 11).

We also cast films of poly(1,2-propylene diisocyanate) (two viscosities) from 96% formic acid (Table 11). Both films were clear and transparent; however, both films were extremely brittle and could not be handled without shattering. Clearly, higher-molecular-weight poly(1,2-propylene diisocyanate) is required to produce coherent films.

We were also unable to solvent cast usable films from the poly(amino acids) (Table 11). Two different molecular-weight samples of poly(L-valine) were cast from trifluoroacetic acid solution. Both films cracked into small pieces upon drying in an N₂ atmosphere. The pieces of film were transparent and free of defects but were extremely brittle.

Films of poly(L-asparagine) cast from water were also optically clear but extremely brittle when dry. The films are plasticized by water and are flexible in this state.

Likewise, we were unable to cast coherent films from poly(L-alanine) with a molecular weight of 25,000 (Table 11). This polymer appears to be the worst film former of all the polymers examined.

2. Preparation of nylon 3 films by coagulation in nonsolvents

We believed that our inability to draw (orient) solvent-cast nylon 3 films resulted from either the low molecular weight of the material or a high degree of intermolecular hydrogen bonding that resisted realignment of the chains, or both. In an attempt to reduce the hydrogen bonding in the nascent films, we investigated the film-forming ability of nylon 3 dope in various coagulants. Depending upon the interaction between the coagulant and the solvent used to prepare the polymer dope, different amounts of coagulant and solvent remain in the resulting films. This plasticization was expected to disrupt the hydrogen bonding of the polymer and allow us to draw the films.

Nylon 3 films were made following the general procedures described by Masamoto et al.⁵⁵ The nylon 3 was dried in a vacuum oven overnight at 110 °C to remove the moisture from the polymer and then prepared as a 25 wt % dope in 96% formic acid. The film-forming ability of this dope in various coagulants was investigated.

The coagulants selected for this investigation included benzene, carbon tetrachloride, ethyl acetate, isopropanol, and toluene. The nylon 3 solution was cast onto a glass plate using a doctor blade and immersed into the coagulant for about 30 min.

We did not obtain usable films from the nylon 3 dope when benzene or carbon tetrachloride was used as the coagulant, but a film rapidly formed when isopropanol was used as the coagulant. This film was white and opaque, and it became brittle when air-dried. We also obtained a film from the nylon 3 dope when ethyl acetate was used as the coagulant; however, film formation was slightly slower from this coagulant. The films obtained from isopropanol and ethyl acetate contained large, visible voids and were deemed unsuitable for poling. The best films were obtained using toluene as the coagulant. These films were translucent, contained no visible voids, and retained their flexibility after drying. However, we were not able to draw these films to any significant extent.

3. Preparation of films by molding under heat and pressure

Because the three polypeptides poly(L-alanine), poly(L-asparagine), and poly(L-valine) did not give good films by solution casting, they were evaluated for their film-forming ability using a Pasadena hydraulic hot press. The polypeptides were pressed in nonplasticized condition and also with glycerol or water present as a plasticizer.

Normally, thermoplastic polymers can be pressed into coherent films by heating above the polymer melting point. However, DSC scans of these polypeptides indicated that they did not melt, and thermogravimetric analysis (TGA) indicated that they thermally decomposed at approximately 250 °C. Therefore, a temperature of 200 °C was selected for the hot-mold pressing of the polypeptides except where water was used as the plasticizer. A temperature of 100 °C was selected for this case.

A mold with a circular cavity 0.5 in. in diameter was filled with the appropriate amount of polypeptide to obtain a film thickness of approximately 10 mils (generally 40 to 60 mg of polypeptide). A load of 20,000 lb, corresponding to approximately 200,000 psi on the sample, was applied to the hot mold for 30 min on the Pasadena hydraulic press.

Poly(L-alanine) formed a brittle film with little or no degradation. The same results were obtained using glycerol as a plasticizer. The use of water as a plasticizer appeared to increase the degradation of poly(L-alanine). Optical microscopic examination of the poly(L-alanine) films showed that the films were composed of tightly packed poly(L-alanine) particles. Poly(L-valine) formed films with the same properties as poly(L-alanine). Because of decomposition, we were unable to hot-mold press films from poly(L-asparagine), even at 100 °C. None of the opaque films formed by this method were amenable to poling trials.

4. Evaluation of plasticizers for nylon 3

Attempts to draw nylon 3 and nylon 5 films at temperatures from 25 to 155 °C resulted in elongations of only 5 to 10%. One possible reason for this low degree of elongation is the extremely high potential for hydrogen bonding in these polymers. In an attempt to obtain nylon 3 films with reduced hydrogen bonding, we evaluated several aliphatic amide plasticizers that are

commonly used in nylon 6,6. Only one of these plasticizers was miscible with a hot formic acid solution of nylon 3, and this amide separated when the solution was allowed to cool to room temperature. In an attempt to prevent this separation, we prepared additional nylon 3 solutions, added the plasticizer, and then evaporated the formic acid at elevated temperatures. However, as the formic acid evaporated, the plasticizer precipitated from solution.

We also attempted to plasticize nylon 3 with tricresyl phosphate (TCP). A strip of film was placed in TCP and heated at 130 °C for 24 h under nitrogen. The film broke into pieces when we attempted to remove it from the TCP, and we were unable to determine if the film had absorbed any TCP.

5. Modification of films by drawing

We briefly examined the drawing at room temperature of nylon 5 films which had been plasticized with TFE and water. Nylon 5 samples (≈ 1.5 by 0.75 in.) were equilibrated overnight at room temperature in air at 65% RH and 100% RH and in a TFE atmosphere at an estimated concentration of ≈ 0.5 g/L (maximum). The weight gain by the previously vacuum-dried films and the applied Instron force at break are given in Table 12.

These data indicate that films plasticized by TFE break at a lower applied force than films plasticized by water. Elongations were not calculated precisely but appeared to be in the range of 5 to 10%. This degree of elongation is probably too low to have much effect on the orientation of the polymer chains. Therefore, we attempted to draw nylon 3 and 5 films above the glass-transition temperatures (T_g s) of the polymers (nylon 3 ≈ 110 °C, nylon 5 ≈ 76 °C).

Strips of film ($\approx 1/4$ in. wide) were drawn in an Instron tensile-testing apparatus, either in an Instron environmental chamber (Model 254) at temperatures up to 155 °C or in a heated pipe at temperatures greater than 155 °C. An initial span length of 1.0 in. was used in conjunction with the environmental chamber, while a 4.0-in. span length was used with the heated pipe. The crosshead speed was 0.02 in./min. Film samples were equilibrated at least 15 min at a given temperature before drawing was begun. The drawing conditions and results of the drawing experiments are given in Table 13.

We were unable to draw either nylon 3 or nylon 5 to any appreciable extent at elevated temperatures. Only modest film elongations (1 to 10%) were noted before the films broke. By comparison with the plasticized cold-drawn films, the heated films broke at much lower applied force. These data are consistent with the observation that the dehydrated films are much weaker and less flexible than the corresponding hydrated films. Based on the observation that we were later able to cold draw a higher-IV sample (1.15 dL/g) of nylon 5 to $\approx 100\%$ elongation, we can conclude that the molecular weights of these nylons were too low to allow drawing.

TABLE 12. WEIGHT GAIN AND FORCE AT BREAK OF COLD-DRAWN^a NYLON 5 FILM

| Equilibration atmosphere | Wt gain, % | Force at break, lb |
|--------------------------|------------|--------------------|
| 65% RH | 3.1 | 5.6 |
| | 3.4 | 6.0 |
| 100% RH | 12.1 | 4.9 |
| | 12.5 | 5.9 |
| TFE | 17.1 | 3.0 |
| | 15.1 | 3.4 |

^aSamples were drawn at room temperature.

^bFilms cast from TFE (13.3% solids) using C934-29-2 (IV = 0.64 dL/g).

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TABLE 13. ATTEMPTS TO DRAW NYLONS 3 AND 5 AT ELEVATED TEMPERATURE

| Sample No. C934 | Polymer ^a | Chamber temperature, °C ^b | Elongation at break, % | Force at break, lb ^c | Comments ^d |
|-----------------|----------------------|--------------------------------------|------------------------|---------------------------------|-----------------------|
| -56-1 | nylon 3 | ≈240 | 6.0 | 0.14 | -- |
| -56-2 | nylon 3 | ≈240 | 1.0 | 0.05 | 40-min equilibration |
| -56-4 | nylon 3 | ≈305 | -- ^e | -- ^e | Decomposed |
| -55-1 | nylon 5 | 140 | 9.7 | 0.17 | -- |
| -55-2 | nylon 5 | 155 | 8.9 | 0.43 | -- |
| -55-3 | nylon 5 ^f | 152 | 4.7 | 0.17 | -- |
| -55-4 | nylon 5 ^f | 155 | 3.0 | 0.22 | -- |
| -56-5 | nylon 5 | ≈170 | 3.2 | 0.28 | Partially scorched |
| -56-3 | nylon 5 | ≈240 | -- ^e | -- ^e | Decomposed |

^aNylon 5 film cast from trifluoroethanol (13.3% solids). Nylon 3 cast from 78:22 (w/w) trifluoroethanol/formic acid (18% solids).

^bAt temperatures <155 °C, an Instron environmental chamber (Model 254) was used. Above 155 °C, a heated pipe was used.

^cInitial span length was 1.0 in. with the environmental chamber and 4.0 in. with the heated pipe.

^dSamples were equilibrated at a given temperature for 15 min unless otherwise indicated.

^eValues not determined.

^fSamples were soaked in glycerol for 10 min and patted dry before testing.

C. Poling and Piezoelectric Testing of Nylon 3 and Nylon 5

During the course of this contract, a poling apparatus and a device for determining the piezoelectric response of poled samples were constructed at SoRI. The latter apparatus worked satisfactorily as judged by our ability to closely reproduce the values of the piezoelectric coefficients for commercially poled films (i.e., Kynar film). However, we found that we were unable to pole either nylon 3 or PVF₂ with our poling equipment. We discussed our difficulties with Dr. Jerry I. Scheinbeim at Rutgers University, and he suggested modifications to our poling equipment. Instead, to save both time and money, we subcontracted Dr. Scheinbeim's services to conduct poling experiments with our polymers. This agreement with Dr. Scheinbeim gave us access to several new poling techniques developed in Dr. Scheinbeim's laboratory and the benefit of his knowledge and experience in the area of poling and piezoelectric testing of polymeric materials. Because all of the piezoelectric test results described in this report were conducted by Dr. Scheinbeim and his co-workers, we will not describe the poling apparatus built at SoRI.

1. Nylon 3

Films of nylon 3 (C840-147-1, 0.45 dL/g) were prepared by solution casting from three different solvents: trifluoroacetic acid, formic acid, and m-cresol. Films were cast onto glass substrates and aluminum substrates; the film properties did not seem to be dependent on the substrate. Films cast from formic acid and trifluoroacetic acid were a hazy whitish color, while those cast from m-cresol were transparent.

All films were brittle, which made measurements quite difficult. Poling of these films often failed by breakdown at surface cracks. Piezoelectric measurements of poled films were not possible because the films cracked when placed in the mechanical grips of the piezotron. The piezotron is an instrument used to measure the piezoelectric coefficients d_{31} and e_{31} . Dielectric and X-ray diffraction experiments were performed, but no useful results were obtained.

It was then decided that the brittle nature of the nylon 3 films might be improved by the addition of a plasticizer. This technique was developed by Scheinbeim et al.²³ at Rutgers University during their studies of nylons 7 and 11 as a means of enhancing piezoelectric response. The nylon 3 films were plasticized by adding plasticizer to the solution before casting. This method of film preparation proved quite successful, although some difficulties with film brittleness were still encountered.

The plasticized films were prepared as follows: 0.9 g of nylon 3 and 0.1 g of 2-ethyl-1,3-hexanediol (the plasticizer) were dissolved in 30 mL of formic acid at 40 °C. Films were cast from this solution onto glass plates, and the dried films were cut to size for poling.

The films were poled by increasing the voltage across the sample until the field reached 350 kv/cm. The temperature was increased to the poling temperature, kept there for 5 min, and then cooled to room temperature.

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The field was then removed. Samples poled easily at 25 °C and at 0 °C. At 60 °C, half the samples (three out of six) broke down under field. At 75 °C, only one sample in six survived poling.

The results of the poling experiments appeared quite promising. As shown in Figure 16, both d_{31} and e_{31} , the piezoelectric strain and stress coefficients respectively, increase rapidly with increasing temperature up to 75 °C. Poling (at 350 kv/cm) at higher temperatures was not possible because of dielectric breakdown. The maximum value obtained for d_{31} was 0.8 pC/N and for e_{31} , 1.1 mC/m². Figure 17 shows the dielectric constant and elastic modulus (both measured at 3 Hz) of the poled films. The rising modulus and decreasing dielectric constant with increasing poling temperature most likely indicates higher crystallinity with increasing poling temperature, a phenomenon observed by Dr. Scheinbeim for both nylon 7 and 11. However, this behavior may also reflect a loss of plasticizer at higher temperatures.

More extensive poling experiments with nylon 3 were not conducted because of the brittle nature of these films. Clearly, higher-molecular-weight samples were needed so that the films could be handled more easily and be oriented by mechanical means. Higher poling temperatures and higher poling fields could probably be employed with flaw-free films cast with higher-molecular-weight material.

2. Nylon 5

Both solution-cast films and solution-cast plasticized films were used to produce polarized nylon 5 films. For the preparation of the solution-cast films, nylon 5 (C934-83-1, 1.15 dL/g) was dissolved in trifluoroethanol at 65 °C for 15 min. A homogeneous solution, ≈15% polymer by weight, was achieved by stirring for an additional 30 min before cooling to room temperature. Films (≈20 μm thick) were obtained by casting onto a clean glass surface. The solvent evaporation rate was limited to a slow rate by use of a glass cover. The films obtained were clear and of uniform thickness and suitable for poling. The films were dried in a desiccator prior to poling.

A poling field of 250 kV/cm was chosen. After application of the field at room temperature, the temperature was slowly increased at a rate 1 °C/min to a number of final temperatures. At the final fixed temperature, the field was maintained for 6 min before the temperature was decreased to room temperature and the field was removed.

The values of the piezoelectric strain constant (d_{31}), the piezoelectric stress constant (e_{31}), the elastic modulus (c), and the dielectric constant (ϵ) were obtained for all the films prepared in this way and are shown in Figures 18, 19, 20, and 21. The values of d_{31} were not high, the highest value being 0.67 pC/N when a final temperature of 75 °C was used. However, these results are promising in that it appears that d_{31} and e_{31} are increasing very rapidly at temperatures above 65 °C. The data obtained for elastic modulus shows some scatter, but higher moduli are also obtained at the higher temperatures, which may indicate additional crystallization or crystal annealing effects at the higher temperatures. Alternatively, some further decrease of water content

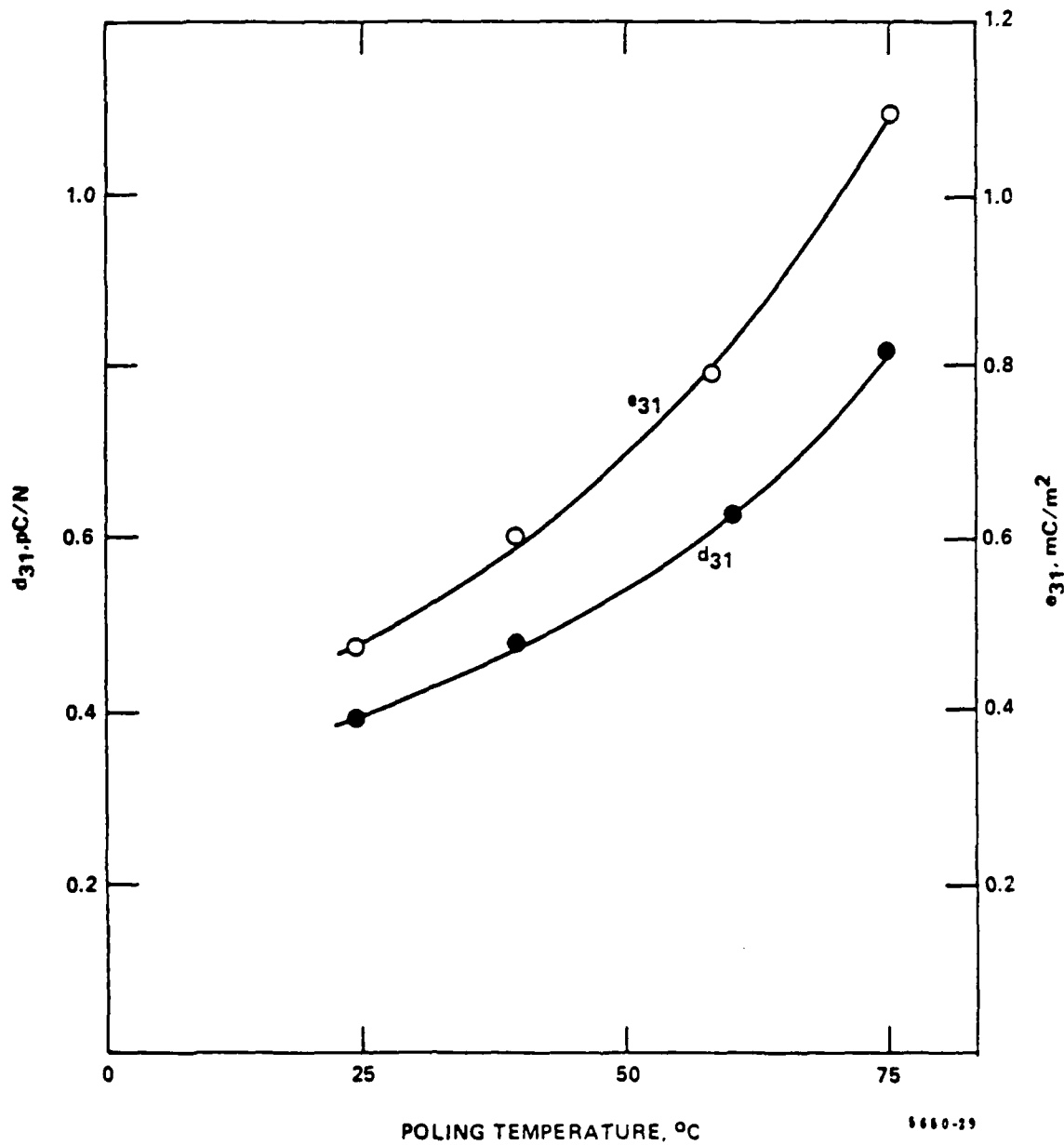


Figure 16. Piezoelectric strain (d_{31}) and stress (e_{31}) constants versus poling temperature for plasticized Nylon 3.

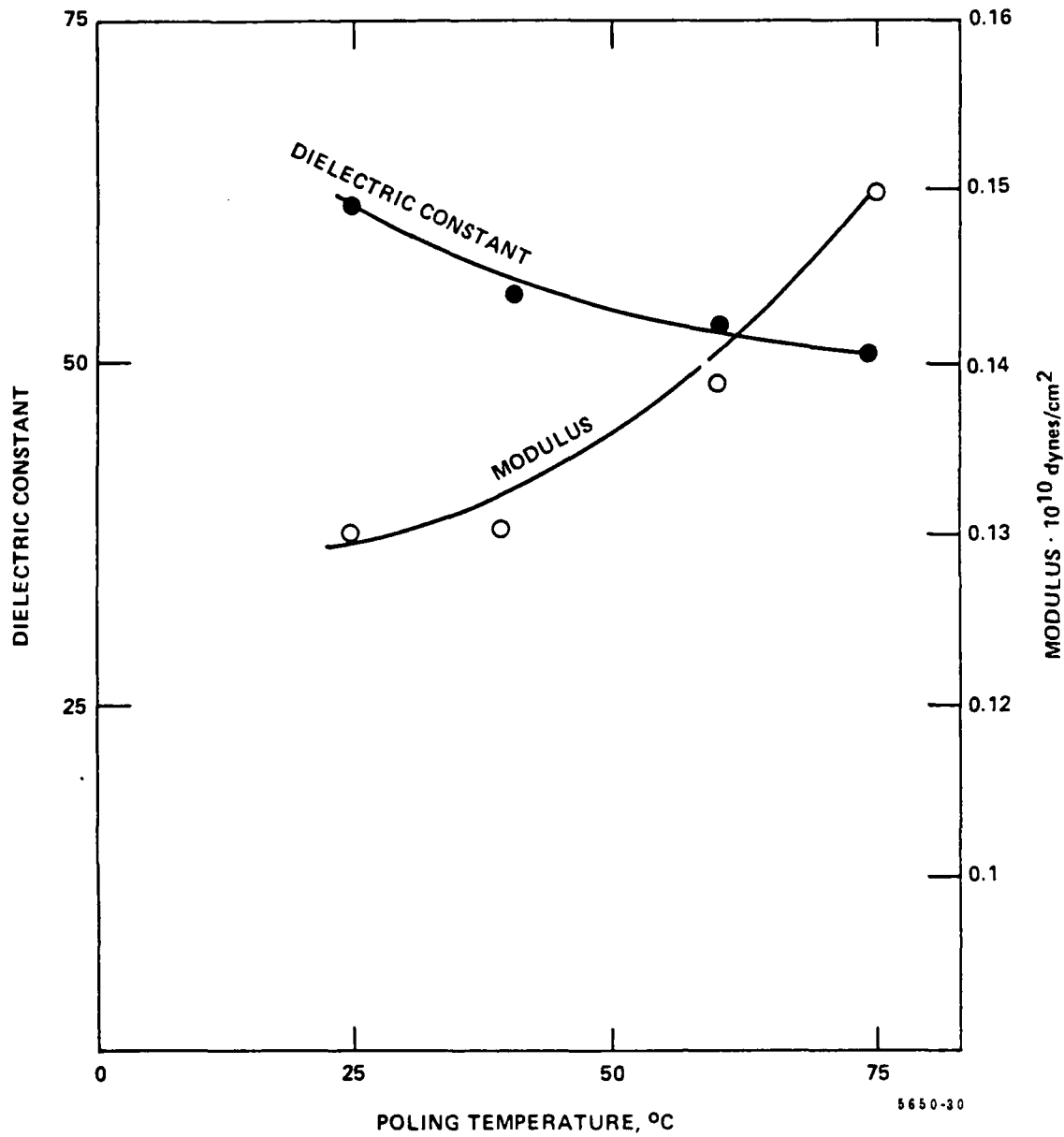


Figure 17. Dielectric constant and dynamic mechanical modulus versus poling temperature for plasticized Nylon 3.

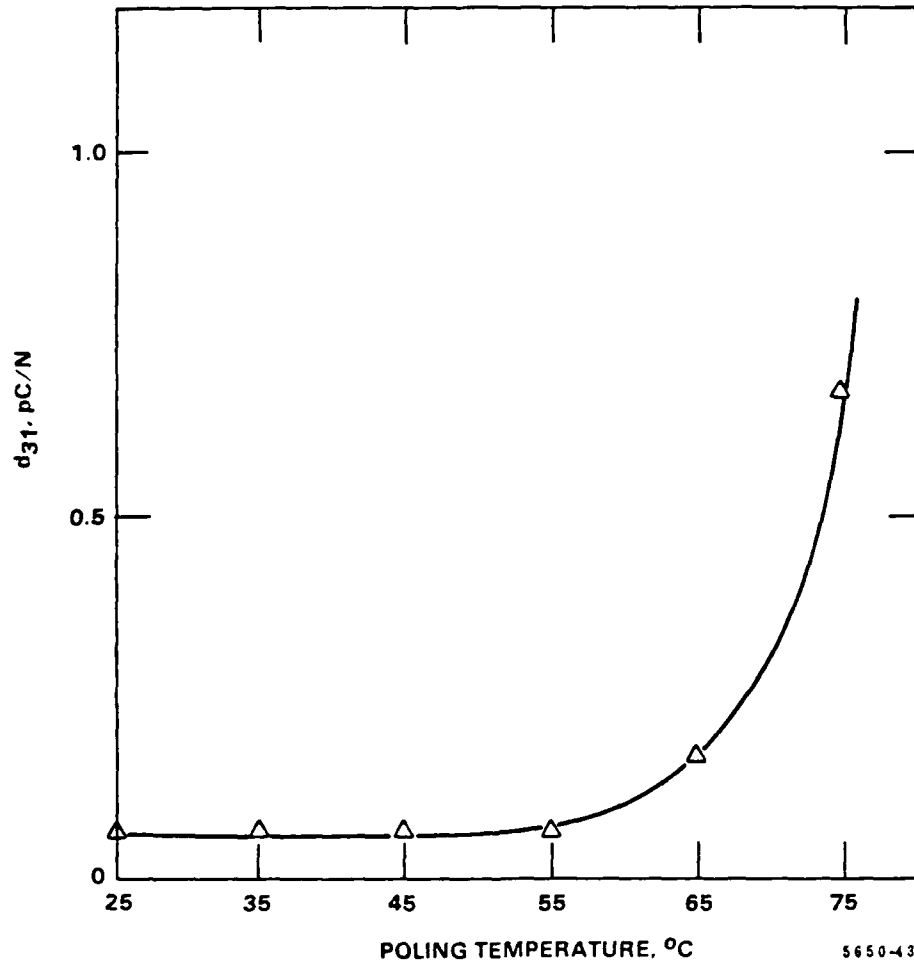


Figure 18. Piezoelectric strain constant (d_{31}) versus poling temperature for nonplasticized Nylon 5.

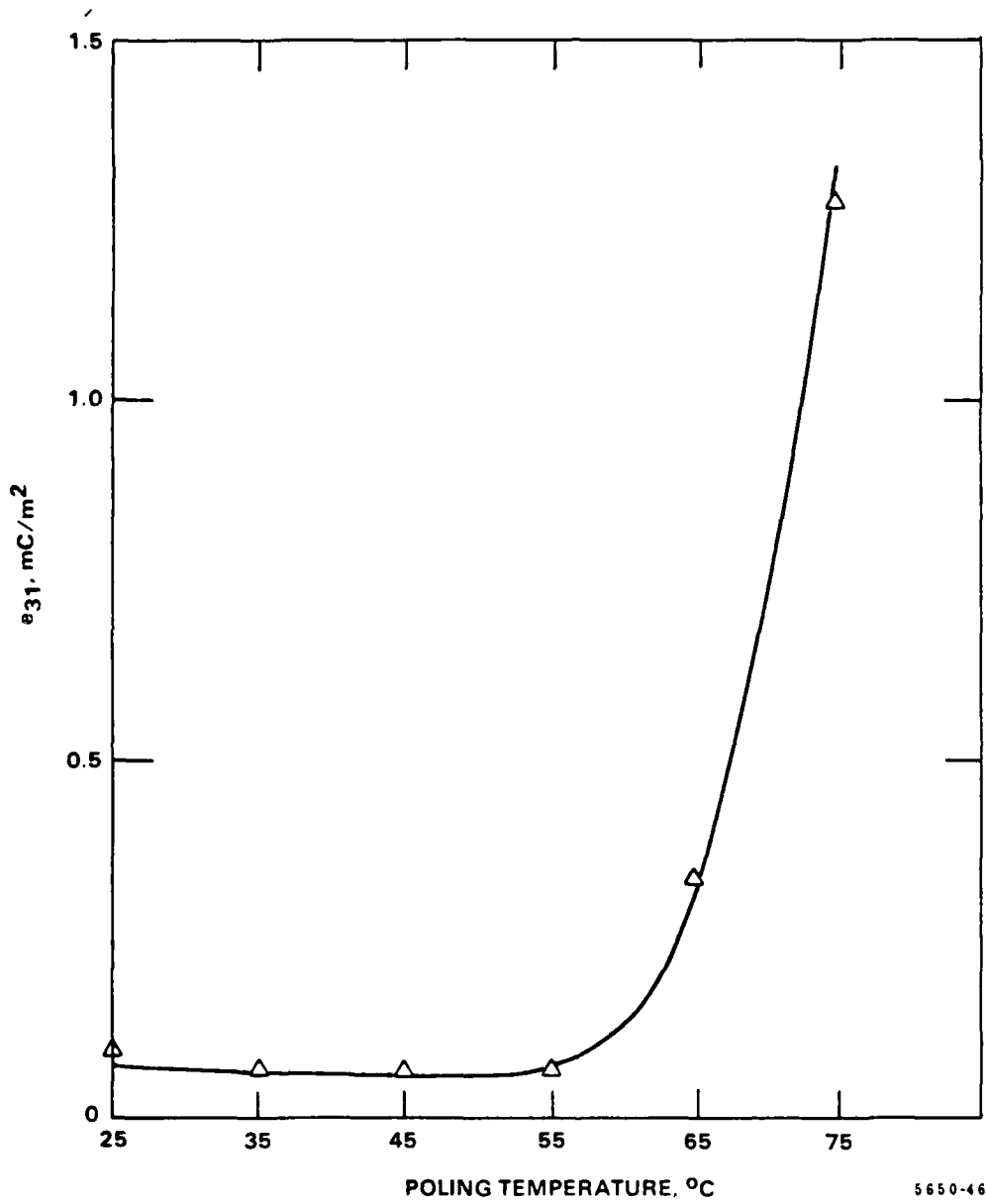


Figure 19. Piezoelectric stress constant (e_{31}) versus poling temperature for nonplasticized Nylon 5.

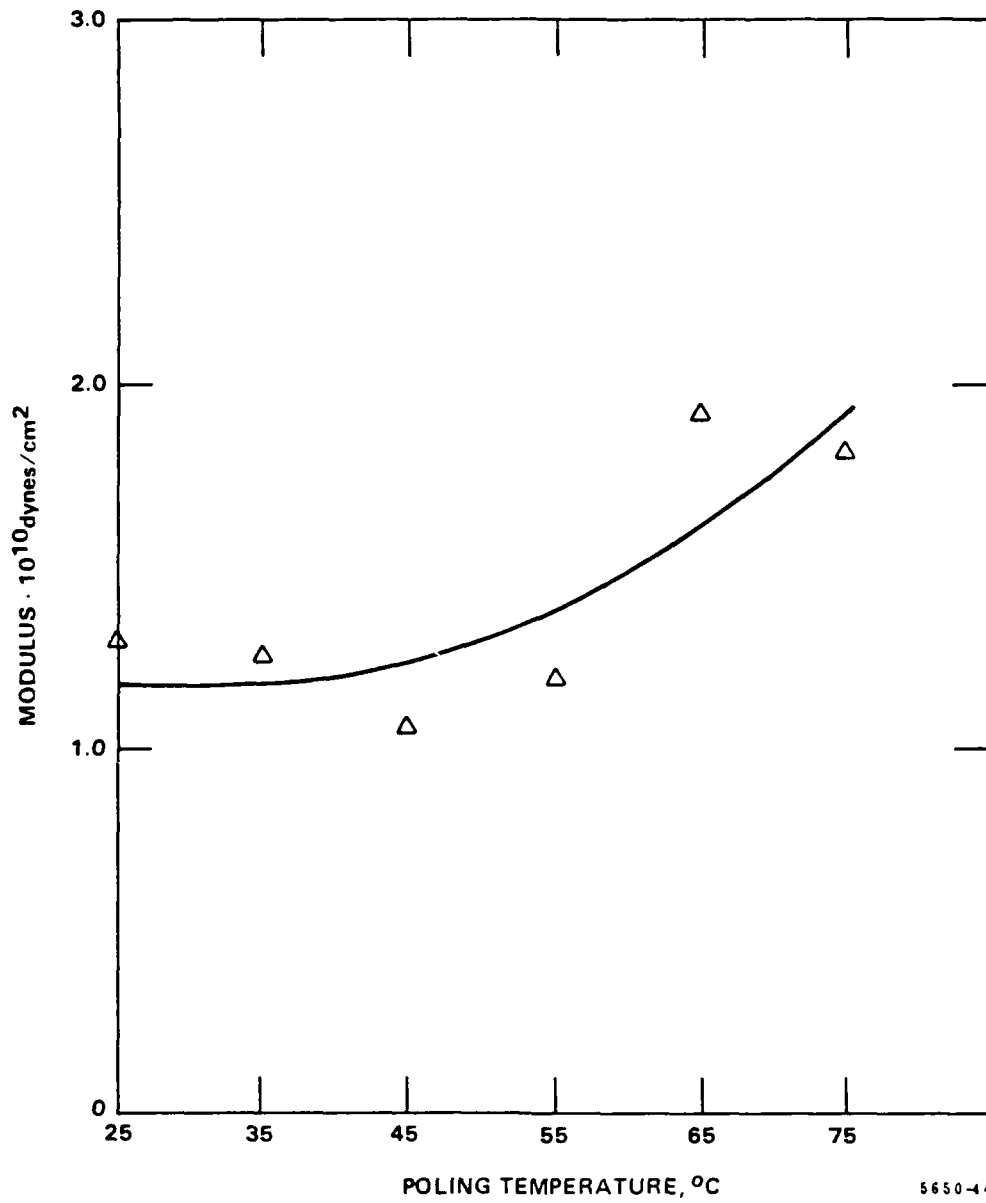


Figure 20. Elastic modulus versus poling temperature for nonplasticized Nylon 5.

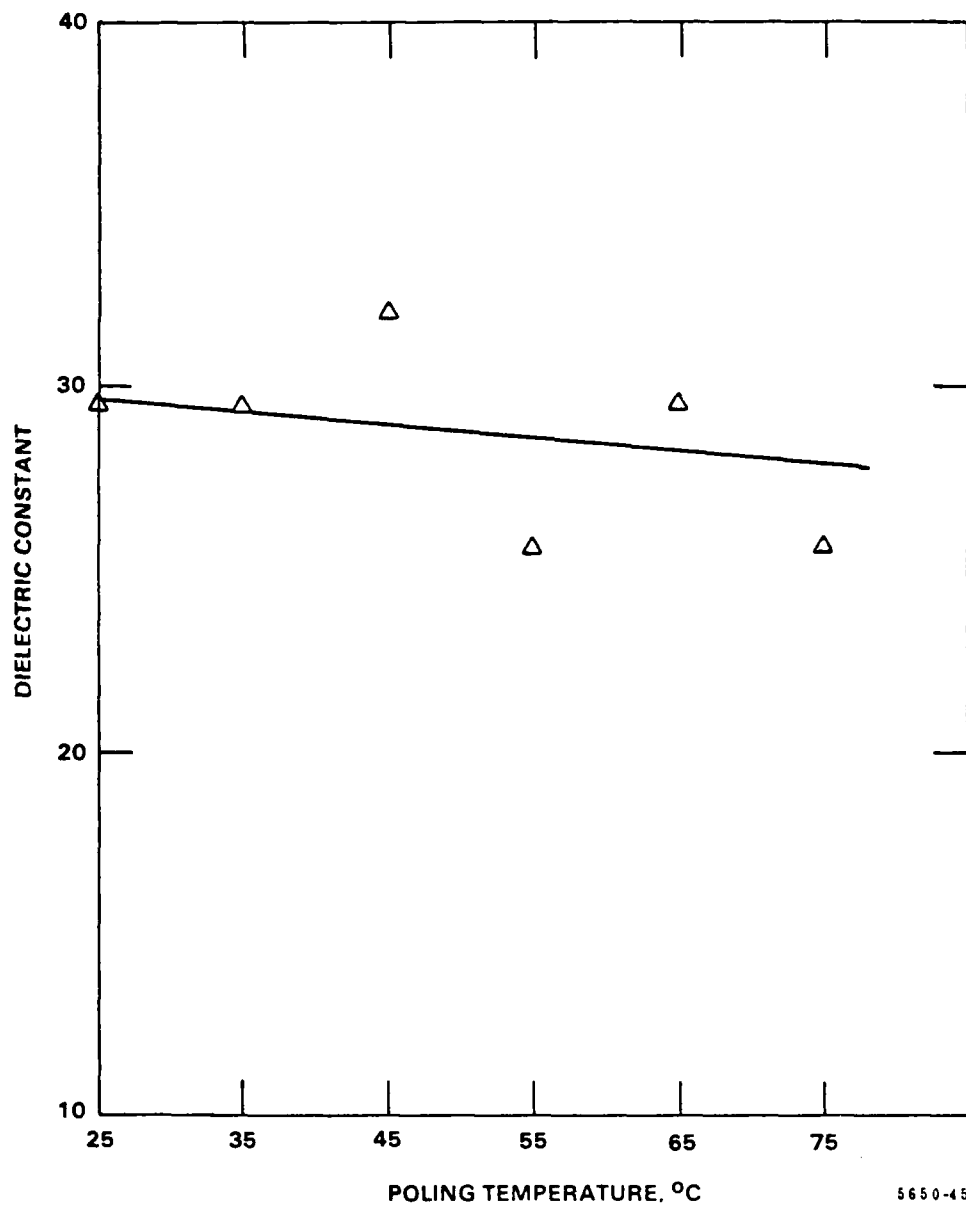


Figure 21. Dielectric constant versus poling temperature for nonplasticized Nylon 5.

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may occur under poling conditions. The values for the dielectric constant also show scatter, but a trend toward lower values at the higher temperatures would be in accord with these explanations.

For the preparation of the solution-cast, plasticized films, nylon 5 was dissolved in trifluoroethanol at 65 °C for 10 min. Then, plasticizer (2-ethyl-1,3-hexanediol) was added to the solution, and stirring to achieve homogeneity was carried out at 65 °C for an additional 30 min. The solution was then cooled to room temperature. The weight ratios of polymer, plasticizer, and solvent were 2:1:7. This solution was cast onto a clean glass surface as before, and solvent evaporation was retarded as before by the use of a cover. The resulting film ($\approx 30\%$ by weight of plasticizer) with a thickness of $\approx 16 \mu\text{m}$ was then poled.

The field was ramped linearly at room temperature to a value of 375 kV/cm in 30 min. When the field reached a value of ≈ 80 kV/cm, a high current (≈ 1 mA) was observed. After 10 min this current decreased to 0.04 mA, and the field ramp was continued. The temperature was then raised at 1 °C/min. As the temperature was increased, an increase in current was noted, until at 55 °C the current was 0.07 mA. At this temperature, the temperature ramp was discontinued for 10 min until the current had decreased to 0.04 mA. Then the temperature ramp was continued at 0.5 °C/min up to 70 °C. The field of 375 kV/cm was maintained at this temperature for 30 min. Then the temperature was reduced to room temperature and the field removed.

A second sample was prepared in a similar way, with the poling field applied being 400 kV/cm. The current during poling behaved in a similar way, being 0.02 mA during most of the poling. The temperature ramp of 1 °C/min discontinued for 20 min at 65 °C to allow the current to decrease from 0.05 mA to 0.02 mA. The subsequent ramp was resumed at 0.5 °C/min and was continued to 90 °C. The field was applied for 30 min at 90 °C before the film was cooled and removed from the field.

The properties of both these samples (at 3.3 Hz) were measured, as for the solvent-cast films, and are shown below.

| | Sample 1 (ramped to 70 °C) | Sample 2 (ramped to 90 °C) |
|--|-------------------------------|-------------------------------|
| d_{31} , pC/N | 0.54 | 1.32 |
| e_{31} , mC/m ² | 1.41 | 2.77 |
| $c \times 10^{10}$, dynes/cm ² | 2.42 | 2.04 |
| ϵ | 91 | 111 |

The highest value of d_{31} obtained, 1.32 pC/N for the sample ramped to 90 °C, is approximately twice the value obtained for the unplasticized sample. However, a higher field and a higher temperature were used. The extremely high values of dielectric constant achieved (≈ 100) are probably partly attributable

to the plasticizer content, which has lowered the glass-transition temperature of the films. X-ray diffraction scans were taken before and after poling for both samples but show very little difference.

D. Literature Search of Piezoelectricity in Polypeptides

An important part of the overall objective of this project was the preparation of strong, flexible films. Because neither poly(L-valine), poly(L-alanine), nor poly(L-asparagine) gave usable films, we were unable to test these polypeptides for piezoelectric properties and obtain guidelines for the biomolecular self-assembly of amino acids. Therefore, we recommended that the proposed biological production of polypeptides be replaced with an extensive literature search to determine which types of polypeptides have the greatest potential for conversion into a flexible film with piezoelectric properties. The results of this literature survey could then be used in future contracts by the Navy to develop polypeptides with the desired mechanical and piezoelectrical properties by genetic engineering.

A thorough search of the literature for research related to piezoelectricity in polypeptides was carried out. The literature was searched from 1966 to 1986 and resulted in 56 articles of interest. A summary of the findings in these articles is given in the following paragraphs.

The piezoelectric effect has been observed in numerous synthetic and biological polymers. Piezoelectricity is an intrinsic property that is possible in materials with noncentrosymmetric geometries. For polypeptides, the effect is attributed to naturally aligned piezoelectric crystallites embedded in amorphous nonpiezoelectric polymer regions. Under external stress, these crystallites are internally strained and polarized. Summation of the polarization of the individual crystallites induces the overall polarization at the electrodes with the same effect being observed for α -helical as well as β -sheet polypeptides. The highest values are produced by the glutamates and are on the same order as some piezoelectric ceramics.^{56,57}

Polarization of the crystallites in a polypeptide is due to mechanical strain of the crystallites themselves, and this can be greatly affected by the nature and extent of the amorphous regions of the polymer. The piezoelectric response of any semicrystalline polymer is time dependent because of the viscoelastic nature of the polymer. Therefore, a piezoelectric dispersion results from cyclical stress caused by the phase difference between stress and strain. This causes the overall polarization to lag behind stress in a complex manner.

Because the viscoelastic response of polymeric materials is temperature dependent, so is the piezoelectric response. Comparison of piezoelectric temperature dispersions to elastic and dielectric dispersions indicates that the piezoelectric effect is closely related to thermal relaxations in polymer structure. Studies of various polypeptides indicate that for polypeptides these dispersions are due to thermal motion in the side chains and disordered regions of the helix.⁵⁸

In attempts to model the piezoelectric response of semicrystalline polymers, Fukada combined fine powders of ceramic piezoelectric crystals within amorphous polymer matrices. A complex response similar to that obtained with the pure semicrystalline polymers was observed. Various mathematical models have been proposed to describe this behavior in semicrystalline polymers.⁵⁹⁻⁶⁵

The piezoelectric effect observed in an oriented and polarized polymer such as poly(vinylidene fluoride) is quite different from that seen in polypeptides. The poly(vinylidene fluoride) is heated and then cooled under an electric field, causing the dipoles to become artificially ordered. Thus, the film becomes a field-induced electret. Crystalline polypeptides on the other hand exhibit a piezoelectric effect that is due to natural ordering as described above, but some of them also exhibit conventional field-induced electret behavior as well. The α -keratins, for example, have exhibited electret behavior as well as a natural piezoelectric effect because of their highly ordered nature.⁶⁶

Piezoelectricity of the α -helix arises mainly from stress-induced deformation of the peptide bond.⁶⁰ This bond has a high dipole moment, ≈ 3.5 D, resulting from its partial double-bond character.⁶⁷ In the α -helix, the peptide dipoles align nearly parallel to the helix axis. Thus, the axial dipole component is 97% of the total peptide dipole. The overall axial dipole moment for the helix is obtained by vector addition of the individual axial components. The overall differences between polypeptides are primarily due to individual amino acids, whereas their sequencing has only a minor effect.⁶⁸

The dipole moment of the peptide bond is theoretically increased 25 to 50% by H-bonding.^{67,69,70} However, the H-bonding severely restricts rotation of the peptide bond and thus reduces strain-induced polarization. Theoretically, a helix without hydrogen bonds would have a piezoelectric strain constant increased by a factor of about 1.6.⁶⁰

Dipoles are also present in some of the side chains of various polypeptides. The contribution from these dipoles is small, but they do add vectorially to yield the total dipole moment for the molecule.⁷¹ We feel that the most important consideration of side chains is their effect on molecular order and packing (which affect the mechanical properties of the material) and not on the small contributions to the dipole concentration.

In addition to the time and temperature dependancies discussed above, the piezoelectric response of polypeptides is also highly affected by hydration. This is primarily due to increases in electrical conductivity and changes in the polymer structure caused by plasticization.⁶³ For example, the piezoelectric constants of collagen vary significantly with temperature and degree of hydration,⁶⁴ which is caused primarily by the dielectric relaxation and electrical conductivity of absorbed water. Collagen is also significantly plasticized by water.

To develop a polypeptide material capable of being made into a useful piezoelectric film, several considerations must be made in light of what is

known regarding the structure of polypeptides. There are four basic levels of polypeptide structure. The primary structure refers to the covalently bonded backbone of the polypeptide chain and denotes the specific sequence of amino acid residues. The secondary structure refers to the extended or helically coiled conformation of the polypeptide chains. The tertiary structure refers to the manner in which the chains are bent or folded to form compact or folded structures and is most important in globular proteins. The quaternary structure refers to the manner in which the chains are arranged relative to one another in space. For example, most proteins contain two or more associated polypeptide chains, and the way these chains are arranged relative to each other is known as the quaternary structure.

Considering the primary structure first, it was stated above that the types and not the sequence of residues is important. Therefore, it seems best to have as high a dipole concentration as possible. For this to occur, there should be short side chains on the individual amino acid residues to increase the mass dipole concentration. Next, the secondary structure should either be helical or sheet to provide a natural orientation of dipoles. Finally, the tertiary and quaternary structures should be conducive to good film-forming and mechanical properties.

The electrostatic effect of the α -helix affects the quaternary structure. In helical proteins the helices tend to be antiparallel because of a favorable interaction of α -helix dipoles, which stabilizes the structure. In α/β proteins a favorable interaction occurs between the dipoles in the center of the molecule and the α -helix dipoles arranged in an antiparallel way around the parallel β strands. This interaction stabilizes the $\beta\alpha\beta$ structure.⁶⁷ Such stabilization aids in increasing crystallinity, but the antiparallel packing of helix dipoles might be counterproductive to piezoelectricity.

The structure of the material should also not sorb large quantities of water because water is a dielectric material that can increase the electrical conductivity of the material and thus lower the polarization. Water also acts as a plasticizer and can modify the viscoelastic properties of the film.^{63,64,72} Unfortunately, most natural polypeptides do sorb large amounts of water. Finally, it would be best for the amorphous regions of the polymer to be capable of being oriented and then readily polarized by application of an electric field to provide a good combination of natural piezoelectricity from the crystalline regions as well as an induced electret effect.

Several natural materials exist which satisfy many of these criteria. Keratin and collagen and modifications of these materials appear to be very good choices for preliminary consideration. Collagen, for example, is a strong film-forming material with good piezoelectric properties. One problem, stated above, that can be anticipated with collagen is its high moisture regain (25 to 30%). Keratins on the other hand are strong, naturally oriented materials, but they are crosslinked and thus would be very difficult to process.

Obviously, no natural material exists that will provide strong, tough films with high piezoelectric response. It is possible, however, to

synthetically prepare or modify polypeptides in several ways. By genetic engineering, various sequences of amino acid residues can be included within the polymer chain. Polypeptide chains can also be extended to higher molecular weights, or various block copolymers can be prepared by using endlinking techniques.^{73,74} It should therefore be possible to prepare block copolypeptides that combine highly crystalline, highly polar segments and excellent film-forming segments. Crosslinking may be used to influence the mechanical and viscoelastic properties and moisture sorption of modified polypeptides. Crosslinking has been shown to be an effective means of retarding the biodegradation of collagen.⁷⁵ This is probably due to lower water uptake and solubilization. Plasticizers may also be used to modify the mechanical and viscoelastic properties as well as influence the ease of polarization of polypeptide films. Care must be taken to avoid the restriction of bond deformation in both cases so that an applied stress will result in effective strain in the dipoles.

It appears feasible based on the literature that a useful, highly piezoelectric polypeptide film can be prepared using the combined approaches described above.⁷⁶⁻¹¹¹ However, to accomplish this goal, both synthetic and natural polypeptides may have to be combined and modified. It also appears from the literature that the basic synthetic techniques for such modifications already exist, but a great deal of work would be required to develop useful materials. The economics of such synthetic procedures may or may not be prohibitive. We recommend that a feasibility program be considered prior to any large-scale development efforts in this area. It appears that a feasibility study based on the preparation of segmented block copolypeptides as described above offers the best chance of success.

IV. EXPERIMENTAL

A. Synthesis of Monomers and Polymers

1. Synthesis of nylon 3

The general procedure used to produce nylon 3 by hydrogen-transfer polymerization of acrylamide is given below.

All polymerization reactions were carried out in a 500-mL, three-neck, round-bottom flask fitted with a stirring rod, a gas-inlet adapter, and a stopper. In a dry box, the flask was charged with the acrylamide, KCl, and *o*-dichlorobenzene (250 mL/25 g acrylamide). Solid *t*-BuOK was weighed under nitrogen and added to the flask in one portion. The flask was placed in a preheated oil bath, and the contents were stirred rapidly. After the contents of the flask had been heated for approximately 15 min, solid polymer, usually in the form of a ball, precipitated. The contents of the flask were heated for a specific time and temperature, then allowed to cool to room temperature. The *o*-dichlorobenzene was decanted, and the polymer was washed twice with 200 mL of acetone. The polymer was crushed into a coarse powder and stirred for 1 h in

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hot water to dissolve the KCl. The polymer was filtered, and the water-insoluble portion was dried in vacuo overnight. IVs were determined in 88% formic acid at 30 °C at a concentration of ≈ 0.5 g/dL.

To provide a sufficient quantity of nylon 3 for piezoelectric evaluation, four samples were combined in solution and reprecipitated. Samples C840-137, -144, -145, and -146 were combined by dissolving 96% formic acid to form a 50:50 (w/w) solution. The polymer was precipitated by pouring the solution into an excess of 90:10 v/v methanol/water solution. The solids were filtered and dried overnight in vacuo. The polymer was then soaked overnight in deionized water and redried in vacuo. Finally, the polymer was redissolved in 96% formic acid, precipitated into excess diethyl ether, and dried in vacuo for several days. The final polymer Sample C840-147 weighed 100 g and had an inherent viscosity of 0.45 dL/g in 88% formic acid.

2. Synthesis of nylon 5

a. With potassium piperidonate/triethylaluminum catalysts

(1) Monomer purification

α -Piperidone (δ -valerolactam) was obtained from Aldrich Chemical Co., Milwaukee, WI. For the early polymerization trials using KAlEt_4 as catalyst, α -piperidone was once distilled from P_4O_{10} (bp 78 to 79 °C, 0.5 to 0.6 mm). For trials C934-15 through -18, α -piperidone was distilled twice from P_4O_{10} . The monomer was distilled directly into tared polymerization flasks during the second distillation. For trials C934-23 through -26, α -piperidone was distilled three times, once from CaCl_2 and twice from P_4O_{10} . The monomer was distilled directly into tared polymerization flasks during the third distillation. The polymerization vessels were stored in a heated desiccator (≈ 45 °C) prior to initiation.

(2) Initiator preparation

N-Acetyl- α -piperidone was prepared by the method of Yoda and Miyake.¹¹² To a dry, 300-mL, three-neck, round-bottom flask fitted with a condenser, N_2 -inlet adapter, and magnetic stir bar was added 10.70 g (0.108 mol) of α -piperidone and 40 g (0.39 mol) of acetic anhydride. The resulting solution was heated at reflux for 4 h and then allowed to stir at room temperature overnight. Excess acetic anhydride was removed at reduced pressure, and the product was distilled (bp 85 to 88 °C, 3 mm). A small amount of sodium bicarbonate was added to the product to neutralize any residual acetic acid. The product was filtered and redistilled (bp 66 to 70 °C, 1.9 to 2.1 mm) onto 3A molecular sieves yielding 9.66 g (63%) of colorless oil. The product flask was fitted with a rubber septum and stored in a desiccator under N_2 .

(3) Catalyst preparation

(a) KAlEt_4

Potassium tetraethylaluminum (KAlEt_4) was prepared by a modification of the method of Tani and Konomi.⁴⁹ To a dry, 500-mL, three-neck, round-bottom flask fitted with an N_2 -inlet adapter, condenser, and addition funnel was added 50 mL of freshly distilled tetrahydrofuran (THF, from CaH_2) and 2.0 g (0.51 mol) of freshly cut potassium metal. The THF was heated to reflux to expose shiny potassium metal and then cooled. The addition funnel was charged with 36 mL of 1.9 M triethylaluminum (AlEt_3) in toluene (0.068 mol), and this solution was added dropwise for 15 min with stirring. The mixture was heated to reflux for 1 h and then cooled. The black mixture was filtered through a fine sintered-glass funnel via N_2 pressure to give a pale-yellow filtrate. The filtrate flask was stoppered with a rubber septum and stored in a desiccator under N_2 . The filtrate was estimated to be $\approx 0.6 \text{ M}$ in KAlEt_4 , based on the amount of potassium consumed and the amounts of solvent employed.

(b) $\text{KAlEt}_3(\text{piperidone})$

Potassium triethylaluminum (piperidone) complex was prepared by a modification of the method of Tani and Konomi.⁴⁹ Into a dry, 250-mL, three-neck, round-bottom flask fitted with two gas-inlet adapters and a stir bar was distilled 10.30 g (0.104 mol) of α -piperidone. The third neck was sealed with a rubber septum after removal of the flask from the distillation apparatus. To the flask was added 65 mL of freshly distilled THF (from CaH_2) and 3.05 g (0.078 mol) of freshly cut potassium metal under N_2 . The mixture was heated to reflux for 1 h to complete the formation of potassium piperidonate and then cooled. The white solid was allowed to settle out, and the THF layer was decanted into a second flask by means of a glass-wool-plugged needle and N_2 pressure. The solid was washed five times with dry THF (30 mL each), and the liquid phase was decanted as described above. After the fourth wash/decant cycle, the solid was dried in vacuo at 115 °C overnight. The flask was subsequently cooled, a solution of 95 mL (0.095 mol) of AlEt_3 (1.0 M in hexane) was added via syringe, and the flask contents were stirred for 24 h. During this time the powdery, white solid was converted to a white semisolid. The semisolid was washed five times with dry hexane (50 mL each), and the liquid phase was decanted after each wash as described previously. After the fifth wash/decant cycle, the semisolid was dissolved in 40 mL of dry benzene. The catalyst was stored in its reaction vessel in a desiccator under N_2 .

(4) Polymerization

All polymerization reactions were carried out in dry, 100-mL, three-neck, round-bottom flasks fitted with two gas-inlet adapters, a stir bar, and a rubber septum. In the first set of experiments, the dry flasks were charged with 10.0 g of once-distilled α -piperidone in an N_2 -flushed glove box. In subsequent trials, monomer was distilled directly into tared polymerization flasks, and the flasks were stored in a heated desiccator until needed.

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For polymerization, the monomer-charged flasks were placed in an oil bath maintained at about 45 °C under N₂, and the desired amount of catalyst [KAlEt₄ or KAlEt₃(piperidone)] was added via dry syringe. A vacuum was then applied to the flask to remove residual catalyst solvent. In early trials, the vacuum was maintained for 2 or 3 h, while in later trials vacuum was maintained for ≈48 h.

Two experiments were carried out in which the catalyst was generated in situ. In these cases, freshly cut potassium metal was added to the molten polymer while purging with N₂. After the metal was consumed, the required amount of AlEt₃ (1.0 M in hexane) was added via dry syringe. A vacuum was applied to the flask to remove residual solvent. When no more solvent remained, polymerization was initiated by addition of N-acetyl- α -piperidone via dry syringe. Initially, polymerizations were carried out in an oil bath at ≈45 °C. Later polymerizations were carried out in a desiccator maintained at ≈45 °C.

Periodically, aliquots of solid polymer were removed from the flasks under N₂, digested in 5% HCl for at least 18 h, washed with water and methanol, and dried in vacuo at 40 to 50 °C for a minimum of 18 h. Better results were obtained when the flasks were left undisturbed.

Inherent viscosity determinations were made at a polymer concentration of ≈0.5 g/dL at 30.0 °C in either 88% formic acid or m-cresol.

Two of the higher-molecular-weight samples (Tables 3 and 4) were precipitated into a nonsolvent in an effort to remove oligomeric products. A 10 or 15 wt % solution of the polymer in formic acid or trifluoroethanol was filtered and added dropwise to a tenfold excess of nonsolvent (methanol, ethanol, or water). The precipitate was filtered and dried in vacuo at 40 to 50 °C for at least 18 h before the IV of the polymer was determined.

b. With tetramethylammonium piperidonate as catalyst

The synthesis of Sample C934-83-1 is described below.

(1) Monomer purification

To a 500-mL, round-bottom flask containing a stir bar was added 200 g of α -piperidone (δ -valerolactam, Lancaster Synthesis) and 150 mL of xylene. A Dean-Stark trap was attached to the flask, and the mixture was refluxed overnight. Approximately 2.0 mL of water was collected in the trap. Next, the xylene was distilled from the mixture at atmospheric pressure under nitrogen. The α -piperidone was then vacuum distilled into three vessels. A cow adapter was used to avoid exposing the collecting receiver to moisture. The distillation apparatus was thoroughly flame-dried under vacuum before starting. A short forerun (≈10 g) was collected in a 100-mL, round-bottom flask. The second fraction was collected in a 250-mL, round-bottom flask (≈29 g) needed for catalyst synthesis (bp 77-79 °C, 0.25 mm). The remainder of the α -piperidone was distilled into a 500-mL, three-neck, round-bottom flask fitted with a stir bar and gas-inlet adapter (bp 79-80 °C, 0.25 mm). This flask

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served as the pot for the second distillation. The distillation was terminated with about 20 g of α -piperidone left in the pot.

The α -piperidone collected in the third vessel was redistilled as described above. The major fraction was collected in a 500-mL, Erlenmeyer flask containing a stir bar (bp 80-83 °C, 0.30 mm, 105.4 g). This vessel served as the polymerization flask.

(2) Initiator preparation

The polymerization initiator, N-acetyl- α -piperidone, was prepared as described in Section IV.A.2.a.(2).

(3) Catalyst preparation

To a 500-mL, Erlenmeyer flask with a ground-glass joint was added 22.2 g (0.203 mol) of tetramethylammonium chloride. The flask was placed in a vacuum oven, and the salt was dried at 45 °C for 11 days in the presence of phosphorus pentoxide.

A solution of sodium ethoxide was made by reacting 4.80 g (0.208 mol) of sodium metal in \approx 100 mL of freshly distilled absolute ethanol [from $\text{Mg}(\text{OME})_2$]. The sodium ethoxide solution was then added to the flask containing the dried TMAC in 100 mL of freshly distilled absolute ethanol in a nitrogen-flushed glovebox. The mixture was allowed to stand for 1 h, and then 200 mL of anhydrous ethyl ether (dried over sodium) was added. The flask was placed in a refrigerator overnight.

The next morning, the flask was warmed to RT in a desiccator and then removed to a nitrogen-flushed glovebox. The majority of the solution was decanted into a 1-L, round-bottom flask. The solvent was evaporated on a rotary evaporator at 30 °C for 5 h using a vacuum pump. The residue was then suction filtered directly into a 4-L filter flask in the glovebox. A solution of \approx 29 g (0.29 mol) of dry, distilled α -piperidone in 150 mL of dry ethyl ether was then added to the filtrate. Approximately 3.5 L of dry ethyl ether was added, and the precipitate was allowed to settle for \approx 0.5 h. The product was collected on a sintered-glass funnel under a cone of nitrogen, immediately transferred to a vacuum desiccator, and dried in vacuo at RT overnight. The product was weighed in a glovebox and subsequently redried in vacuo over phosphorus pentoxide. The yield of product was 15.9 g (45%).

(4) Polymerization

The flask containing 105.4 g (1.06 mol) of α -piperidone was placed in an oil bath at 45 °C to melt the monomer. The flask was then immediately transferred to a nitrogen-flushed glovebox, and 14.59 g (0.085 mol) of TMAP was added. The flask was replaced in the 45 °C oil bath and maintained under N_2 backpressure. After the catalyst had dissolved (\approx 15 min), \approx 1.5 mL (0.0106 mol) of N-acetyl- α -piperidone was added via syringe. The stirred mixture solidified in \approx 5 min. The flask was transferred to a heated (45 °C) desiccator and allowed to stand for 4.75 days. The flask was then broken to remove the

product, and the polymer was dissolved in 500 mL of 88% formic acid. The solution was filtered through glass wool and added dropwise to 5 L of ethyl ether. The precipitated polymer was allowed to stand over 2 L of fresh ether overnight. The filtered polymer was dried for four days in vacuo at 70 °C. The yield was 62.4 g, IV = 1.15 dL/g (m-cresol, 0.5 g/dL, 30 °C).

3. Synthesis of odd,odd nylons

a. Melt polymerization

Salts of nylon 3,5, 3,7, 5,5, 5,7, and 7,7 were prepared by mixing methanolic solutions of the appropriate diamine and diacid (Table 6). For example, to prepare nylon 7,7 salt, solutions of 1,7-diaminoheptane and pimelic acid were combined at room temperature. The resultant mixture was stirred at ambient temperature for 1 h, and the precipitate was then filtered, washed with methanol, and dried in vacuo. When a salt was discolored or had a wide melting range, as was the case with nylon 7,7 salt, it was stirred in refluxing methanol, hot filtered, washed, and dried in vacuo. Yields and melting ranges of the salts are given in Table 6.

Nylon salts were polymerized by first heating the salt under N₂ pressure to form a prepolymer. The temperature used during this step was generally 15-20 °C above the melting point of the salt. In some cases, the nylon salts were melted under N₂ backpressure (slightly above atmospheric pressure) in lieu of a pressure step in order to prepare the prepolymer. The nylon prepolymer was then heated under vacuum (≈ 0.1 mm) at a specified temperature. For example, nylon 7,7 prepolymer was prepared by heating the salt at 212 °C under N₂ pressure at 105-195 psig for 2 h. The prepolymer (IV = 0.35 dL/g) was then converted to high polymer by heating under vacuum at 250-252 °C for 4 h. This nylon 7,7 polymer had an IV in trifluoroethanol of 1.76 dL/g. The IVs of nylon 5,5 and 3,5 were low when they were heated in vacuo to their melting temperatures, so vacuum heating was also conducted below the melting temperature of these nylons. Polymerization conditions for the nylons prepared by melt polymerization are given in Table 7.

b. Interfacial polymerization of nylons

Nylons 3,5, 3,7, and 5,5 were prepared by adding a dichloromethane or tetrachloroethane solution of diacid chloride to a rapidly stirred, aqueous solution of diamine, using the molar ratios of dichloride and diamine indicated in Table 8. Sodium hydroxide or excess diamine was added to the aqueous layer to scavenge HCl. Stirring was continued for 15 min, the precipitate was filtered, washed several times with water and then acetone, and dried in vacuo. A maximum IV of 0.55 dL/g was obtained for nylon 5,5 when the reaction was carried out at 0 °C using a 2:1 ratio of diamine to diacid chloride and an equivalent amount of sodium hydroxide as an acid acceptor. These conditions were also used to prepare nylons 3,5 and 3,7 as shown in Table 8.

c. Solution polymerization of nylon 5,5

The solution polymerization of nylon 5,5 was carried out with equimolar amounts of 1,5-diaminopentane and glutaryl dichloride. All reactants and solvents were distilled before use. Diaminopentane (0.10 mol) was dissolved in N-methylpyrrolidone (100 mL), and triethylamine (0.10 mol) was added to act as an acid acceptor. The solution was cooled to 0 to 2 °C. Glutaryl dichloride (0.10 mol) was added dropwise to the cold diamine solution, and the solution was stirred at 0 to 2 °C for 1 h and then at room temperature for 1 h. A white precipitate formed before the addition of the diacid chloride was complete. The polymer solution was stirred into an equal volume of water and the precipitate was filtered, washed several times with water and then with acetone, and dried in vacuo. An IV of 0.39 dL/g in trifluoroethanol was obtained. The polymer was redissolved in trifluoroethanol to give a 15 wt % solution. An approximately equal volume of water was added to precipitate the polymer which was washed and dried as before. The IV of the reprecipitated polymer was 0.46 dL/g in trifluoroethanol.

4. Polyureasa. Preparation of poly(trimethyleneurea)

(1) Monomer preparation

(a) Glutaric dihydrazide

To a 5-L flask fitted with an addition funnel, a stirring rod, and a reflux condenser was added 299 g of hydrazine hydrate, 2.4 L of absolute ethanol, and 484 mL of water. While this solution was being stirred, 160 g of dimethyl glutarate was added. After the addition was completed, the resultant solution was concentrated under reduced pressure, and the crystalline glutaric dihydrazide precipitated. The solid was filtered and dried in vacuo to give 155 g (82%) of white, crystalline solid that was identified by its IR spectrum.

(b) TMDI

Glutaric dihydrazide (114 g), 1200 g of ice, 299 mL of carbon tetrachloride, and 140 mL of concentrated HCl were weighed into a 4-L beaker. A solution of 100 g of NaNO_2 in 200 mL of water was slowly added, while stirring the contents of the beaker. After the addition was completed, the contents of the beaker were stirred for 30 min, and then the liquid layers were allowed to separate. The upper aqueous layer was extracted twice with 200 mL of benzene, and the benzene was added to the organic layer. The organic layer was then dried overnight over CaCl_2 . This solution was filtered under dry nitrogen to remove the CaCl_2 and then refluxed for 4 h to convert the diazide to the diisocyanate. The solvents were removed under reduced pressure, and the residue was distilled at 3.8 mmHg and 66 °C. A clear liquid, 24.6 g (32% yield), was obtained that was identified as TMDI by its IR and NMR spectra.

(2) Polymerization

An oven-dried, 250-mL flask was fitted with a stirring bar, an addition funnel, and a thermometer. TMDA (3.697 g) and 150 mL of dry DMF were added to the flask. The addition funnel was charged with 6.306 g of TMDI and 20 mL of dry dioxane. The flask was cooled in an ice bath, and the TMDI solution was added slowly. A white precipitate formed immediately during the addition of the TMDI solution. After the addition was completed, the contents of the flask were stirred for 10 min and then heated to reflux. The slurry was refluxed at 100 to 130 °C for 4 h and filtered while hot. The filtrate was poured into 1 L of hot ethanol, and no additional solid precipitated. The solid obtained from the filtration of the hot slurry was dried under reduced pressure to give 7.0 g of white, crystalline solid that melted between 250 to 259 °C with decomposition. The molecular weight of this product was 4500 as determined by end-group analysis, and the IV, determined in HFIP at 30 °C, was 0.20 dL/g.

b. Preparation of poly(1,2-propylene diisocyanate)

(1) Monomer preparation

A sample of 1,2-propylene diisocyanate was prepared by the same procedure used to prepare trimethylene diisocyanate. Dimethyl 2-methylsuccinate was added to hydrazine hydrate in ethanol and H₂O and the mixture refluxed overnight. The solution was concentrated under reduced pressure, and the precipitated α -methylsuccinic dihydrazide was filtered and dried. The α -methylsuccinic dihydrazide was converted to 1,2-propylene diisocyanate via the α -methylsuccinic diazide. The 1,2-propylene diisocyanate, 22.04 g, 60% yield, was vacuum distilled at 3.4 mmHg and 59 °C, and the freshly distilled product was stored at -78 °C.

(2) Polymerization

A freshly distilled sample of 1,2-propylene diisocyanate was maintained under dry nitrogen for four days at 0 °C. The monomer gradually polymerized to a hard, transparent mass that was reprecipitated from 88% formic acid. This polymer softened with decomposition between 260 and 300 °C and had an IV of 0.32 dL/g.

c. Preparation of poly(pentamethyleneurea)

(1) Monomer preparation

(a) Pimelic dihydrazide

To a 3-L flask fitted with an addition funnel, stirring rod, and a reflux condenser, was added 92.6 g of hydrazine hydrate, 1.2 L of absolute ethanol, and 240 mL of water. While this solution was being stirred, 100 g of diethyl pimelate was added. After the addition was completed, the resultant solution was concentrated under reduced pressure, and the crystalline dihydrazide precipitated. The dihydrazide was filtered and dried in vacuo to

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give 70.43 g (70% yield) of white, crystalline solid that was identified by IR spectroscopy.

(b) PMDI

Pimelic dihydrazide (50 g), 600 g of ice, 100 mL of carbon tetrachloride, and 70 mL of concentrated HCl were weighed into a 4-L beaker. A solution of 28.64 g NaNO_2 in 78 mL of water was slowly added while stirring the contents of the beaker. After the addition was completed, the contents of the beaker were stirred for 30 min, and then the liquid layers were allowed to separate. The upper aqueous layer was extracted twice with 200 mL of benzene, and the benzene was added to the organic layer. The organic layer was dried overnight over CaCl_2 and then refluxed for 4 h to convert the diazide to the diisocyanate. The solvents were removed under reduced pressure, and the residue was distilled at 70 °C (1.5 mm). A clear liquid, 10.7 g (30% yield), was obtained that was identified as PMDI by IR spectroscopy.

(2) Polymerization

An oven-dried, 250-mL flask was fitted with a stirring bar, addition funnel, and thermometer. PMDA (3.93 g) and 150 mL of dry DMF were added to the flask. The addition funnel was charged with 5.93 g of PMDI and 30 mL of dry dioxane. The flask was cooled in an ice bath, and the PMDI solution was added slowly. A white solid formed immediately upon addition of the PMDI solution. After the addition was completed, the contents of the flask were stirred for 10 min and then heated to reflux. The slurry was refluxed at 100 to 130 °C for 4 h and filtered while hot. The filtrate was poured into 1 L of methanol, and no additional solid precipitated. The solid was dried in the vacuum oven to give 8.69 g of white, crystalline solid that melted at 281 °C as determined by differential scanning calorimetry. The IV of the solid was 0.42 dL/g as determined in 88% formic acid at 30 °C.

V. CONCLUSIONS AND RECOMMENDATIONS

During this program, we were able to evaluate the piezoelectric potential of nylons 3 and 5 only. Our efforts to evaluate the other polyureas and polypeptides were thwarted by our inability to obtain materials of sufficiently high molecular weight to provide usable films. The highest values of d_{31} obtained for nylons 3 and 5 were 0.8 and 1.3 pC/N respectively, while the highest values obtained for e_{31} were 1.1 and 1.8 mC/m² respectively. These values are not as high as that achieved for PVF₂ and need to be increased by an order of magnitude to reach commercial values. However, these values are higher than those reported for most other polymers.

Our results suggest that a threshold phenomenon exists, in that the applied field must exceed a certain critical value, which depends on temperature and the detailed state of the polymer (i.e., solvent and plasticizer content, degree of crystallinity, crystal form and morphology, glass

transition, etc.). It should be realized that this threshold field may be higher than the dielectric strength of the polymer in many cases. Similar results have been observed by other workers with other polymers. In this preliminary study, we approached the threshold conditions for only a few samples without the samples undergoing dielectric breakdown. Such experimental probing of the critical processing and poling conditions results in the destruction of a large number of samples by dielectric breakdown. A detailed study is needed to correlate the threshold field with the state of the polymer and to ascertain the processing and poling conditions when the dielectric strength of the polymer exceeds the threshold field.

Given the dipole densities of nylon 3 and nylon 5 and our relatively early position on a learning curve, we believe that our results to date show great promise. We recommend that additional research be carried out to maximize the piezoelectric coefficients of nylons 3 and 5. Studies should be directed toward the synthesis of nylon 3 with a sufficiently high molecular weight so that films can be prepared which are not brittle. A great deal of effort was expended in this study because of difficulties encountered during film preparation, poling, and sample measurements caused by film splitting and cracking. While the use of plasticizer greater ameliorated these problems, a great expenditure of time occurred. Also, further exploration of sample processing before poling must be carried out to find the optimum conditions (crystallinity, crystal form, conductivity, plasticizer type and content, etc.) for polarization.

Judging from our literature survey, the polypeptides are also deserving of additional research. Problem areas in the field of polypeptides appear to be an inability to prepare strong, flexible films from these materials and an inability to properly align and maintain the alignment of dipoles in these films because of strong intermolecular forces and preferred molecular configurations. If these constraints can be overcome, the polypeptides should make excellent piezoelectric materials.

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