Wettability and Multiple Attenuated Internal Reflection Infrared Spectroscopy of Solvent-Cast Thin Films of Polyamides

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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) using new techniques of drop-solvent casting. 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. Results were confirmed by MAIR spectroscopy on solvent cast thin films of each polymer. Elimination of the hydrogen-bonding ability at nylon surfaces might accompany polymer fractionation in different solvents, slight configuration changes, or a combination of both.

Very thin films of natural macromolecules are increasingly recognized as contributing significantly to various forms of biological adhesion, ranging from the adhesion of blood platelets to synthetic materials (resulting in thrombus formation) and the adhesion of dental and surgical adhesives to biological substrates, to the tenacious underwater adhesion of marine organisms (*e.g.*, barnacles) to ships and docks. In most instances, proteinaceous components dominate these films. Since adhesion is highly dependent upon the surface properties of the actual outermost layer exposed, and particularly the wettability of this layer, our investigation seeks to broaden the applicability of already successful contact angle techniques (for determining polymer wetting behavior) to very thin films of macromolecules. Hoping to avoid, initially, the ambiguity of working with complex natural materials which contain numerous monomers in unknown sequences, and which can often not be easily cleaned of surface-active contaminants because of their water solubility, we chose to establish base-line wetting behavior on a series of water-insoluble nylons. These polymers have the virtue of sharing the common feature of a polyamide backbone, with one another, with the polypeptides, and with all proteins. As will be evident in the following, these polymers can be readily cast from solvents and, so, should in many ways mimic those natural films which deposit from solution. As a first investigation of the applicability of these methods, this report necessarily focuses on techniques of surface preparation, their validity, and the interpretation of the contact angles.

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 polyamide films. Since the polypeptides, and some of the nylons, cannot be melted without being charred, a technique 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.

Four water-insoluble polyamides have been investigated, including nylon 11, nylon 6, and nylon 66, and polyglycine (also known as nylon 2). 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 with either dichloroacetic acid (DCA) or formic acid. 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 to the parameters used to characterize the wettability of the polyamides.

Experimental Section

Materials and Methods. Nylon 11 and nylon 6 samples in pellitized form were used which had been made available for earlier investigations[2] by W. R. Turner as samples 81649 and 81650 from the polymer collection of the Research and Development Department, Atlantic Refining Co. Our nylon 11 sample was originally made by the Societé Organico,

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(2) (a) A. H. Ellison and W. A. Zisman, *J. Phys. Chem.*, **58**, 503 (1954); (b) R. C. Bowers, W. C. Clinton, and W. A. Zisman, *Lubric. Eng.*, **9**, 204 (1953).

TABLE I

CONTACT ANGLES ON POLYAMIDE FILMS SPREAD FROM SOLUTION IN VARIOUS SOLVENTS ON PLATINUM PLATES

Wetting liquid	Surface tension at 20°, γ_{LV}	Average contact angle,[a] θ, deg				
		Nylon 11[b]	Nylon 6[b]	Nylon 11[c]	Nylon 6[c]	Polyglycine (nylon 2)[b]
Water	72.8	61	63	61	69	49
Glycerol	63.4	65	60	70	72	38
Formamide	58.2	48	50	47	61	30
Thiodiglycol	54.0	35	36	34	58	23
Methylene iodide	50.8	42	42	32	50	30
Ethylene glycol	47.7	41	35	31	46	25
1-Bromonaphthalene	44.6	21	23	14	35	10
Hexadecane	27.7	0	0	0	0	0

[a] Reported values are averages of at least ten readings on at least two independently prepared films of each type. [b] Cast from DCA. [c] Cast from formic acid.

France, and was procured as BCI nylon 1107 from Belding Corticelli Industries, New York, N. Y. 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 24,000, number-average molecular weight 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 Co., Plastics Division; its characterization by gel permeation chromatography yielded the following results: weight-average molecular weight 42,000, number-average molecular weight 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.[2]

Polyglycine was obtained in granular form from Mann Research Laboratories, Inc., New York, N. Y., 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.

After initial experiments had shown that no differences in film properties were observed with redistilled DCA and formic acid, reagent-grade materials were selected for use throughout this investigation. As will be shown in subsequent sections, no systematic effect of the use of either of these 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.

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° and a variety of structural types. Their sources, purification, and surface tensions have previously been reported.[3,4] For convenience, these and their liquid/vapor surface tensions are listed in Table I.

Procedures. Thin films of each polymer were formed on polished platinum plates or sheets by the technique illustrated in Figure 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, 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. 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° in a grease-free, covered, glass container.

The slowly advancing contact angles on the specimen surface 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 10–20 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 much longer 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° 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

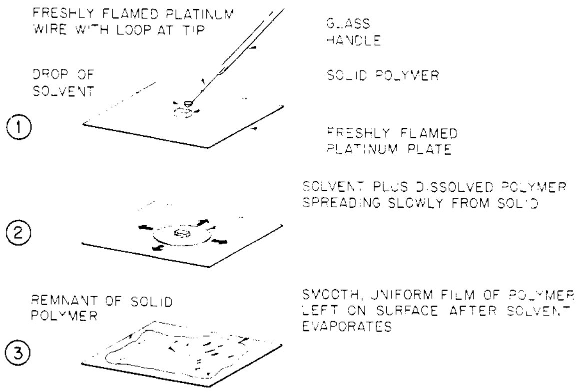

Figure 1. Technique for film formation.

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

(4) H. W. Fox and W. A. Zisman, *ibid.*, 7, 428 (1952).

(5) E. G. Shafrin and W. A. Zisman, *ibid.*, 7, 166 (1952).

(6) NRL contact angle goniometer, commercially available from Ramé-Hart, Mountain Lakes, N. J.

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 1 μ 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.

Validation of Methods. 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, but would affect the contact angles reported, additional checks for surface cleanliness were made. 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 degergent 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. The application of a detergent solution of Tide to a polyamide specimen surface using a clean soft brush followed by thorough water rinsing completely removed signs of any organic contamination. Germanium plates always were returned to their initially clean condition after such treatment.

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[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.[2a] 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° 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. Once each of these modified nylon surfaces had been cleaned with Tide and rinsed with water before measurements were made, no detectable contamination remained in any instance. It should be noted that the original NRL contact angle investigation of nylon 66[2a] and a companion publication of the frictional properties of this polymer[2b] had also established earlier that no detergent residues remained on nylon surfaces after rinsing.

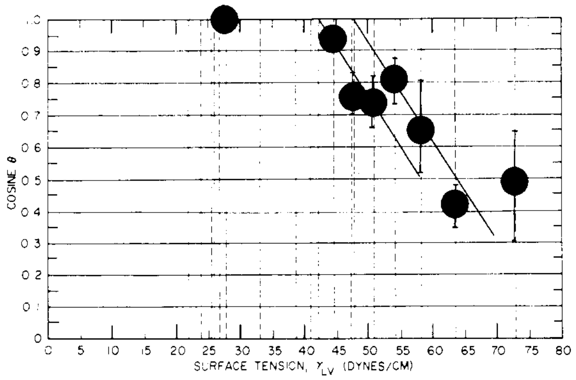

Figure 2. Nylon 11 film spread on platinum from DCA solution.

All of the liquids used in making the contact angle measurements were of high purity and behaved reliably, and all organic films examined by the contact angle method were investigated at least in duplicate using independently prepared samples. The measured contact angles on each plastic surface were routinely reproducible within 3°. 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 dyn/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.[2a] 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.[2a]

Results with Contact Angles. 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 I. A plot of $\cos\theta$ *vs.* the liquid surface tension γ_{LV} is given in Figure 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 II.

The results for nylon 6 films cast from DCA are listed in column 4 of Table I and row 3 of Table II, and the data plot is given in Figure 3. These nylon 6 films were smooth and

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(7) G. I. Loeb, *J. Colloid Interfac. Sci.*, **26**, 236 (1968).

(8) G. I. Loeb and R. E. Baier, *ibid.*, **27**, 38 (1968).

(9) N. J. Harrick, "Internal Reflection Spectroscopy," Interscience Publishers, New York, N. Y., 1967.

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

TABLE II

CRITICAL SURFACE TENSIONS FOR POLYAMIDE FILMS (DETERMINED GRAPHICALLY FROM PLOTS OF θ *vs.* γ_{LV})

Polymer	Solvent	Critical surface tension intercept: Hydrogen-bonding liquids	Critical surface tension intercept: Non-hydrogen-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

transparent and adhered well to the platinum backing plates.

Contact Angles on Nylon Films Cast from Formic Acid. Column 5 of Table I 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 Figure 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 II. It is possible that these milky white films are partially crystallized, and hence an X-ray diffraction comparison of the nylon films cast from formic acid with those from DCA might be helpful.

Column 6 of Table I and Figure 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 dyn/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° as the equilibrium value), the slowness of the spreading could reflect the trapping of some oleophobic contaminant of unknown 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 II) 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 not be caused by surface roughness but 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 Polyglycine 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 I and row 5 of Table II and plotted in Figure 6.

MAIR Spectra of Nylons and Polyglycine. Nylon 11, nylon 6, and polyglycine form a 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 7, 8, and 9 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

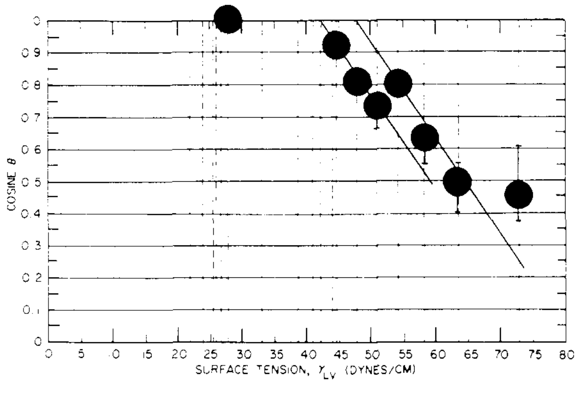

Figure 3. Nylon 6 films spread on platinum from DCA solution (average of three runs).

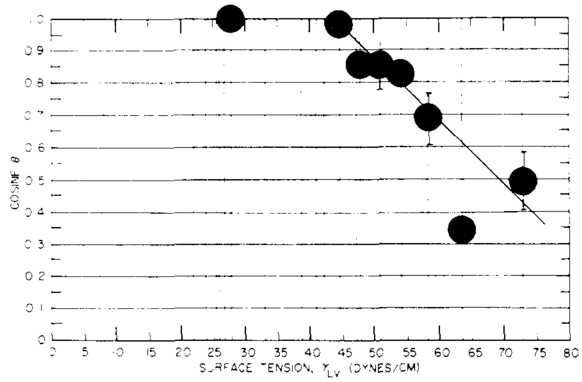

Figure 4. Nylon 11 film spread on platinum from formic acid solution.

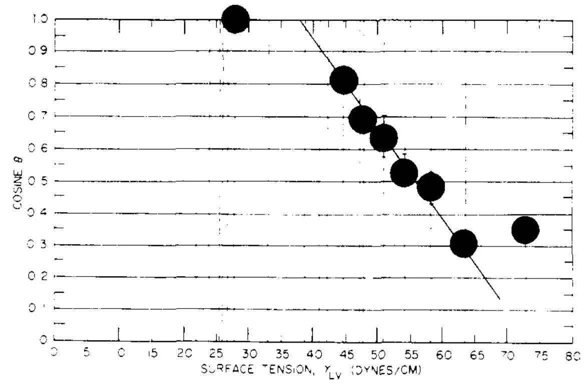

Figure 5. Nylon 6 film spread on platinum from formic acid solution.

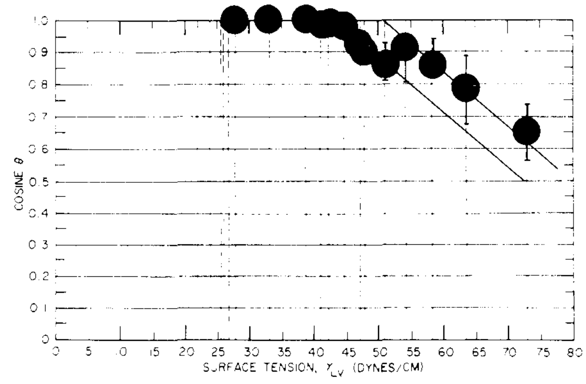

Figure 6. Polyglycine (nylon 2) films spread on platinum from DCA solution (average of four runs).

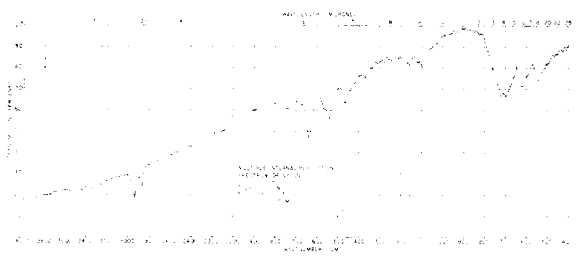

Figure 7. Multiple internal reflection spectrum of nylon 11.

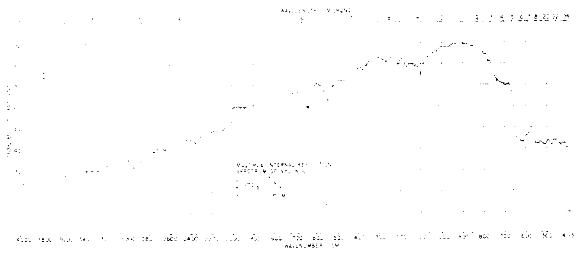

Figure 8. Multiple internal reflection spectrum of nylon 6.

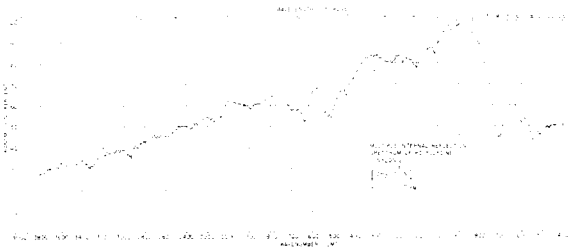

Figure 9. Multiple internal reflection spectrum of polyglycine.

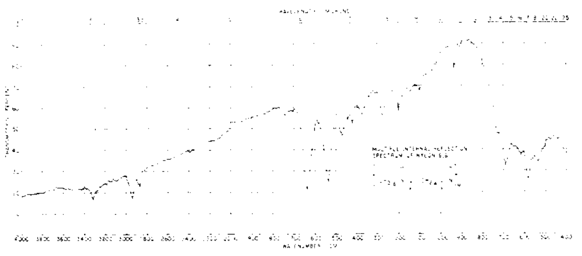

Figure 10. Multiple internal reflection spectrum of nylon 66.

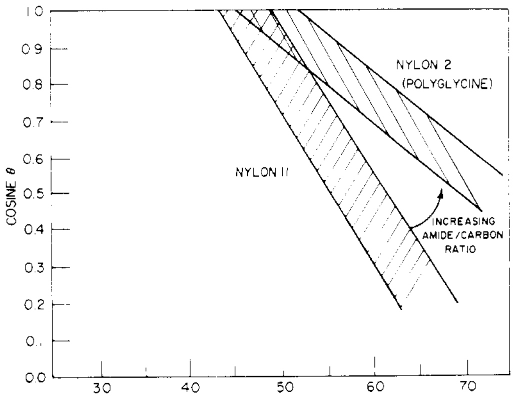

Figure 11. The wettability band for polyamides of the nylon series shift in the direction shown as the number of methylene carbons between successive amide links is reduced.

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 contract of the specimen surface with the surface of the internal reflection prisms. 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, Figure 10 shows the MAIR infrared spectrum of the surface of the nylon 66 disks used in this investigation.

The spectra recorded in Figures 7–10 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.

Discussion

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 θ *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. It should be noted here that the data points in Figures 2–6 represent the total range of contact angles on independently prepared specimens and that where the error range is the greatest, this range reflects variations among many replicates and not on a single surface. The two features reported 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 II and shown as the intercepts at cos $\theta = 1$ on Figures 2–11, 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[2a] 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 never before been observed with any class of polymers not having hydrogen-bonding sites, and is in strong contrast with the earlier work of Fort;[11] however, Ellison and Zisman did observe

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(11) T. Fort, Jr., *Advan. Chem. Ser.*, **No. 43**, 302 (1964).

another type of split[2a] 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 very near the polymer/air interface. Figures 7, 8, 9, and 10 show the MAIR spectra for the polyamides nylon 11, nylon 6, nylon 2, and nylon 66, respectively, and they are examples of the quality of the spectra obtainable from the surface zone of extremely thin films. Attention should be directed to the absorption bands in the regions of 3300 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 Figures 7 and 8, 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 Figure 9, the N–H and C–H characteristic frequencies are equally prominent, reflecting the nearly equal amide-to-methylene ratio in nylon 2. Figure 10 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;[11] 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 θ *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; another explanation might lie in the differing preparative techniques. In any case, the critical surface tension range of 42–46 dyn/cm obtained here for nylon 11, which contains 10% amide groups, is not unreasonable when it is recalled that values as high as 33 dyn/cm have been obtained with polyethylene, which contains no amide groups at all.

Figure 11 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 θ *vs.* γ_{LV} plots for nylon 11 and polyglycine are superposed. The critical surface tension range covered is from about 40 to 50 dyn/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 Figure 11, one boundary of each "wettability band" is formed by the data points for the hydrogen-bonding liquids and the other by the data 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 Figure 11 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 Figure 11 is the marked 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.

Surface spectroscopy does not appear as sensitive to changes in the surface orientation as contact angle measurements. Figures 2–6 and columns 3–7 of Table I 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 and 1530 cm^{-1}, respectively, are characteristic of materials in which all possible hydrogen bonds are made intermolecularly between predominantly extended chains.[12] 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.[13] Contact angle results may help to distinguish between these structures.

Summary and Conclusions

A drop-solvent-casting method which required the use of minute amounts of sample and solvent was devised to form very thin polyamide films on platinum sheets. Such films were suitable, as prepared, for both contact angle and MAIR ir spectroscopic measurements. MAIR spectroscopy, sensitive to monolayer levels of contamination, also was used to validate the preparative and cleaning procedures. When cast from dichloroacetic acid, nylon 11, nylon 6, and polyglycine all exhibited wetting behavior similar to that reported earlier by Ellison and Zisman and verified here. This wetting behavior is different from that regularly found with nonamide polymers in that (a) contact angle values plot as two separate and nearly parallel straight lines in graphs of cos θ *vs.* γ_{LV}, one line characterizing hydrogen-bonding liquids and the other nonhydrogen-bonding liquids, and (b) these lines intercept the $\cos \theta = 1$ axis to give higher critical surface tension intercepts which range from 40 to 50 dyn/cm. It is proposed that these wetting features may be exploited as diagnostic indicators of the presence of accessible hydrogen-bonding sites at a polymer surface. A systematic variation in the slopes of the contact angle graphs appears to be additionally useful as an indicator of the relative proportion of these surface sites. Formic acid-cast films of nylon 11 and nylon 6 do not show the dual wettability feature, presumably because of polymer fractionation, configuration, or crystallinity changes which remain to be identified. MAIR spectroscopy is not as sensitive to differences in casting solvent as contact angle measurements. These data encourage similar investigations of more complex polypeptides[14] and eventually of complex biological macromolecules themselves.

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Notes

Diffusion of Radioactively Tagged Small Molecules through Biaxially Stretched Rubbers

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The question of whether local molecular mobility in rubbery polymers is affected by large deformations is important in interpreting viscoelastic properties of such materials subjected to large strains.[1,2] For example, natural rubber and butyl rubber were studied by Mason[1] with superposition of small oscillating deformations in extension on large static tensile strains; and a styrene–butadiene rubber was studied by Smith and Dickie[2] with stress–strain measurements at different strain rates in uniaxial extension up to high elongations. From both investigations, it was deduced that the monomeric friction coefficient depends very little on the uniaxial extension ratio up to moderate-to-high values (2, 6, and 6, respectively, for natural, butyl, and styrene–butadiene rubber). Of course, the behavior can be expected to depend on the degree of cross-linking and other factors.

Another gauge of local mobility can be obtained from the diffusion of a radioactively tagged small molecule (*i.e.*, molecular weight of the order of 200) in trace amounts through the polymer.[3-5] The translational friction coefficient of the penetrant, obtained from the diffusion coefficient, can be closely correlated with the monomeric friction coefficient of the polymer itself in many cases. In the present note, the effect of large static strain on the diffusion coefficient on *n*-hexadecane (HXD) and 1,1-diphenylethane (DPE) in several rubbery polymers is reported.

The penetrants, tagged with ^{14}C, have been described in previous publications.[4,5] The rubber samples—natural rubber (NR), styrene–butadiene rubber (SBR), and *cis*-polybutadiene (PB-*cis*)—were cross-linked by dicumyl peroxide; they are identified by code numbers which correspond to previous reports,[5,6] except for PB-*cis* 116-150, which has a somewhat higher degree of cross-linking[7] than the polybutadiene PB-*cis* 116-30 investigated earlier.

Biaxial stretching was performed by clamping a disk-shaped sample in the jig shown in Figure 1, without the cell base. An expandable rubber plug was temporarily placed in the middle of the plunger assembly

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