NRL Report 6755

Wettability and Mair Infrared Spectroscopy of Solvent-Cast Thin Films of Polyamides and Polypeptides

R. E. Baier and W. A. Zisman

Laboratory for Chemical Physics

September 16, 1968

NAVAL RESEARCH LABORATORY
Washington, D.C.

This document has been approved for public release and sale; its distribution is unlimited.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
MATERIALS AND METHODS	2
EXPERIMENTAL PROCEDURES	2
RESULTS	4
Validation of Methods	4
Contact-Angle Results	5
MAIR Infrared Spectroscopy	11
DISCUSSION	15
Freedom from Artifacts	15
Diagnostic Features in the Data	17
Influence of Polymer Configuration	18
SUMMARY AND CONCLUSIONS	21
ACKNOWLEDGMENTS	22
REFERENCES	22

ABSTRACT

Polyamides, such as the nylons, polypeptides, and proteins, may have variable surface properties as the result of the masking or exposure of surface hydrogen-bonding sites which may greatly influence their behavior. Our earlier investigation with the polyamide nylon 66, showing a wettability difference by hydrogen-bonding and nonhydrogen-bonding liquids, was confirmed and extended in the present work with nylon 11, nylon 6, and nylon 2 (polyglycine). This difference in wettability behavior seems diagnostic, when present in conjunction with a high critical-surface-tension range, for the presence of accessible amides in a polymer surface. Investigations of the more complex polypeptides, polymethylglutamate, and polybenzylglutamate by contact-angle determination and multiple attenuated internal reflection (MAIR) infrared spectroscopy on solvent-cast thin polymer films showed that the hydrogen-bonding capacity of the common polyamide backbone could be masked by either bulky side-chain substituents or by certain configuration changes of the polymer chain. Elimination of the hydrogen-bonding ability at nylon surfaces might also accompany polymer fractionation in different solvents, slight configuration changes, or a combination of both.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem C02-10
Project RR 001-01-43-4751

Manuscript submitted June 7, 1968.

WETTABILITY AND MAIR INFRARED SPECTROSCOPY OF SOLVENT-CAST THIN FILMS OF POLYAMIDES AND POLYPEPTIDES

R.E. Baier* and W.A. Zisman

INTRODUCTION

The nylons are relatively simple polymers made up of segments of chains of methylene ($-CH_2-$) groups (having variable lengths but no substitutions) connected by planar, covalent amide (-CONH-) links. Polypeptides can be classed as members of a separate polyamide family derived by making substitutions to the simplest nylon, which has only one $-CH_2-$ group separating amide links. The surface properties of nylons and polypeptides are of much interest, especially since these polymers can potentially exhibit or mask a hydrogen-bonding functionality by either exposing or masking the amide groups in the polymer backbones; a polyamide backbone and many of the side chains available in synthetic polypeptides are also common to the proteins so important to biology and technology.

This investigation attempted to determine any characteristic features in the contact-angle results that might be diagnostic for the presence or absence of accessible amide groups at the surface of thin polymer films. Since the polypeptides, and some of the nylons, cannot be melted without being charred, a techinque of solvent casting of thin films has been developed and used here. Solvent casting also has the advantage that only extremely small amounts of expensive research polymers need to be used. As will be shown, this technique also allows the induction of differing polymer configurations by varying the solvents. However, solvent casting introduces potential problems with solvent entrapment, fractionation of the polymer by selective solubilization of certain molecular-weight components, and addition of difficultly removed surfactant contaminants. Consideration of these disadvantages were problems of major concern in this investigation.

Six water-insoluble polyamides have been investigated, including three nylons and three polypeptides. These materials were nylon 11, nylon 6, nylon 66, polyglycine (also known as nylon 2), poly-γ-benzyl-L-glutamate (PBG), and poly-γ-methyl-L-glutamate (PMG). Because of their water insolubility, each polymer coating could be cleaned prior to measurements with an aqueous detergent solution. These coatings were cast on a smooth, solid surface as thin films or were modified after casting with each or all of the following three solvents: dichloroacetic acid (DCA), formic acid, and chloroform. Contact-angle measurements were employed as the most sensitive of the surface-chemical techniques available for characterizing the outermost chemical composition of any organic solid surface. Multiple attenuated internal reflection spectroscopy (MAIR), at infrared wavelengths, was used to monitor the polyamide specimens for constitution and configuration and to validate the experimental methods of film formation and cleaning. The simultaneous use of these two powerful tools for determining surface structure has allowed us to draw new and definite conclusions about the relation of polymer constitution and configuration to the parameters used to characterize the wettability of the six polyamides investigated.

*NRC-NAS Postdoctoral Fellow 1966-1968.

MATERIALS AND METHODS

Nylon 11 and nylon 6 samples in pellitized form had been generously made available to one of us for earlier investigations (1,2) by W.R. Turner as samples 81649 and 81650 from the polymer collection of the Research and Development Department, Atlantic Refining Company. Our nylon 11 sample was originally made by the Societé Organico. France, and was procured as BCI nylon 1107 from Belding Corticelli Industries, New York City. This polymer specimen was characterized by gel permeation chromatography (by Waters Associates, Framingham, Mass.), using a meta-cresol solvent and polystyrene standards, as having a weight-average molecular weight of 24,000, number-average molecular weight of 13,000, and heterogeneity ratio (weight average/number average) of about 1.8. The nylon 6 specimen was produced as Plaskon 8200, Natural, by Allied Chemical Company, Plastics Division; its characterization by gel permeation chromatography yielded the following results: weight-average molecular weight of 42,000, number-average molecular weight of 21,000, and heterogeneity ratio of about 2. Nylon 66 was in the form of 1-in.- diameter disks cut from unplasticized rod stock; this material had been described in connection with earlier NRL investigations (1,2).

Polyglycine was obtained in granular form from Mann Research Laboratories, Inc., New York, with the following physical characteristics (as determined by the supplier): molecular weight, 19,200; degree of polymerization, 256; and specific viscosity (in DCA), 0.40. PBG was also obtained in granular form from Mann Research Laboratories. Gel premeation chromatography (using dimethylformamide as the carrier solvent) of this material yielded a weight-average molecular weight of 300,000 to 400,000 and a heterogeneity ratio of about 5. PMG was received as a cast sheet of 4-mil thickness (from solution in tetrahydrofuran) as a generous gift from Dr. F. Reeder of Courtaulds, Ltd., Coventry, England. Gel permeation chromatography of this sample (in dimethylformamide) showed it to have an extremely broad range of molecular lengths. The weight-average molecular weight was about 300,000, but a heterogeneity ratio of nearly 26 indicated a considerable fraction of lower-molecular-weight polymer.

After initial experiments had shown that no differences in film properties were observed with redistilled DCA, formic acid, and chloroform, reagent-grade materials were selected for use throughout this investigation. As will be shown in subsequent sections, no systematic effect of the use of any of these three solvents was observed; if impurities derived from the solvents had remained in the polyamide films, a systematic dependence of wettability on the solvent used would be expected. A concentrated water solution of the detergent Tide was used throughout this work for cleaning the solid polymer surfaces. Copious rinsing with singly distilled water followed in all cases.

Liquids used as sessile drops in the contact-angle measurements included hydrogen-bonding and nonhydrogen-bonding compounds, and the entire group covered a wide range of surface tensions at 20°C and a variety of structural types. Their sources, purification, and surface tensions have previously been reported (3,4). For convenience, these liquids and their liquid/vapor surface tensions are listed in Table 1 in the first and second columns.

EXPERIMENTAL PROCEDURES

Thin films of each polymer were formed on polished platinum plates or sheets by the technique illustrated in Fig. 1. This drop-spreading method consisted in placing a few grains (or a small piece) of the polymeric solid in the center of a freshly flamed platinum plate and transferring drops of the chosen solvent to this material with a freshly flamed platinum wire. The solvent drops dissolved a portion of the polymer and spread spontaneously over the clean platinum plate. After the plate had dried in the air inside of a large, covered, grease-free container, a smooth, shiny film covered most of the platinum plate,

Table 1
Contact Angles on Polyamide and Polypeptide Films Spread from Solution in Various Solvents on Platinum Plates

Wetting Liquid	Surface Tension at 20°C, γ_{LV}	Average Contact Angle, θ* (degrees)									
		Nylon 11†	Nylon 6†	Nylon 11‡	Nylon 6‡	Polyglycine (Nylon 2)†	PMG†	PBG†	PMG§	PMG¶	PMG‡
Water	72.8	61	63	61	69	49	69	71	66	76	49
Glycerol	63.4	65	60	70	72	38	59	63	65	69	47
Formamide	58.2	48	50	47	61	30	48	63	52	62	34
Thiodiglycol	54.0	35	36	34	58	23	39	44	40	46	29
Methylene iodide	50.8	42	42	32	50	30	42	38	39	35	32
Ethylene glycol	47.7	41	35	31	46	25	31	44	38	37	23
1-Bromo naphthalene	44.6	21	23	14	35	10	25	25	26	24	13
Hexadecane	27.7	0	0	0	0	0	0	0	0	0	0

*Reported values are averages of at least 10 readings on at least two independently prepared films of each type.
†Cast from DCA.
‡Cast from formic acid.
§Cast from chloroform.
¶Swelled in formic acid.

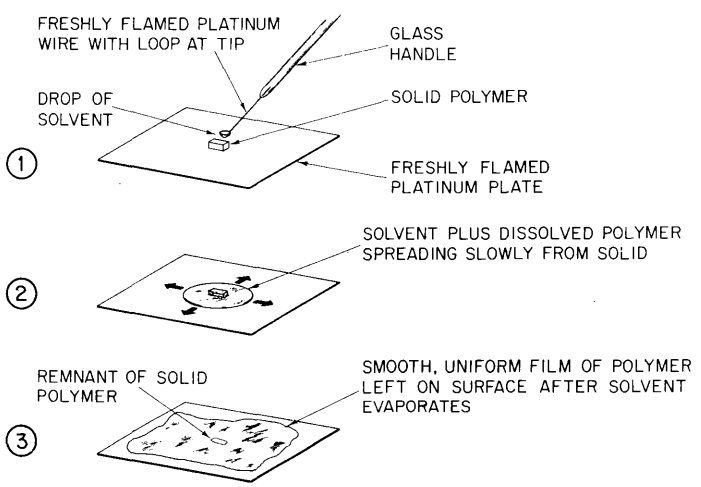

Fig. 1 - Technique for film formation

and remnants of the solid polymer remained in the middle. This simple technique was found generally applicable, the resultant thin films were more readily freed from trapped solvent, and problems with slow diffusion of contaminants to the surface from the bulk phase were rare. PMG films, once cast on platinum sheets, were further modified by soaking each, while still adhering to the platinum, in formic acid to induce configurational changes. Surfaces of all polymer samples were cleaned immediately prior to our measurements by washing each with a concentrated Tide solution applied with a soft, clean, camel's hair brush. After each sample was thoroughly rinsed with distilled water, it was air-dried for 4 hr at 20°C in a grease-free, covered glass container.

On the specimen surface the slowly advancing contact angles of each of many pure liquids were determined using the slow, drop-buildup method (5) and a goniometer telescope (6). Each contact-angle value recorded is that which occurred reproducibly within

the first 10 to 20 sec after slowly advancing the sessile drop over a fresh surface region. Contact angles exhibited by water, formamide, and ethylene glycol changed after this time as the result of the gradual penetration of liquid into the plastic solid. The contact angle of glycerol changed more slowly and that for thioglycol was often constant for many minutes. Contact angles exhibited by the nonhydrogen-bonding organic liquids were generally constant for many minutes and, in most instances, showed no significant hysteresis when slowly receding contact angles were measured. All measurements reported here were made with samples and liquids equilibrated in a clean room at 20°C and 50% relative humidity.

MAIR spectroscopy at infrared wavelengths was used to confirm the identity of the polymers, monitor the induced structural transformations, and validate the preparative and cleaning procedures. A Wilks Scientific Corp. Model 9 Internal Reflection Accessory was used in conjunction with Beckman IR-12 and Perkin-Elmer 21 infrared spectrometers. Reflection spectra characteristic of only the first fraction of a micron of each specimen surface were obtained by clamping the specimen against a KRS-5 multiple internal reflection prism and mounting it in the accessory mentioned above. Reflection spectra characteristic of as little as monolayer amounts of the solvents, cleaning agents, and adventitious organic contaminants were obtained by exposing a clean germanium prism to each of the various materials and then mounting the prism in the internal reflection accessory.

RESULTS

Validation of Methods

It was essential to verify that the various polymer solvents and cleaning agents used did not remain in the film or leave residues which would strongly influence the observed contact angles. Because it was conceivable that MAIR spectra, even though they characterize only the first few molecular layers of a sample surface, might allow a monolayer of adsorbed contamination on a plastic surface to go undetected, additional checks for surface cleanliness were made. That the simple combination of air drying and thorough water rinsing was sufficient to completely remove the solvents and cleaning compounds was established as follows: detergent-washed, water-rinsed, internal reflection prisms of germanium showed a blank spectrum in the infrared. It has been shown at NRL (7,8) and other laboratories (9) that such spectra are sensitive to a single monolayer of deposited organic material. When clean germanium prisms (i.e., those with blank ir spectra) were contacted with the detergent solution or the various solvents but were not rinsed with water, they were found by the MAIR technique to have retained at least a contaminating monolayer of organic material after simple air drying. Thus, our technique could readily detect a monolayer of organic surface contaminant.

In a similar fashion, polyamide films dried from solvent onto clean germanium prisms, and not further washed or rinsed, were found to include solvent to a slight extent. In general, copious water rinsing completely removed traces of Tide from these surfaces as well as most of the organic solvent residues, and the application of a detergent solution to a specimen surface using a clean soft brush followed by thorough rinsing completely removed signs of any organic contamination. Germanium plates always were returned to their initially clean condition after such treatment. In conclusion, it was possible to establish that the MAIR technique was sensitive to monolayer amounts of material and that both the preparative procedures and cleaning procedures adopted were satisfactory for producing contaminant-free polyamide surfaces.

The various solvents used did not introduce artifacts of roughness during the casting of films or their surface modification. Disk specimens of nylon 66 prepared for earlier

investigations (1,2) were used to check this effect. Contact angles of a number of pure liquids of interest on the same specimen of nylon 66, prepared by polishing the specimen with a dry silk cloth, are known (1). Additional specimens of this same polymer were treated in this investigation with the various solvents selected for film casting, and the contact angles were determined in each case. Although some variance, at the most 5 degrees for a given liquid, was introduced by treatment of the surface with the solvents, the values did not alter significantly the trend of the results or modify the important features of the data plots.

It is of interest to note that each of these modified nylon surfaces was cleaned with Tide and rinsed with water before measurements were made, and no detectable contamination remained in any instance. The original NRL contact-angle investigation of nylon 66 (1) and a companion publication of the frictional properties of this polymer (2) established earlier that no detergent residues remained on nylon surfaces after rinsing. All organic films examined by the contact-angle method were investigated at least in duplicate using independently prepared samples.

All of the liquids used in making the contact-angle measurements were of high purity and behaved reliably. The experimental determinations of the contact angles on each plastic surface were routinely reproducible within 3 degrees. Regular checks of both the experimental technique and the liquid purity were made by placing sessile drops of these liquids on a smooth flat Tide-cleaned, water-rinsed, Teflon surface. The plot of $\cos\theta$ vs surface tension for this system always intercepted the $\cos\theta = 1$ axis at between 18 and 19 dynes/cm, in good agreement with the earlier reported values (3,10).

Ethylene glycol behaved anomalously on all of the surfaces investigated here and, in the case of the polyamide specimens, was more nearly in line with the nonhydrogen-bonding liquids than with the hydrogen-bonding liquids when plotted in the standard $\cos\theta$-vs-γ_{LV} graph. Since ethylene glycol is very hygroscopic, a possible explanation for this anomaly is that the presence of some water in this liquid increases its surface tension. If this were the case, the data point for ethylene glycol should be plotted at a higher surface tension, and the point would be more nearly in line with the other hydrogen-bonding liquids.

Some judgment was needed in the choice of a straight-line fit through the data points for each class of liquids and in its extrapolation to the $\cos\theta = 1$ axis to obtain the critical surface tension intercept γ_c. Since the contact angles for thiodiglycol and glycerol were the most stable among the hydrogen-bonding liquids, the line chosen to represent hydrogen-bonding liquids was influenced most strongly by these two data points. As a result the data point for water fell above the plotted line, in the direction consistent with the rapid penetration of water into the polyamide specimens, and with the resultant difficulty in accurately estimating the largest initial contact angle. This choice also had the virtue of being consistent with the earlier plot for nylon 66 and allowing ready comparison of the results reported here with those given by Ellison and Zisman (1). Similarly, the line drawn through the data points for nonhydrogen-bonding liquids was most strongly influenced by the values for methylene iodide and α-bromonaphthalene, which were also the nonhydrogen-bonding liquids used earlier (1).

Contact-Angle Results

Contact Angles on Nylon Films Cast from DCA – The mean observed contact angle θ for each liquid on the surface of a nylon 11 film cast from DCA is listed in column 3 of Table 1. A plot of $\cos\theta$ vs the liquid surface tension γ_{LV} is given in Fig. 2. These films were very smooth and translucent in appearance and adhered very poorly to the

platinum sheets on which they were cast. The critical surface tension intercepts γ_c obtained for the hydrogen-bonding and nonhydrogen-bonding liquids are given in row 1 of Table 2.

The results for nylon 6 films cast from DCA are listed in column 4 of Table 1 and row 3 of Table 2, and the data plot is given in Fig. 3. These nylon 6 films were smooth and transparent and adhered well to the platinum backing plates.

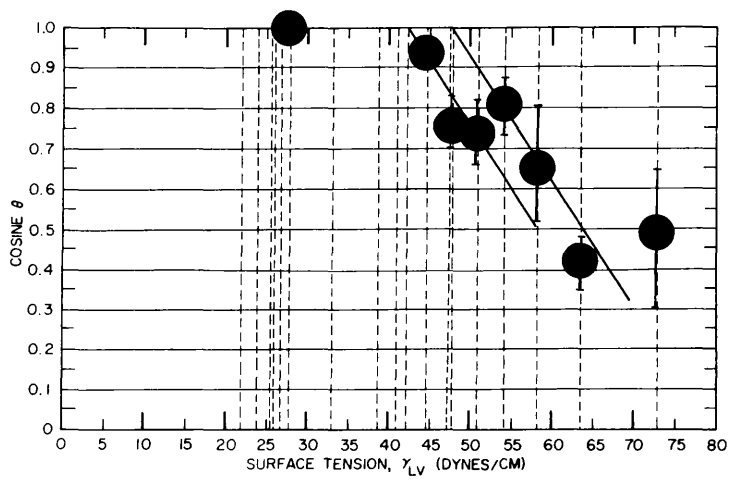

Fig. 2 - Nylon 11 film spread on platinum from DCA solution

Table 2
Critical Surface Tensions for Polyamide and Polypeptide Films
(determined graphically from plots of cos θ vs γ_{LV})

Polymer	Solvent Treatment	Critical Surface Tension Intercept	
		Hydrogen-Bonding Liquids	Nonhydrogen-Bonding Liquids
Nylon 11	DCA	46	42
Nylon 11	Formic acid	44	44
Nylon 6	DCA	46	42
Nylon 6	Formic acid	38	38
Polyglycine (Nylon 2)	DCA	51	44
PMG	DCA	48	42
PMG	Chloroform	48	43
PMG	Formic acid	50	43
PMG	Formic acid (soak)	42	42
PBG	DCA	40	40

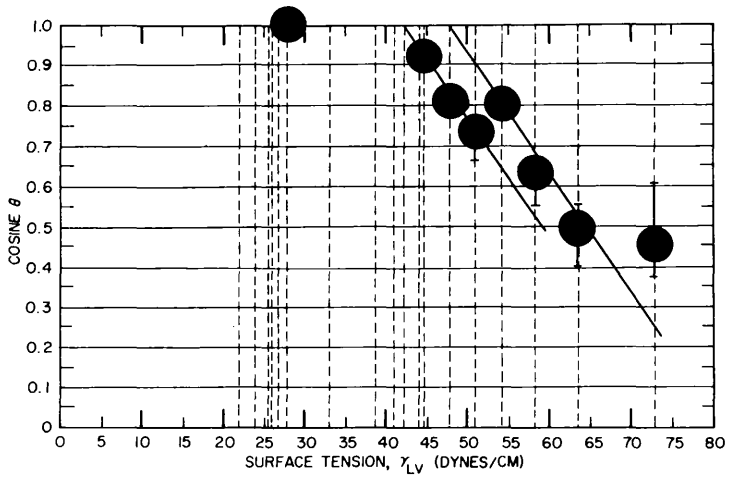

Fig. 3 - Nylon 6 films spread on platinum from DCA solution (average of 3 runs)

Contact Angles on Nylon Films Cast from Formic Acid – Column 5 of Table 1 lists the experimental data for each pure liquid in contact with the surface of nylon 11 films cast from formic acid by the drop-spreading method; the resulting plot of cos θ vs γ_{LV} is found in Fig. 4. These films were smooth, milky white in appearance and adhered tenaciously to the platinum sheets. They did not show a difference in wetting by hydrogen-bonding and nonhydrogen-bonding liquids but did have high γ_c values as recorded in row 2 of Table 2.

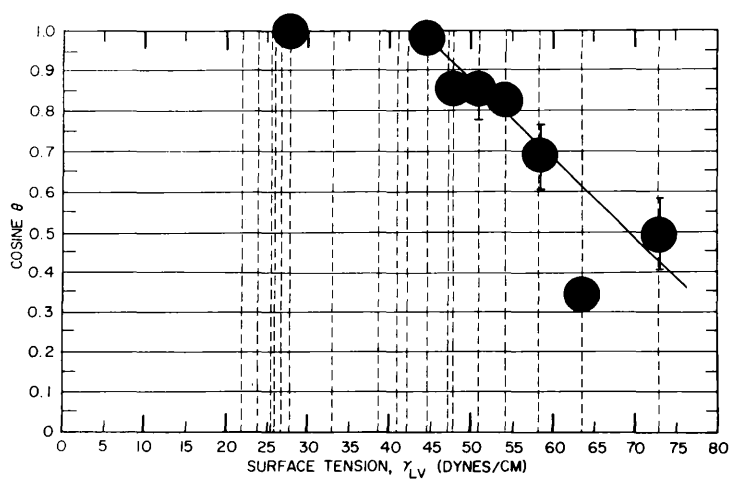

Fig. 4 - Nylon 11 film spread on platinum from formic acid solution

Column 6 of Table 1 and Fig. 5 report the experimental results for nylon 6 cast from formic acid. There was one anomaly in these results which remains difficult to explain. Although pure hexadecane (γ_{LV} = 27.7 dynes/cm) spread rapidly over the surface of every other polyamide film investigated here, it crept rather slowly over the nylon 6 films cast from formic acid. Since such spreading was spontaneous and eventually went to completion (thus warranting the reported θ of 0 degree as the equilibrium value), the slowness of the spreading could reflect the trapping of some oleophobic contaminant of unknown

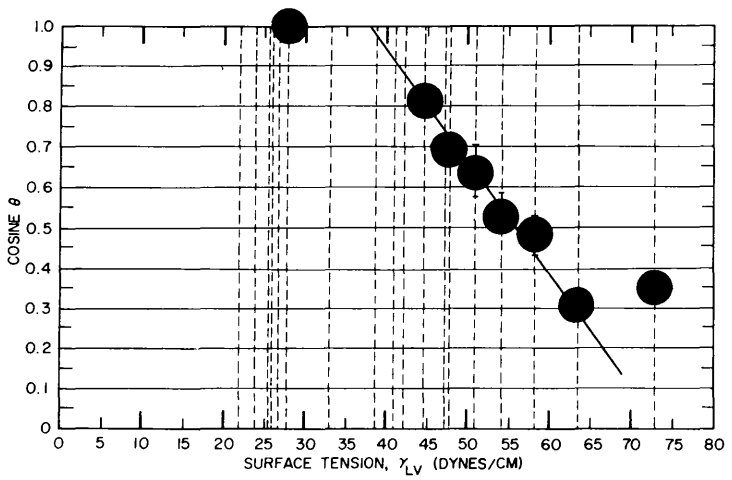

Fig. 5 - Nylon 6 film spread on platinum from formic acid solution

source in the film surface. The lower γ_c intercept and lack of differentiation between hydrogen-bonding and nonhydrogen-bonding liquid wetting behavior (row 4, Table 2) would support this suspicion; on the other hand, the film appearance was smooth and translucent (not transparent as when cast from DCA) and so could reflect a molecular configuration change which might give this wetting behavior independent of any oleophobic contaminant. Since there was no other evidence linking oleophobic contaminants to the formic acid, a configuration change is considered probable.

Contact Angles on Polypeptides Cast from DCA – Polyglycine formed smooth translucent films which adhered tenaciously to the platinum sheets when spread from a solution in DCA. Experimental observations are recorded in column 7 of Table 1 and row 5 of Table 2 and plotted in Fig. 6.

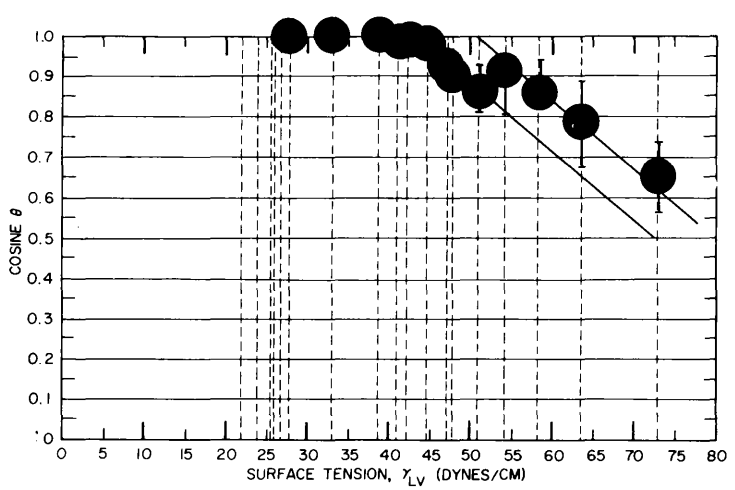

Fig. 6 - Polyglycine (nylon 2) films spread on platinum from DCA solution (average of 4 runs)

PMG, which differs from polyglycine only in having a methylglutamate ester side chain substituted for one of the hydrogen atoms on the carbon separating amide links, formed smooth transparent films when cast from solution in DCA. Contact-angle results for these films are given in column 8 of Table 1 and row 6 of Table 2 and plotted in Fig. 7.

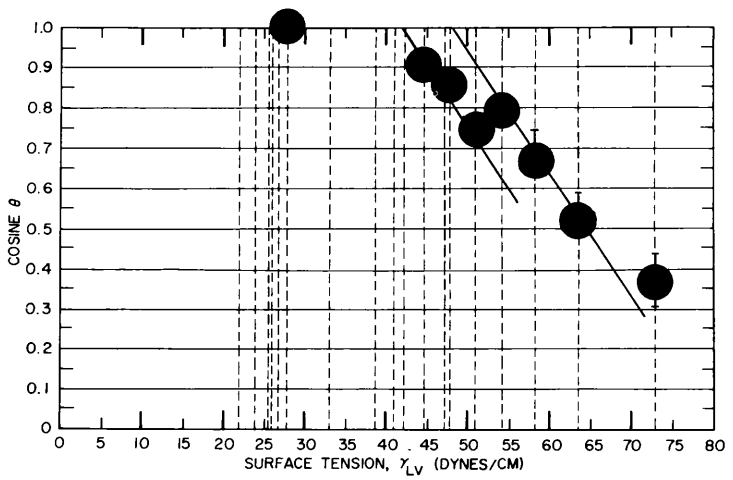

Fig. 7 - PMG film spread on platinum from DCA solution

PBG differs from DMG only in that benzyl ester side chain of glutamic acid is present rather than the methyl ester. The contact-angle results obtained with the thin, transparent films formed by drop spreading PBG from DCA are reported in column 9 of Table 1 and row 10 of Table 2 and graphed in Fig. 8. These were also smooth, transparent films which adhered well to the platinum foils.

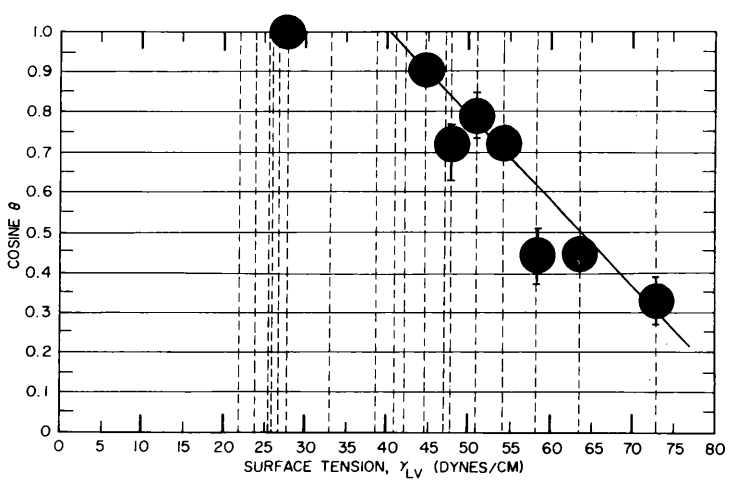

Fig. 8 - PBG film spread on platinum from DCA solution

Contact Angles on PMG Films Cast from Chloroform – Whereas the strong solvent action of DCA is thought to induce the normal statistical random-coil type of configuration in polypeptide solutions, there is good evidence (8) that PMG dissolved in chloroform possesses a high degree of the ordered α-helix chain structure. Contact-angle results obtained with PMG films cast from chloroform are given in column 10 of Table 1 and row 7 of Table 2 and plotted in Fig. 9.

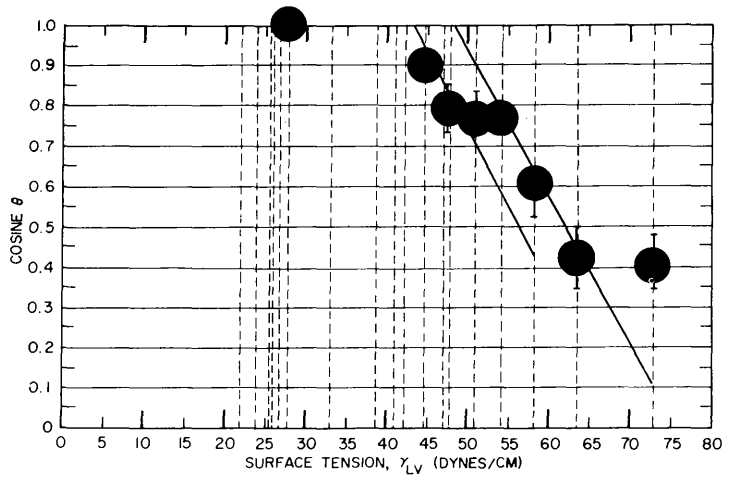

Fig. 9 - PMG films spread on platinum from chloroform solution (average of 3 runs)

Contact Angles on PMG Films Swollen in Formic Acid – Highly polymerized PMG is not soluble in formic acid; it does swell in this reagent, however, and on drying assumes an extended chain configuration characterized as the β or extended structure on the basis of x-ray and infrared investigations (11,8). It was thus possible by formic acid swelling of PMG films cast from chloroform to obtain contact angles results for both extreme forms of polymer configuration (the as-cast α-helical form and the after-swelling β-structure form) from the same thin cast film. Column 11 of Table 1, row 9 of Table 2, and Fig. 10 summarize the results on the films of PMG swollen by formic acid. The swelling was accomplished in the following sequence. PMG films on platinum sheets, after being cast from chloroform, were immersed halfway in 100% formic acid for 24 hr. The immersed portion of the film swelled to about 1-1/2 times its initial dimensions and became quite cloudy in appearance. The formic acid was poured off and replaced again with fresh acid; this step was important, because the low-molecular-weight fraction of the PMG film apparently dissolved in formic acid and, if not eliminated, imparted different properties to the film when allowed to dry on the surface. After a second 24-hr soak in formic acid, the PMG film was allowed to air dry and was then cleaned with the standard detergent solution in water. The upper portion of the film remained unmodified and so could serve as an internal control for each experiment. The unmodified portion of each film retained its original transparent appearance and gave the same contact angles as reported in column 10 of Table 1 and Fig. 9, whereas the portion modified by formic acid assumed a translucent appearance and gave different contact angles as recorded in column 11 of Table 1, row 9 of Table 2, and Fig. 10.

Contact Angles on PMG Cast from Formic Acid – Since low-molecular-weight fractions were abundant in the PMG sample, and since these fractions showed an apparent ready solubility in formic acid, it was possible to drop-spread PMG films from formic acid directly. The formation of such films illustrates an important feature of the drop-spreading technique outlined in Fig. 1: fractionation of the polymer by differential solubility occurred, particularly when poor solvents were used. Films of the formic-acid-soluble fraction of the PMG were formed by allowing drops of the solvent to swell and partially dissolve a piece of the bulk PMG film placed in the center of a flamed platinum sheet. The formic acid which spontaneously spread to cover the metal sheet carried with it some of the dissolved polypeptide and, after being air dried, left PMG deposited as a very smooth outermost translucent film. Films indentical in all respects could be formed by allowing the formic acid soaking bath to evaporate to dryness on any clean flat surface. Column 12 of Table 1, row 8 of Table 2, and Fig. 11 summarize the results obtained from contact-angle measurements on these films.

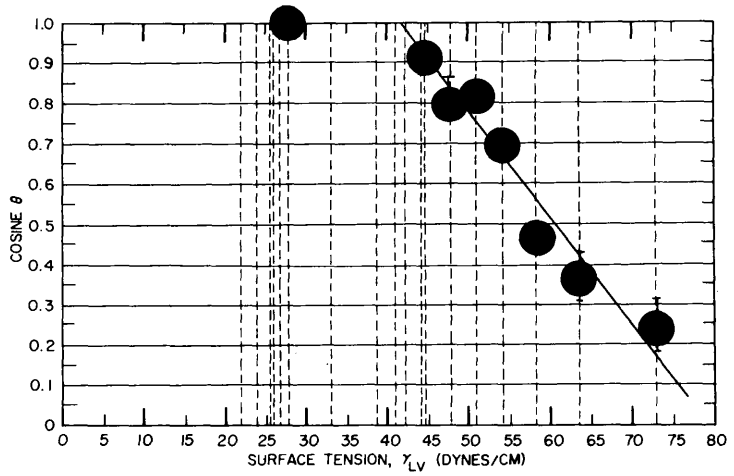

Fig. 10 - PMG film spread on platinum from chloroform solution and then swollen in formic acid solution

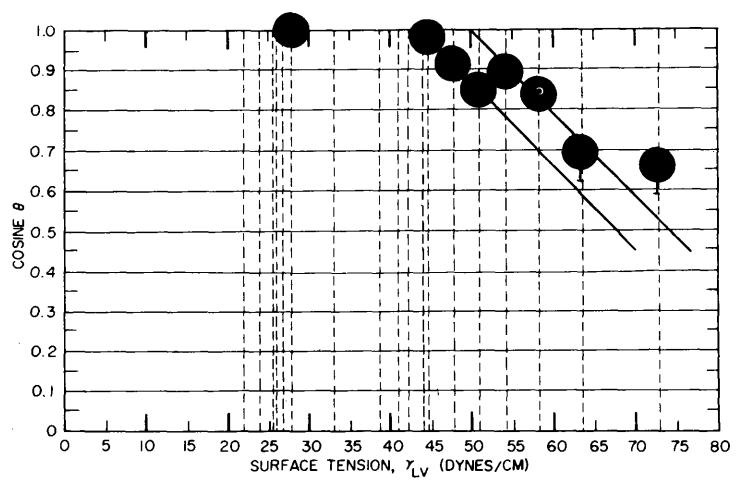

Fig. 11 - PMG film spread on platinum from formic acid solution

MAIR Infrared Spectroscopy

MAIR Spectra of the Nylons and Polyglycine - Nylon 11, nylon 6, and polyglycine form an homologous series of polyamides in which the number of $-CH_2-$ groups intervening between sequential amide links is 10, 5, and 1, respectively. Each member of this series may be thought of as a polypeptide (or polymer of amino acids). Figures 12, 13, and 14 are the infrared spectra characterizing the outermost molecular layers of films of these polyamides on platinum sheets. These spectra were obtained for all samples included in the contact-angle phase of the investigation (after removing the solid polymer remnants in the center of each film).

Only because of the recent advances (9) in MAIR spectroscopy have such spectra been obtainable. In many instances excellent spectra were recorded with films so thin that interference colors were evident in reflected light. The quality of the spectra (i.e., the intensity and separation of diagnostic peaks) depends heavily on the degree of intimate molecular contact of the specimen surface with the surface of the internal reflection prisms.

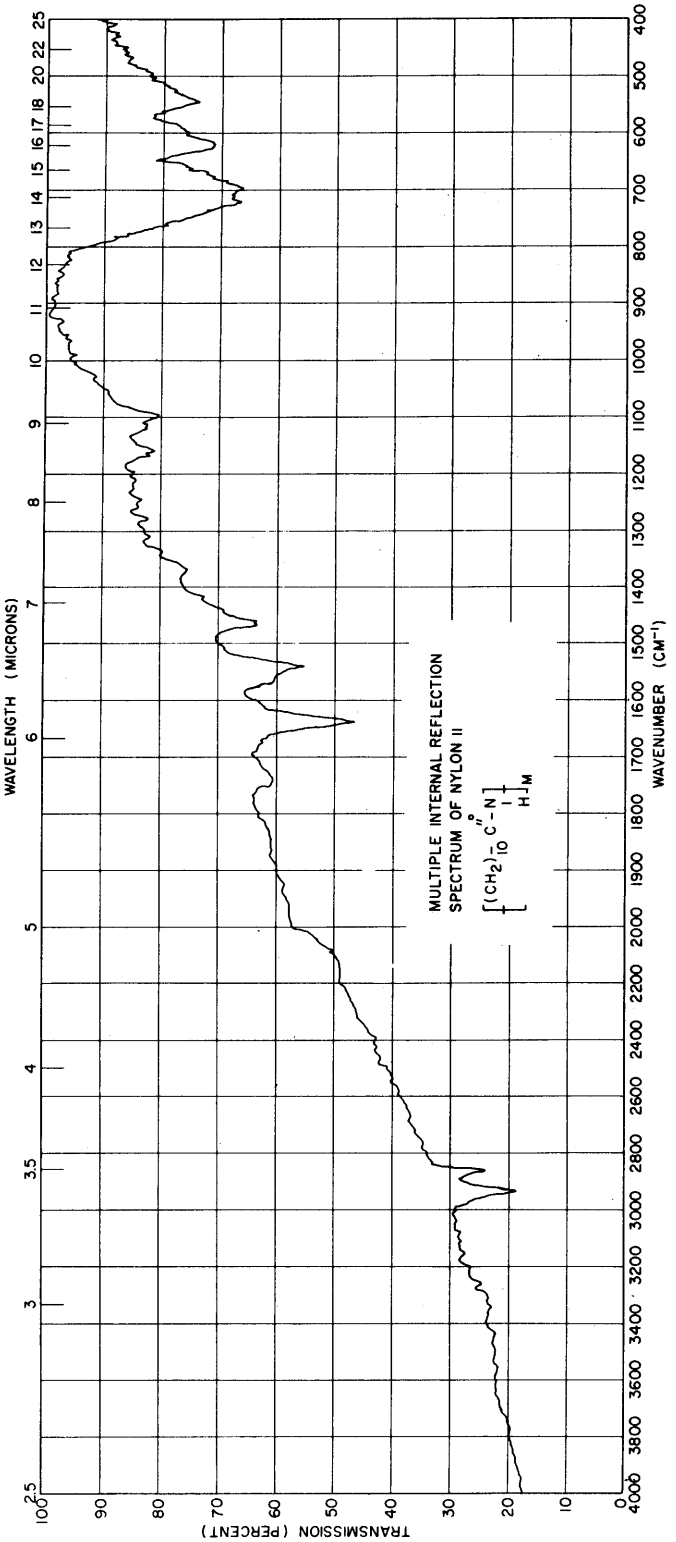

Fig. 12 - Multiple internal reflection spectrum of nylon 11

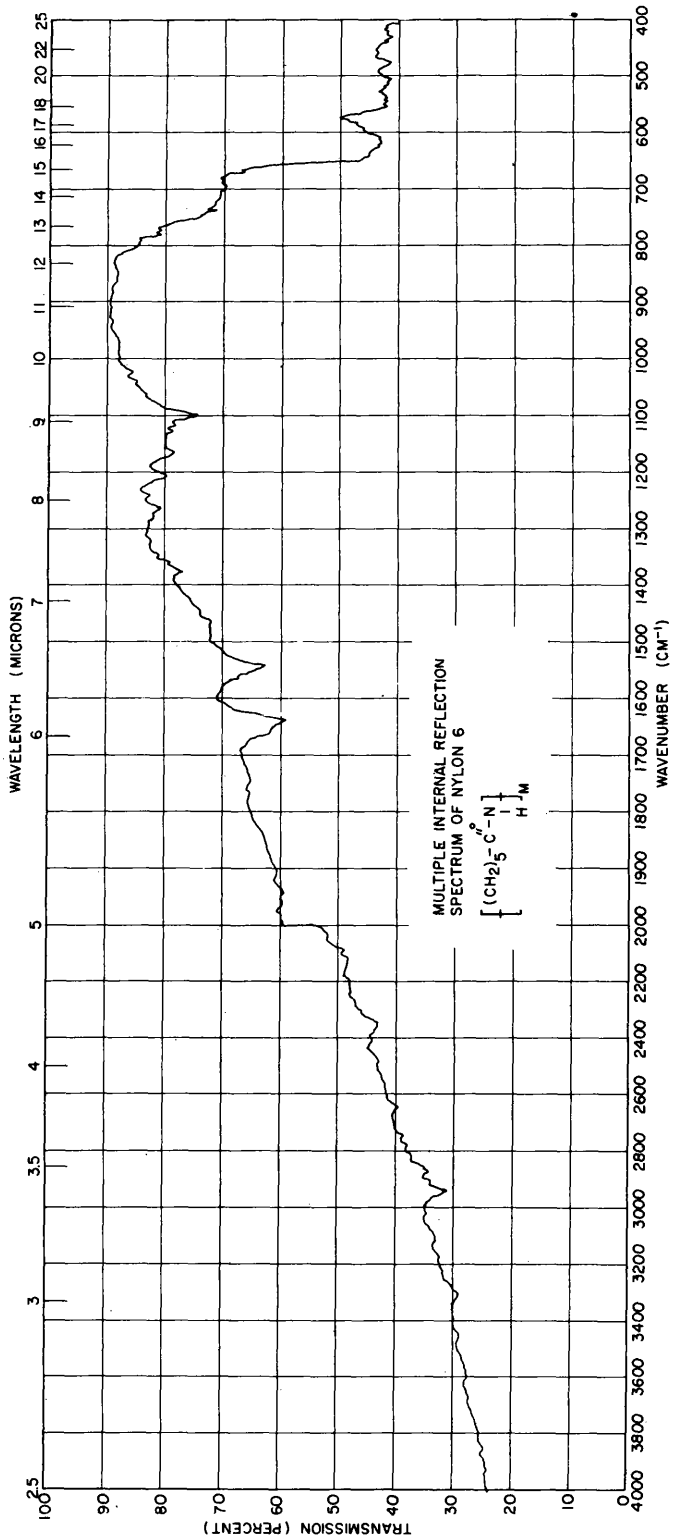

Fig. 13 - Multiple internal reflection spectrum of nylon 6

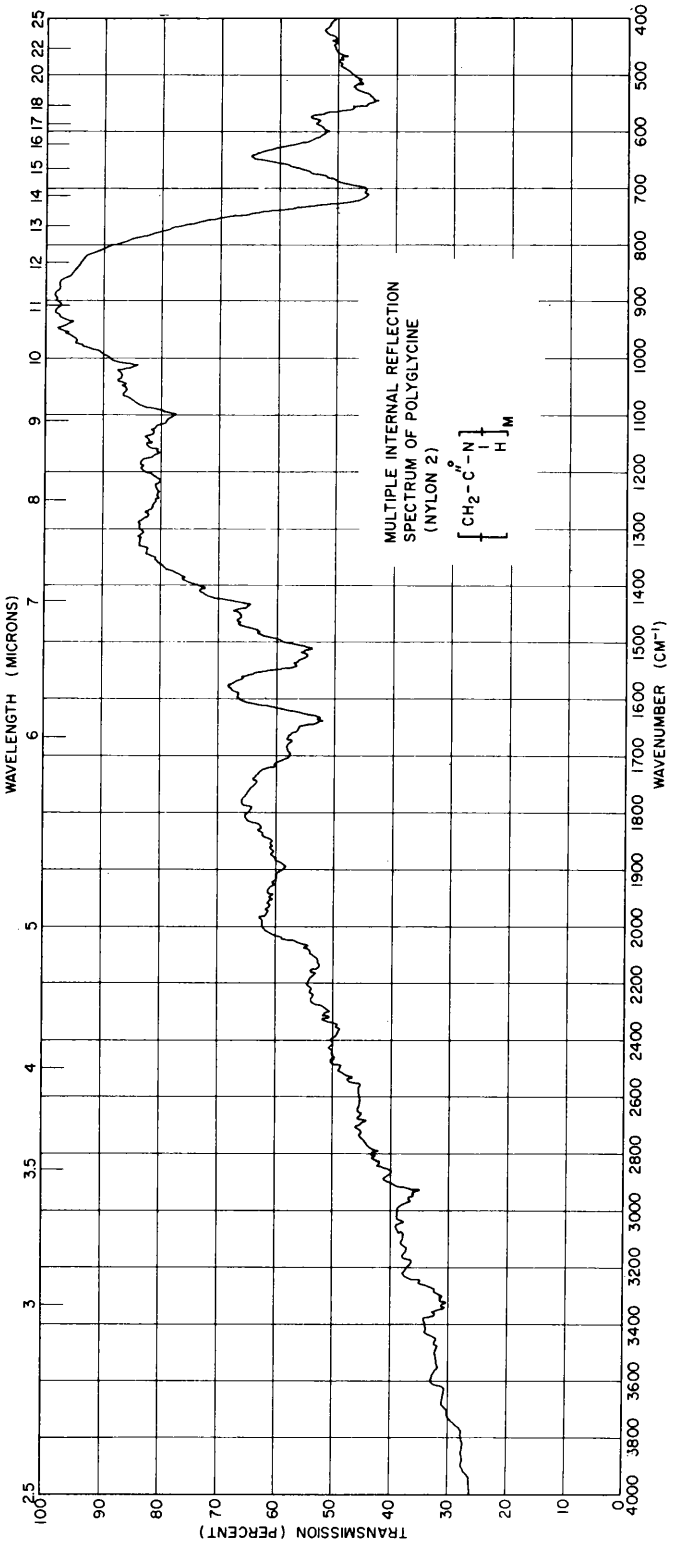

Fig. 14 - Multiple internal reflection spectrum of polyglycine

In the present work, good results were obtained. We had to accept the constraint of using very thin polymer films mounted on metal backing plates, because stripping of the films prior to spectral analysis might have given rise to artifacts.

As an example of the improvements which can be obtained when (a) bulk plastic specimens are used and (b) additional surface contact can be created by pressure extrusion of the sample in the clamping device, Fig. 15 shows the MAIR infrared spectrum of the surface of the nylon 66 disks used in this investigation.

The spectra recorded in Figs. 12 through 15 are typical of all nylon (and polyglycine) films investigated, regardless of the casting solvent used. No obvious spectral differences were recorded for these polyamides when cast from DCA and from formic acid. The contact-angle results showed that some differences in surface properties were produced, however, and additional analysis of infrared patterns may yet yield a correlation.

MAIR Spectroscopy of PBG and PMG – In the case of the more complex polypeptides, especially PMG, variations in the solvents produced variations in the polymer configuration in the dried film. MAIR infrared spectra have proven remarkably effective in indicating these alterations in surface configuration (8), and this aspect of the research has been pursued further in a companion investigation (12). The results from these studies will be used here but without repeating the graphs exhibiting the spectral shifts diagnostic of the structure changes.

PBG films cast from DCA produced spectra typical of the α-helix (or random-coil chain) configuration. PMG cast from DCA, chloroform, and formic acid also gave this α-type spectral pattern—indicative of coiled chains which were intramolecularly hydrogen bonded. The formic-acid-cast films of PMG, in particular, gave sharp narrow absorption bands typical of highly α-helical polypeptides. On the other hand, PMG swollen in formic acid (but not soluble in this reagent) converted to the β-type spectrum typical of extended chains predominantly intermolecularly hydrogen bonded to each other. The extended-chain molecular configuration constrained the methylglutamate side chains to lie at right angles to the main chain and in such a manner as to mask the polyamide backbone from the outermost atomic layer of β-structure films. These considerations are reported in greater detail elsewhere (12).

DISCUSSION

Freedom from Artifacts

The results reported in the previous section reveal that the contact-angle measurements contain no systematic errors, and it is particularly convincing that DCA and formic acid induced both types of polyamide wettability with the various polymers. In many cases wettability behavior is characterized by a split of the cos-θ-vs-γ_{LV} plot into two lines, one through the hydrogen-bonding liquids and one through the non-hydrogen-bonding liquids. The wettability characteristic of the solid polymer surfaces reported in the past has been a single-line fit with a characteristically rectilinear segment through the data points for the nonhydrogen-bonding liquids and a curved segment through the hydrogen-bonding liquids. But we now find that DCA-cast films of nylon 11, nylon 6, polyglycine, and PMG (as well as the DCA-solvated surface of a nylon 66 disk) all showed the two nearly parallel line graphs, with the right-hand line indicating the hydrogen-bonding capability at the polyamide surface. DCA-cast PBG, on the other hand, showed a normal cos-θ-vs-γ_{LV} plot comprising a single straight line. Formic acid induced a two-line graph when the surface of nylon 66 disks were solvated with this reagent and similarly for the drop-spread films of PMG. In contrast, films of nylon 11 and nylon 6 drop-spread from formic acid, as well as PMG films swollen in formic acid (but not dissolved in it) exhibited only

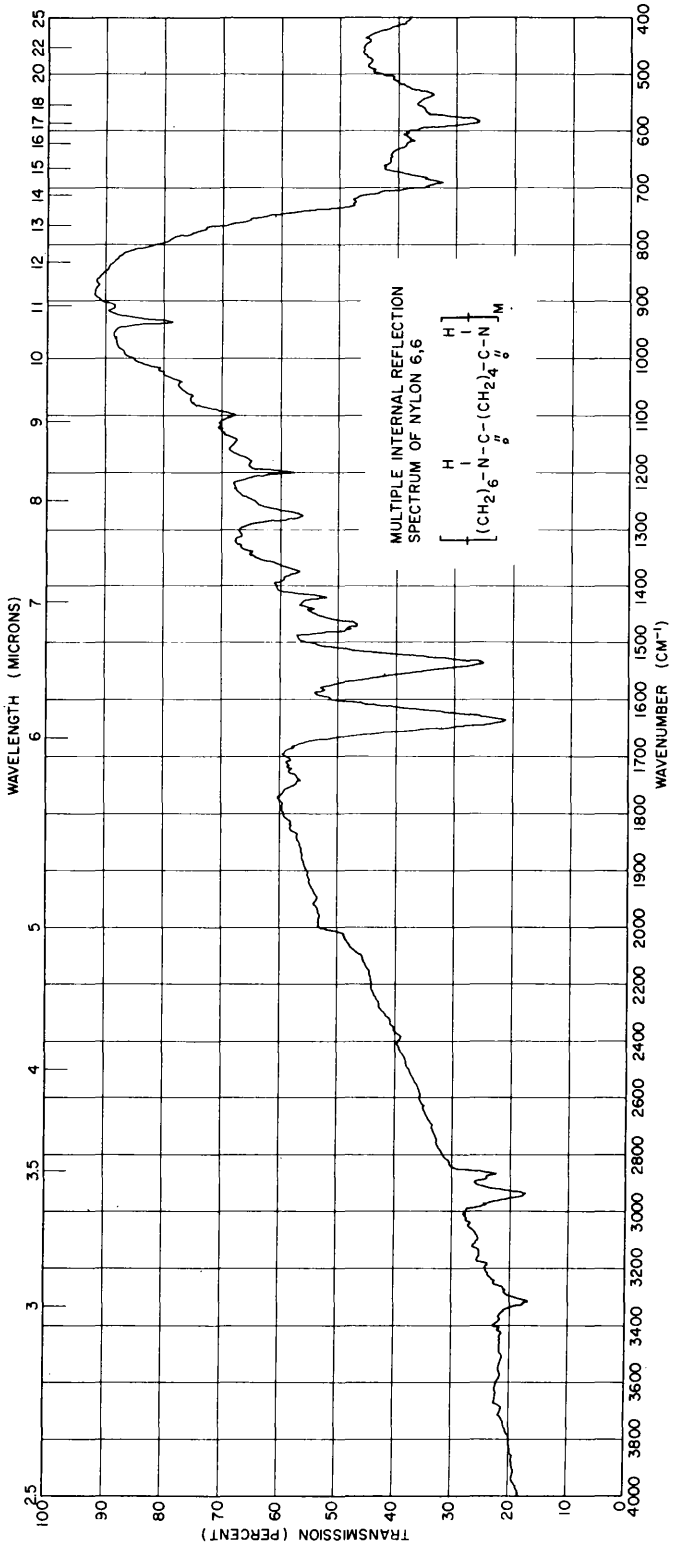

Fig. 15 - Multiple internal reflection spectrum of nylon 66

the normal wettability behavior. Polyglycine was totally insoluble in formic acid and so could not be included in this series. If the solvents alone, or any suspected contaminants, were responsible for the ultimate wettability of the polymer films cast from them, this diversity of behavior would not have occurred. The simplest remaining interpretation of the data is that a combination of polymer constitution and polymer configuration most strongly influenced the makeup of the outermost atomic layers at the surfaces of solvent-cast polyamide films.

Diagnostic Features in the Data

The polyamide films drop-spread from DCA form an homologous series identical in all respects except for the relative proportions of amide and hydrocarbon groups in the polymer backbone. It is useful to consider the common nature of the results on nylon 11, nylon 6, and polyglycine, as well as the unique features.

Two striking features are noted in the contact-angle data: first, $\cos\theta$ vs γ_{LV} for the hydrogen-bonding and nonhydrogen-bonding liquids fell on separate (but nearly parallel) lines, and, second, the slopes of the lines were smaller than is common with solids of low surface energy. These features suggest a high degree of liquid-solid interaction and a special interaction for the hydrogen-bonding liquids. The critical surface tensions determined by these straight lines, reported in Table 2 and shown as the intercepts at $\cos\theta$ - 1 on Fig. 2 through 11, are substantially higher than those for polymers free from amide groups. In other words, the introduction of amide groups in the polymer surface increased the free surface energy per unit area.

The two separate γ_c values, depending on the class of liquids chosen, can also be extrapolated from the earlier results of Ellison and Zisman (1) with nylon 66. It appears that this split of the data points into two rectilinear groupings may be used to diagnose for the presence of hydrogen-bonding groups in polymer surfaces. This type of split has not been observed with any class of polymers not having hydrogen-bonding sites; however, Ellison and Zisman did observe another type of split (1) in the cos-θ-vs-γ_{LV} plot for polystyrene where the halogenated organic liquids showed anomalous behavior and the hydrogen-bonding liquids showed no evidence of special interactions.

In a similar manner, the change in slope in the cos-θ-vs-γ_{LV} lines may reflect the density of hydrogen-bonding sites in the surface. This conjecture follows from the observed decrease in the slope of the lines in going from nylon 11 to nylon 2, and it is consistent with the increase in γ_c as the surface amide density increased in this same series. Neither the slope nor the γ_c values changed greatly in going from nylon 11 to nylon 6, which was a surprise, and this makes the above suggested correlation tentative.

It was at this juncture that the MAIR infrared spectra became particularly useful, since they allowed us to verify the chemical constitution and (in many cases) the chain configuration at the polymer/air interface. Figures 12, 13, 14, and 15 show the MAIR spectra for the polyamides nylon 11, nylon 6, nylon 2, and nylon 66, respectively. Attention should be directed to the absorption bands in the regions of 3300 cm^{-1} and 2900 cm^{-1}, which are diagnostic, respectively, for N-H and C-H groups. Although the absolute intensities of these bands will vary from one repeat experiment to another, depending on the clamping pressure applied in the film-to-prism mounting device, the relative intensities of bands within a single spectrum are directly comparable. Comparison of these band heights yields the relative proportions of the various chemical groups in each of the nylon samples. Inspection of Figs. 12 and 13, for nylon 11 and nylon 6, confirms the sample identifications and proves that nylon 11 films did have a greater proportion of hydrocarbonlike groups in their surfaces than did nylon 6. Whereas in the nylon 6 spectrum the CH:NH (stretching frequencies) ratio is not much greater than unity, it is quite clear that the nylon 11 films

contained a much larger number of methylene groups for each amide group present in the surface region. In Fig. 14, the N-H and C-H characteristic frequencies are equally prominent, reflecting the nearly equal amide-to-methylene ratio in nylon 2. Figure 15 shows that nylon 66 has essentially the same band ratios as nylon 6, as expected, albeit with greater band intensities at all wavelengths because of the more efficient contact this specimen made with the internal reflection prism surface.

These spectra show that the sample identifications were reliable and that no apparent reason exists to distrust the contact-angle data on the nylon 11 films used here. Both nylon 11 and nylon 6 had previously been studied, after preparation from the melt, by Fort (13); his results for nylon 6 are comparable to those obtained here. His value of γ_c for nylon 11 was considerably lower than ours, however. Unfortunately, too small a number and variety of liquids were used in his work to observe a pair of straight lines for $\cos\theta$ vs γ_{LV}. One possible explanation for the disparity in the nylon 11 results might be the small amount of contaminant stated to be present in Fort's sample (13); another explanation might lie in the differing preparative techniques. In any case, the critical surface tension range of 42 to 46 dynes/cm obtained here for nylon 11, which contains 10% amide groups, is not unreasonable when it is recalled that values as high as 33 dynes/cm have been obtained with polyethylene, which contains no amide groups at all.

Figure 16 is a graph pertaining to some of the preceding discussion and illustrates the suggested diagnostic features in the contact-angle data. In this diagram, results from the $\cos\text{-}\theta\text{-vs-}\gamma_{LV}$ plots for nylon 11 and polyglycine are superposed. The critical-surface-tension range covered is from about 40 to 50 dynes/cm, which is considerably above the intercepts characteristic of most other polymers; this indicates the presence of some high-surface-energy constituents in the plastic surface. A major diagnostic feature is the split of the data into two well-defined groups. In Fig. 16, one boundary of each "wettability band" is formed by the data points for the hydrogen-bonding liquids and the other by the data points for the nonhydrogen-bonding liquids. This graph, with the hydrogen-bonding liquids defining the lower contact-angle boundary, indicates that hydrogen-bonding sites are accessible for interactions at the plastic surface. The hatching filling the spaces between the limiting lines for each class of liquid in Fig. 16 serves to indicate that the contact angles for more complex liquids, perhaps those containing varying ratios of hydrogen-bonding and nonhydrogen-bonding groups, might fall in this intermediate zone rather than at either extreme. A combination of a high critical surface tension with an obvious split in the wetting data into hydrogen-bonding and nonhydrogen-bonding classes would immediately mark this polymer, if unknown in constitution, as a probable polyamide. MAIR spectroscopy would confirm or disprove this identification.

The remaining diagnostic feature disclosed in Fig. 16 is the change in slope of the "wettability band" with changing amide content in the polymer. The more shallow slope, with the band closer to and more nearly parallel with the $\cos\theta = 1$ axis, indicates a greater interaction of the liquids, especially by the hydrogen-bonding liquids, with the polymer surface. This we interpret as evidence of the greater proportion of high-energy amide links available at the polymer surface; the interpretation is supported by the increase in critical surface tension which accompanies the change in slope.

Influence of Polymer Configuration

Although there is no obvious structural regularity among the natural proteins, certain configurations of the polyamide backbone common to all proteins are found frequently in segments of the molecules. It is important to learn if the influence of the polyamide backbone on the surface properties of proteins differs as the polymer configuration changes. The polypeptide PMG could be formed into films having two different but well-defined configurations known to occur in natural molecules. Films of PMG in its α-helical

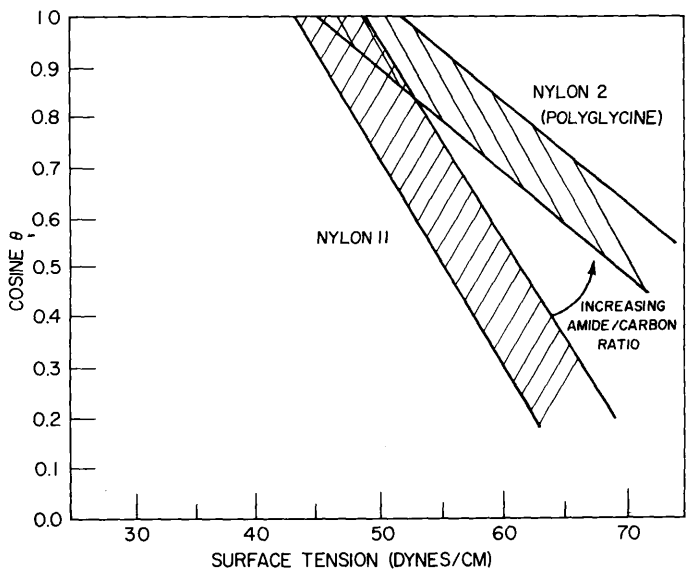

Fig. 16 - The wettability band for polyamide of the nylon series shifting in the direction shown as the number of methylene carbons between successive amide links is reduced

chain configuration were those produced by drop-spreading from chloroform. The polypeptide molecules were shown to be predominantly in this configuration when dissolved in chloroform (8), and the MAIR spectra interpreted according to criteria outlined elsewhere (8,12) confirmed that this configuration dominated the dried films. An experimental diffculty in forming these films was the rapid evaporation of the chloroform.

In many cases, specimen surfaces were unsuitable for contact-angle measurements, because they were not at all smooth; instead they were rough and chalky in appearance. This difficulty was overcome by saturating the air in a closed container with chloroform vapor and then adding a considerable excess of chloroform to the PMG specimen in the center of a platinum sheet so that evaporation was slow enough to result in the formation of smooth and transparent films. Figure 9 is the plot for the contact-angle data (recorded in column 10 of Table 1) for these α-helical film specimens. The dual wettability feature, the high critical-surface-tension intercepts, and the overall similarity of the results to those characterizing polyamides without side chains (i.e., the nylons) demonstrate unambiguously that in the polypeptide the molecules in the screwlike helical configuration allow ready access of hydrogen-bonding liquids to the polyamide backbone. The regular spiral arrangement of the ester side chains around the helical polyamide core is apparently open enough to allow small molecules, such as water, formamide, glycerol, and thiodiglycol, to penetrate to and hydrogen-bond with the amide links.

As illustrated in column 8 of Table 1 and Fig. 7, PMG drop-spread from DCA exhibited wettability behavior not significantly different from the films spread from chloroform. DCA is considered to be a general randomizing solvent for polypeptides and should have produced a random tangle-type configuration in the dried films. However, the infrared spectra for random tangle polypeptide structures and for α-helical structures are nearly the same, and in the present investigation these two coiled types of configuration were not differentiated by MAIR spectroscopy. One would expect ready accessibility of the liquid to the polyamide backbone as the polypeptide was randomized, and

such was the observation by contact-angle methods. The possibility remains that in the course of being dried to a thin film the polypeptides convert from their randomized solution structure to the more regular helical configuration. Whichever the case, it is interesting to note that a simple change in the nature of the side chain—replacing the methyl ester of glutamic acid with the more bulky benzyl ester—blocked the access of hydrogen-bonding liquids to the polyamide backbone chain. Since the MAIR spectra for PBG films cast from DCA were practically identical with those for PMG cast from DCA, and yet the wettability results differed, it can be concluded that the bulky benzyl substituents masked the amides from the film surface by steric hindrance and not by a configuration change. The contact-angle results are summarized in Fig. 8 and coulmn 9 of Table 1 for PBG. Note also that the critical-surface-tension intercept of 40 dynes/cm is consistent with the earlier value of 39 dynes/cm for surfaces containing ester groups, obtained with polymethylmethacrylate (14) but is slightly augmented by the benzyl group. No hydrogen-bonding functionality attends the presence of esters in plastic surfaces, as judged by criteria outlined in the previous section of this discussion.

Although it was not possible to drop-spread the β-structured form of PMG, since formic-acid-soluble PMG gave rise to films of the helix type by both wettability and MAIR spectra (Fig. 11 and column 12 of Table 1), films predominantly composed of this interesting model protein structure were obtainable by a soaking procedure. Soaking of the specimens originally drop-spread from chloroform, which by every indicator were α-helical in nature, resulted in structural transformation of the coiled polypeptide chains into extended chains. Column 11 of Table 1 and Fig. 10 contain the results of contact-angle measurements on the transformed films. It is immediately apparent that the criteria established for the presence of accessible amides in the surface of the solid polymer are not met. The high value of γ_c of 42 dynes/cm suggests that hydrophilic groups were present in the surface, however. The most plausible interpretation of the data is that the β-structured surface was comprised predominantly of ester groups, probably supplemented by occasional amides exposed in incompletely transformed chain segments. In a companion study (12), where free films of the PMG sample were similarly transformed with formic acid, a more complete conversion to the β structure was achieved (perhaps because the polymer chains were free from constraints associated with their attachment to a metallic foil), and the value of γ_c obtained was identical with that for polymethylmethacrylate (14). Analysis of Corey-Pauling-Koltun molecular models for the various configurations showed that the wettability features obtained were consistent with the chain structures determined by surface spectroscopy (12). Here we have a convincing demonstration of the diagnostic value of contact-angle results as discussed previously and also have evidence of how changes in the backbone configuration of a polypeptide or protein can strongly influence its surface properties.

Our preceding conclusion appears to hold also for the simpler polyamides, such as the nylons, but surface spectroscopy does not appear as sensitive to changes in the surface orientation as contact-angle measurements. Figures 2 through 6 and columns 3 through 7 of Table 1 show that nylon 11 and nylon 6 cast from DCA differed considerably in wettability by hydrogen-bonding liquids from similar films cast from formic acid. These film differences may be attributed either to polymer fractionation, to structure transformation, or to both causes.

There were obvious differences in the film appearance and strength of adhesion to the platinum plates, which suggest differences in molecular configurations. Surface spectroscopy, while not differentiating solvent-cast films of a given nylon sample from one another, did provide some additional useful information about the polymer structure. The positions of the N-H stretching frequencies at about 3300 cm^{-1}, and the amide I and amide II absorption bands at about 1630 cm^{-1} and 1530 cm^{-1}, respectively, are characteristic of materials in which all possible hydrogen bonds are made intermolecularly between predominantly extended chains (11). A number of slight modifications of these extended chain structures

involving less coiling as compared to the polypeptides and proteins have been postulated for certain members of the nylon family (15). Contact-angle results may help to distinguish between these structures.

Additional research on the wetting behavior of nylon samples prepared from the melted state will be reported separately (16).

SUMMARY AND CONCLUSIONS

1. A new drop-solvent-casting method which required the use of minute amounts of sample and solvent was used to form very thin polyamide films on platinum sheets suitable for contact-angle and MAIR spectroscopic measurements.

2. The preparative and cleaning procedures used were validated by experiments with MAIR spectroscopy techniques, which were found sensitive to monolayer levels of contamination.

3. Nylon 11, nylon 6, and polyglycine, when cast from DCA, showed contact-angle results similar to those reported earlier by Ellison and Zisman for nylon 66 and verified here. Features in the wetting data were (a) a split in the cos-θ-vs-γ_{LV} graphs into a straight line for hydrogen-bonding liquids and a separate and nearly parallel line for nonhydrogen-bonding liquids and (b) high critical surface tensions of about 40 to 50 dynes/cm.

4. These similarities in the data were exploited as diagnostic indicators of the presence of accessible amide groups in the surface of a polymer. A systematic variation in the slopes of the graphs of cos θ vs γ_{LV} for the members of the nylon family appears to be useful as an indicator of the relative surface proportions of amide vs hydorcarbon groups.

5. Samples of the synthetic polypeptide PMG were prepared with different chain configuration by casting or soaking the solid form with different solvents—namely chloroform, formic acid, and DCA. The α-helical structure, the β- or extended-chain structure, and, presumably, the random-tangle structure were each produced, with the structural assignments derived by MAIR spectroscopy on the same specimens.

6. The helical and random configurations of PMG, but not of the very similar PBG, had wettability characteristics similar to those of the nylons, indicative of accessible amides at the free surface of the solid polymer according to the hypothesized diagnostic criteria. The benzyl ester, in PBG, apparently shielded the polyamide backbone more efficiently than did the less bulky methyl ester (in PMG).

7. The β- or extended-chain films produced by formic acid soaking of PMG, had wettability behavior similar to that of the PBG films, with no evidence of accessibility to the polyamide backbone for the hydrogen-bonding liquids. These results demonstrated that the masking effects of side chains can considerably alter the surface properties of solid polypeptides and proteins; in our work the wettability behavior of a polyamide containing esterified side groups was very much like that obtained with a similarly esterified polymethylmethacrylate, which contains no amide group at all.

8. Nylon 11 and nylon 6 films drop-spread from formic acid did not show the expected dual wettability for hydrogen-bonding and nonhydrogen-bonding liquids, presumably because of polymer fractionation, slight configuration changes, or both. MAIR spectroscopy did not differentiate between nylon films cast from different solvents as well as contact-angle measurements did.

9. Formic-acid-soluble fractions of PMG formed films of the α-helical type by both contact-angle and spectroscopic criteria. It was thus established that no systematic effect due to the various solvents used could have been responsible for the results obtained.

10. This investigation using the two powerful surface-chemical techniques of wettability determination, and MAIR spectroscopy has led to the conclusion that the solid surface properties of polyamides, polypeptides, and proteins are strongly influenced by the polymer configuration. These changes in the polymer structure are manifested by alterations of the chemical constitution of the outermost atomic layers of these complex molecules.

ACKNOWLEDGMENTS

Helpful suggestions by members of the Surface Chemistry Branch, especially George I. Loeb, Elaine G. Shafrin, N. Lynn Jarvis, and Marianne K. Bernett, are gratefully acknowledged; Dorothy S. Cain of the Spectroscopy Section, Physical Chemistry Branch, was particularly helpful in the work on MAIR infrared spectra. This investigation was carried out during the tenure of Robert E. Baier as an NRC-NAS Postdoctoral Research Associate at NRL.

REFERENCES

1. Ellison, A.H., and Zisman, W.A., J. Phys. Chem. 58:503 (1954)

2. Bowers, R.C., Clinton, W.C., and Zisman, W.A., Lubrication Eng. 9:204 (1953)

3. Fox, H.W., and Zisman, W.A., J. Colloid Sci. 5:514 (1950)

4. Fox, H.W., and Zisman, W.A., J. Colloid Sci. 7:428 (1952)

5. Shafrin, E.G., and Zisman, W.A., J. Colloid Sci. 7:166 (1952)

6. NRL Contact Angle Goniometer, commercially available from Rame-Hart, 43 Bloomfield Ave., Mountain Lakes, New Jersey

7. Loeb, G.I., "A Study of the Conformation of Surface Films of Polybenzyl-L-glutamate by Multiple Internal Reflection Spectroscopy," J. Colloid and Interface Sci., 26:236 (1968)

8. Loeb, G.I., and Baier, R.E., "Infrared Spectra of Surface Films of Poly-γ-Methyl-L-Glutamate," NRL Report 6554, July 1967; also "Spectroscopic Analysis of Polypeptide Conformation in Polymethylglutamate Monolayers," J. Colloid and Interface Sci. 26:236 (1968)

9. Harrick, N.J., "Internal Reflection Spectroscopy," Interscience, New York, 1967

10. Bernett, M.K., and Zisman, W.A., J. Phys. Chem. 66:1207 (1962)

11. Bamford, C.H., Elliott, A., and Hanby, W.E., "Synthetic Polypeptides," New York: Academic, 1956

12. Baier, R.E., and Zisman, W.A., "The Influence of Polymer Conformation on the Surface Properties of Polymethylglutamate," in preparation

13. Fort, T., Jr., Adv. in Chem. Ser. 43:302 (1964)

14. Jarvis, N.L., Fox, R.B., and Zisman, W.A., Adv. in Chem. Ser. 43:317 (1964)

15. Vogelsong, D.C., J. Poly. Sci. A1:1055 (1963)

16. Baier, R.E., and Zisman, W.A., "Contact Angle Investigation of the Surface Properties of Polyamides of the Nylon Family," in preparation

This page intentionally left blank.

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Research Laboratory Washington, D.C. 20390	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

WETTABILITY AND MAIR INFRARED SPECTROSCOPY OF SOLVENT-CAST THIN FILMS OF POLYAMIDES AND POLYPEPTIDES

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Interim report; work is continuing

5. AUTHOR(S) *(First name, middle initial, last name)*

R.E. Baier and W.A. Zisman

6. REPORT DATE September 16, 1968	7a. TOTAL NO. OF PAGES 28	7b. NO. OF REFS 17
8a. CONTRACT OR GRANT NO. NRL Problem C02-10 b. PROJECT NO. RR 001-01-43-4751 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6755 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research), Washington, D.C. 20360

13. ABSTRACT

Polyamides, such as the nylons, polypeptides, and proteins, may have variable surface properties as the result of the masking or exposure of surface hydrogen-bonding sites which may greatly influence their behavior. Our earlier investigation with the polyamide nylon 66, showing a wettability difference by hydrogen-bonding and nonhydrogen-bonding liquids, was confirmed and extended in the present work with nylon 11, nylon 6, and nylon 2 (polyglycine). This difference in wettability behavior seems diagnostic, when present in conjunction with a high critical-surface-tension range, for the presence of accessible amides in a polymer surface. Investigations of the more complex polypeptides, polymethylglutamate, and polybenzylglutamate by contact-angle determination and multiple attenuated internal reflection (MAIR) infrared spectroscopy on solvent-cast thin polymer films showed that the hydrogen-bonding capacity of the common polyamide backbone could be masked by either bulky side-chain substituents or by certain configuration changes of the polymer chain. Elimination of the hydrogen-bonding ability at nylon surfaces might also accompany polymer fractionation in different solvents, slight configuration changes, or a combination of both.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Nylons						
Multiple attenuated internal reflection infrared spectroscopy						
Contact angles						
Critical surface tension						
Polyamides						
Polypeptides						
Wettability						
Thin films						
Polymers						
Polyglycine						

DD FORM 1 NOV 65 1473 (BACK)
(PAGE 2)

Security Classification