mophores are traps produces a lower limit to the trapping rate constant. Hopefully an independent method for evaluating the concentration of trap sites can be developed to yield quantitative values for these important rate constants.

Conclusions

When time resolution in the submicrosecond regime is used, it has been possible to determine some important rate constants related to the triplet-state processes of PVCA in fluid solutions. These include the rate of triplet–triplet annihilation and the rate of trapping of triplet excitons by the excimer-forming sites. The lifetime for first-order relaxation of triplets is 300 μs and the trapping of triplet excitons, which apparently controls the shape and the position of the maximum in the def–time profile, takes place on the time scale of several hundred nanoseconds. Solid films of PVCA at 10 K also produce a buildup in the intensity of delayed excimer fluorescence as a function of time in the nanosecond time regime. It is proposed that this buildup in def results from a corresponding buildup in the concentration of trapped triplet excitons. Also, from the knowledge of the position of the maximum in the intensity of def as a function of time it has been possible to evaluate the trapping rate constant of the triplet excitons by excimer-forming sites.

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Registry No. PVCA, 25067-59-8.

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Monomeric Surfactants for Surface Modification of Polymers

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ABSTRACT: The surfaces of poly(methyl methacrylate) and a UV-curable acrylic lacquer have been modified by the addition of small amounts of polymerizable, monomeric surfactants and a surface-active polymer. In the system used, the surfactants concentrate at interfaces toward less polar phases. Addition of 1% w/w of a monomeric surfactant to an acrylic lacquer gives a surface concentration of 50% at the interface toward air. The rate of surface enrichment is primarily dependent on the size of the surfactant molecules and on the viscosity of the bulk material to which it is added. Comparison shows that the surfactant-modified surface layers are thicker than monolayers made by the Langmuir–Blodgett technique. The behavior of monomeric surfactants in the outmost surface layer of a modified film is, however, similar to that of a monolayer formed in a Langmuir–Blodgett balance. Contact angle hysteresis measurements show that the surface-active monomers concentrating in the surface of a modified lacquer film become more and more closely packed when the total surfactant concentration is increased.

Introduction

Many properties of a material are dependent primarily on the surface structure and on the chemical composition of the outmost surface layer. Wetting and coating characteristics, frictional behavior, and physiological compatibility are examples of such properties. In several applications is difficult to find a material with both appropriate bulk properties and required surface properties. It is therefore often desirable to combine the surface properties of one material with the bulk properties of another. With polymers, this can be done through surface modification, i.e. by altering the chemical structure of a thin surface layer without affecting the bulk properties of the material. Several methods for modification of polymer surfaces have been developed,[1] including chemical methods,[2] plasma treatment,[3] and grafting reactions involving UV irradiation.[4] The latter technique is made even more effective if the bulk samples is doped with a small amount of a photoinitiator which, on

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exposure to irradiation, creates a catalytic surface.[5] In this paper we describe an alternative method for surface modification, using surface-active materials, surfactants.

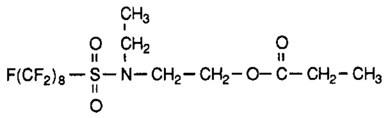
Surface-active molecules, being amphiphilic, are soluble in both polar and nonpolar media. The solubility in a particular medium depends on the balance between the hydrophilic and hydrophobic groups.[6] Because of their dual nature, surface-active molecules tend to concentrate at interfaces between media of different polarities. There the molecules orientate themselves in an energetically favorable way, with the hydrophilic parts located toward the polar phase and the hydrophobic parts toward the nonpolar phase.[7] The phenomenon of surfactants concentrating at interfaces is primarily a result of diffusion, caused by thermal motion. Having reached the surface, the surfactant molecules are energetically favored by their orientation at the interface and have a low tendency to diffuse back into the bulk of the material.

The use of surfactants is an integral surface modification method. It has long been known that certain surface active agents incorporated during polymer fabrication concentrate at the surface and alter the surface structure and properties of the polymer material.[8] Other, often costly and complicated, surface treatments steps after fabrication then become unnecessary. Even at low concentrations, addition of surfactants to a polymer gives rise to a considerable change in surface composition. The low amount needed makes it possible effectively to remodel the surface structure without affecting the bulk properties.

Various surface active agents have been studied with respect to their usefulness in surface modification of polymers. Most common are surface-active block copolymers[9] or well-defined graft copolymers[10] that can be synthesized by using macromers.[11-13] Irreversibly modified polymer surfaces have been achieved with a surface-active photoinitiator[14] and by using surface-active macromers as polymer-supported membranes.[15] Polymer surfactants have the advantage that they cannot be removed from the surface by rinsing or evaporation, as is the case with low molecular weight surfactants.[8] However, Gaines[16] has shown that if the molecular weight is doubled, the diffusion constant is reduced by a factor of about 6. The surface concentration of polymer surfactant therefore takes a long time to reach its maximum, due to slow diffusion through the bulk of the material.

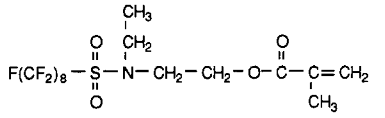
In the work reported here, polymerizable, monomeric surfactants with relatively low molecular weight were synthesized and used without prepolymerization for surface modification in polymer films. Modified surface layer is thus rapidly formed due to fast diffusion through the bulk of the films. Once at the surface the monomeric surfactants can be made to react and become chemically bonded to the surface. The new surface layers formed this way were found to be stable.

The effect of monomeric surfactants as surface modifiers in polymers is compared with the effects of a low molecular weight, nonreactive surfactant and of a surface-active polymer. The modified polymer films are compared with monolayers of the monomeric surfactants. The monolayers were prepared by using the Langmuir–Blodgett technique. This LB technique has been known for a long time and is now experiencing a renaissance as a method for preparing ultra thin films for various applications.[17] Variations in surface structure due to differences in molecular structure of the monomeric surfactants are also studied.



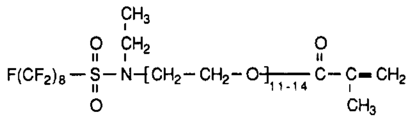
I

$F(CF_2)_8-SO_2-N(CH_2CH_3)-CH_2-CH_2-O-C(=O)-CH_2-CH_3$



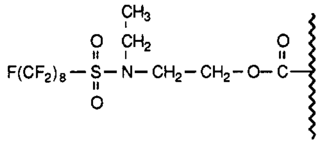
II

$F(CF_2)_8-SO_2-N(CH_2CH_3)-CH_2-CH_2-O-C(=O)-C(CH_3)=CH_2$



III

$F(CF_2)_8-SO_2-N(CH_2CH_3)-[CH_2-CH_2-O]_{11-14}-C(=O)-C(CH_3)=CH_2$



IV

$F(CF_2)_8-SO_2-N(CH_2CH_3)-CH_2-CH_2-O-C(=O)-$

Figure 1. Chemical structures of the surfactants studied. The surface-active polymer IV is a graft copolymer with an acrylic main chain.

Experimental Section

Materials and Apparatus. Three low molecular weight surfactants (I–III, Figure 1) and one surface-active polymer (IV, Figure 1) have been studied. The low molecular weight surfactants were synthesized from fluorinated alcohols that were kindly supplied by 3M. The compound used for the synthesis of I and II was used as received. The compound used to synthesize III was dissolved in THF, and the solution was passed through a column packed with 4-Å molecular sieves. The surface-active polymer was a graft copolymer with an acrylic main chain (M_n = 2600, M_w/M_n = 8.7). It was also supplied by 3M and was used as received.

Methacrylic acid chloride, pyridine, and all solvents were distilled before use. Propionic acid chloride and 4-(dimethylamino)pyridine was used as received. $Na_2SO_4 \cdot 10H_2O$ was prepared by recrystallization of sodium sulfate from water. Celite was used as received. Silica gel 60 (230–400 mesh ASTM) was used as column material for liquid chromatography.

ESCA spectra were recorded on a Leybold Heraeus ESCA/Auger spectrometer LH 2000, with an Al Kα X-ray radiation source. The IR analyses were performed with a Perkin-Elmer 1710 infrared Fourier transform spectrometer. Contact angle hysteresis was measured with a Ramé-Hart Inc. A-100 goniometer. The measurements were made in air at about 40% relative humidity. A simplified method for measuring contact angles was used when only advancing contact angles were measured: A 10-μL drop of an aqueous solution containing 25% ethanol by volume was placed on the film surface and assumed to be a truncated sphere. From measurements of the diameter of the droplet, it is possible to calculate the contact angle.[18] This method was found to give results that compared well with the measurements made with the goniometer. Films were spin-coated on glass or single-crystal silicon wafers at 3000 rpm for 40–60 s by using a spin-coater from Headway Research Inc.

Poly(methyl methacrylate) (PMMA) (M_n = 133 000, M_w/M_n = 2.3) was dissolved in cyclohexanone to 10% w/w concentration. The acrylic lacquer used was a 40/60 mixture of hexanediol diacrylate and an epoxy acrylate oligomer with 3% w/w Irgacure 184 (Ciba-Geigy), 2% w/w methyldiethanolamine, and 0.5% w/w isopropylthioxanthone (Ward Blenkinsop). The viscosity of the lacquer was approximately 200 cps at 23 °C. The lamp used for irradiation was an OSRAM Ultra-Vitalux 300W sunlamp that emits light in the near-UV ($\lambda > 300$ nm).

Molecular weight measurements were made on a Waters Associates GPC system with μ-Styragel columns and chloroform as a solvent. In the case of the surface active polymer IV calibration was made with PS standards.

Synthesis Procedure. Three low molecular weight surfactants were synthesized (Figure 1), one nonreactive (I) and two monomeric (II and III), by the reaction of fluorinated alcohols with an acid chloride in the presence of pyridine. Propionic acid chloride was used to synthesize the nonreactive surfactant (I), while methacrylic acid chloride was used in the other syntheses. The general procedure was to dissolve the alcohols in THF and add a 10 times excess of pyridine. A catalytic amount of 4-(dimethylamino)pyridine was also added to the mixture in the synthesis of the monomeric surfactants. The mixture was cooled in an ice bath, and the acid chloride was then slowly added to the reaction solution under stirring. Acid chloride was added in an 2.5 times excess of the alcohol.

The reaction solution was stirred for 24 h. In the synthesis of the monomeric surfactants (II and III) a 1:4 by weight mixture of $Na_2SO_4 \cdot 10H_2O$ and Celite was added, so that the amount of crystal water corresponded to the excess of acid chloride and the reaction solution was stirred for another 24 h. The reaction solution was filtered and extracted three times with water to which NaCl was added to prevent the formation of a stable emulsion.

The nonreactive surfactant (I) was pure after evaporating the solvent and drying, but the two monomeric surfactants (II and III) had to be purified by liquid chromatography on a column packed with silica gel.

IR spectra show a singlet carbonyl peak at 1746 cm^{-1} for the nonreactive surfactant (I) and singlet carbonyl and vinyl peaks respectively at 1722 and 1640 cm^{-1} (II) and 1719 and 1637 cm^{-1} (III) for the two monomeric surfactants.

Film Formation. Films of poly(methyl methacrylate) (PMMA) containing various concentrations of surfactants were spin-coated on glass or single-crystal silicon wafers from 10% cyclohexanone solutions. The films were dried at 100 °C for 15 min. The surfactants were also added to a UV-curable acrylic lacquer. Films were spin-coated and placed in a nitrogen atmosphere for 1 min, after which they were cured by exposure to UV light in a nitrogen atmosphere for another 4 min. Films of PMMA containing monomeric surfactant II and the surface-active polymer were also cast on glass. All films were rinsed with water and allowed to dry before analysis.

Langmuir–Blodgett monolayers of the monomeric surfactants were prepared on water by spreading a 1 mg/mL solution of surfactant in chloroform on the water surface, after which the surface area was continuously decreased. This was done in the presence of a silicon wafer spin coated with acrylic lacquer, which had been lowered into the water in advance. The wafer was then slowly raised so that a monolayer was deposited on the solid lacquer surface. The surface pressure was held constant at 30 mN/m during the deposition. This was done at KSV Chemicals, Finland, with a KSV 2200 LB equipment.

Environmental Influence

Surface-active molecules concentrate at interfaces between media when this is energetically more favorable than solution in either media. The criteron for surface activity is that either the hydrophobic or the hydrophilic part of the amphiphilic molecule is compatible with the host medium. If this is not the case, phase separation will occur. In addition to the nature of the surfactant, the environment also plays an important role in the final surface behavior of a modified polymer. Azrak[19] has shown that the nature of the molding substrate has a significant effect on the surface properties of block copolymers, and Allmér and co-workers[20] recently showed that the structure of the outmost surface layers of polymer films modified through grafting reactions is intimately related to the nature of the environment.

PMMA and the acrylic lacquer used are both more polar than the hydrophobic parts of the surfactants in this study. In these media the surfactant molecules concentrate at interfaces toward less polar phases, with the hydrophobic part orientated toward the neighboring medium. At interfaces toward more polar phases, one might expect that the surfactants would concentrate with the hydrophilic part orientated toward the surrounding, more polar, phase. However, no such enrichment takes place. A lacquer film containing 1% w/w of the monomeric surfactant II was prepared on a glass wafer. The surfaces toward both air and glass were analyzed with ESCA (Figure 2). The large F_{1s} peak indicates an enrichment of surfactant at the coating-air interface. The content of surfactant molecules in the air-side surface is approximately 50% w/w or 56 times larger than in the bulk of the lacquer film, but there is no sign of surfactant at the film surface toward the glass or at the glass surface. The hydrophobic part of the surfactant is energetically even less favored in the vicinity of the glass surface than in the bulk of the lacquer. Further, the hydrophilic part, being compatible with the lacquer film, has nothing to gain by concentrating at the coating-glass interface. As a consequence, the surfactant concentration near the glass surface is decreased rather than increased (Figure 3). This environmental influence on the surface activity of amphiphilic agents can be utilized to modify polymer surfaces selectively.

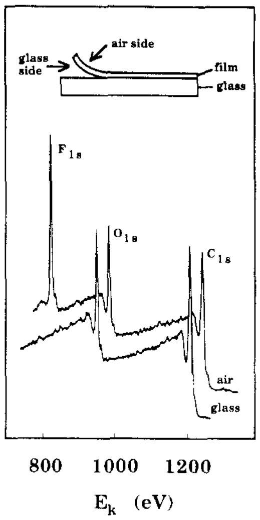


Figure 2. ESCA spectra taken at the surfaces toward air and glass of an acrylic lacquer film containing 1% w/w monomeric surfactant II.

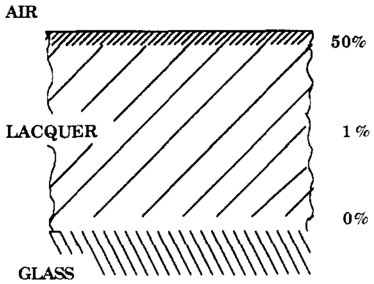


Figure 3. An example of selective modification. A schematic view of the cross section of an acrylic lacquer film with a total content of 1% w/w monomeric surfactant II. Local concentrations in various parts of the film are derived from ESCA measurements.

The Nature of the Surfactant

The rate of surfactant adsorption at an interface depends on the nature of both the bulk material and the surfactant. Large and bulky surfactants take longer to migrate through the bulk into the surface than do small surfactants. Further, a specific surfactant migrates faster through a low viscosity bulk material than through a polymer matrix.

The nonreactive surfactant I, the monomeric surfactant II, and the surface active polymer IV have identical hydrophobic groups and similar structures, but they behave

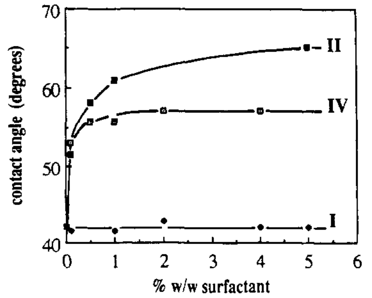


Figure 4. Advancing contact angles of 25% v/v ethanol in water on modified PMMA versus surfactant concentration for nonreactive surfactant I, surface-active polymer IV, and monomeric surfactant II.

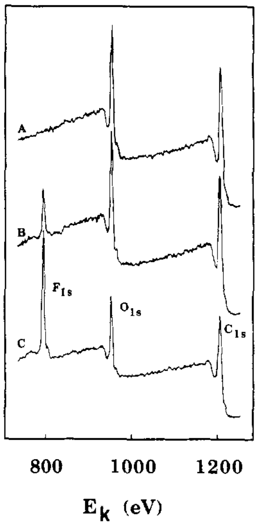


Figure 5. ESCA spectra of (a) PMMA containing 1% w/w nonreactive surfactant I, (b) PMMA containing 1% w/w monomeric surfactant II, and (c) acrylic lacquer containing 1% w/w monomeric surfactant.

quite differently when added to polymer systems as a result of basic differences in their sizes and reactivities (Figure 4). The low molecular weight, nonreactive surfactant is easily removed from a polymer surface by rinsing with water, leaving the original surface properties unchanged. Although it has approximately the same size as the nonreactive surfactant, the surface-active monomer leads to a change in the surface properties of PMMA. The effect is even more evident in a lacquer film (Figure 5). The surface-active polymer also brings a permanent change in the surface properties of PMMA. It stays in the surface due to chain entanglements and cannot be removed by rinsing with water. The surface effect of the polymer surfactant in PMMA is not, however, as great as the effect of the reactive monomeric surfactant. The reason for the differences between monomeric and polymer surfactant is primarily that the smaller monomer diffuses faster through the bulk material. This is specially the case in the rather low viscosity uncured lacquer.

Theoretically, given sufficient time to migrate through the bulk and up to the surface, the surface-active polymer should have the same effect as the monomeric surfactant. In order to confirm this, lacquer films containing 1% w/w of the polymer surfactant were prepared and stored for various periods of time, up to 72 h, at room temperature before being cured. No further changes were noticed; the diffusion rate of the relatively large and bulky surface-active polymer is apparently too slow. When a number of films were stored at different temperatures for 1 min before curing, however, it was evident that the rate of diffusion increased with temperature (Figure 6). The amount of surface-active polymer concentrating at the surface of a modified lacquer film is nearly doubled in this time at 100 °C. This effect can be explained partly by a decrease in viscosity of the lacquer and partly by an increase in mobility of the surfactant. The combined effect results in a diffusion rate of the polymer surfactant comparable with that of the surface-active monomer II (Figure 7). The same improved effect of the polymer surfactant was observed when films of PMMA were cast at room temperature, allowing the solvent to evaporate at low rate and thereby slowly increasing the viscosity of the film.

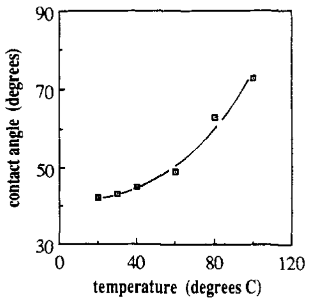


Figure 6. Contact angles of 25% v/v ethanol in water on lacquer films modified with 1% w/w surface-active polymer IV as a function of temperature at which the films were stored for 1 min before curing.

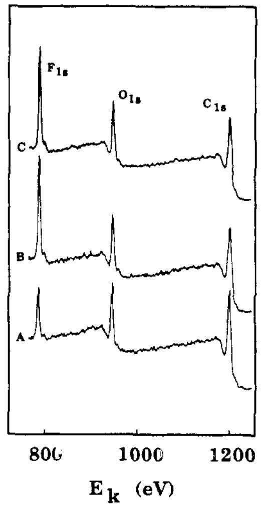


Figure 7. (A and B) ESCA spectra of acrylic lacquer containing 1% w/w surface-active polymer IV. The film was stored at (A) 20 °C and (B) 100 °C, for 1 min before curing. (C) ESCA spectrum of an acrylic lacquer film with 1% w/w monomeric surfactant II.

No changes in surface structure were observed as a result of the different ways of preparing PMMA and lacquer films modified with monomeric surfactant, although the effect of the surface-active monomer is larger in the lacquer films. In PMMA, the monomer partly reacts and leads to a permanent change in the surface, probably due to thermally induced polymerization. In the lacquer system the surface-active monomer reacts with the lacquer monomers during the curing process and becomes part of the cross-linked lacquer network. A maximum and irreversible effect is reached within seconds.

Surface Structure

Contact angle measurements show that addition of less than 1% w/w surface-active monomer is sufficient to dramatically change the surface properties of a polymer film

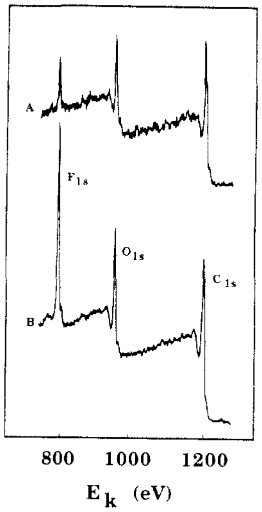


Figure 8. ESCA spectra of (A) a monolayer of monomeric surfactant II deposited on an acrylic lacquer and (B) a lacquer film containing 1% w/w monomeric surfactant II.

(Figure 4). With ESCA it is possible to measure the average surface composition of a film to approximately 50-Å depth. Calculations from the ESCA spectra show that a lacquer film containing 1% w/w monomeric surfactant II has an average surface concentration of surfactant of approximately 50% w/w. The overall bulk concentration of surfactant is still approximately 1% w/w, since the modified surface region is a very thin layer compared to the thickness of the whole film. At this low concentration however, the effects on the bulk properties are negligible in most cases.

Monomolecular layers of monomeric surfactant II deposited on lacquer films by the Langmuir–Blodgett technique were also studied with ESCA (Figure 8). The average surface concentration of surfactant in such a film was calculated from ESCA spectra to be 20% w/w, which means that the ESCA spectrum refers to a deeper layer than the LB monolayer. This indicates that the surface-active molecules concentrated at the surface of the modified lacquer film are not located in a single molecular layer. There is probably a gradient in surfactant concentration increasing considerably toward the outmost surface layers, although neither the advancing contact angles nor the ESCA measurements made permit any conclusion to be drawn concerning the composition and homogeneity of the very top surface layer.

At higher surfactant concentrations the effects on the bulk properties can no longer be neglected. Nevertheless, concentrations up to 5% were also used in order to study the effect on the very top surface layers as the surfactant concentration is increased. The chemical and physiological properties of a solid material surface are dependent primarily on the structure of a few outmost molecular surface layers. Advancing contact angles of water on lacquer films modified with the two monomeric surfactants II and III slightly increase when the amount of added surfactant is further increased above 1%, being comparable with the contact angle on Teflon at higher concentrations.[21] The surface of a film containing 5% w/w monomeric surfactant is more hydrophobic than a film with 1%. Evidently, no micelles are formed in the range of concentrations studied. Light-scattering measurements on monomeric surfactant II in solution support this conclusion.

An effective surface modification method should result not only in a stable modification but also in a homogeneous top surface layer. A powerful method of studying the characteristics of the outmost surface layers is that of contact angle hysteresis, i.e. the difference between advancing and receding contact angles.[22] Most surfaces, particularly those with both hydrophobic and hydrophilic groups present, show contact angle hysteresis. There are three main reasons:[23] the first being the possibility that droplet molecules can penetrate and swell the surface region of the material (this is particularly the case if water is used); second, surface heterogeneity caused by regions of different surface structures; and third, reorientation of the surface structure under the droplet. It is often difficult to separate the three effects. The contribution of reorientation can, however, be neglected in the case of UV-cured lacquer films containing monomeric surfactant, since these systems are presumably highly cross-linked, and the measurements were made within a short period of time.

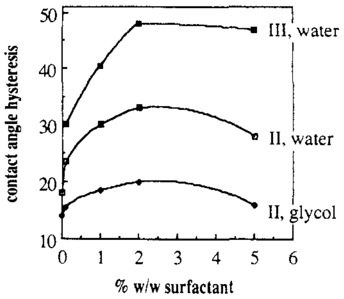


Figure 9. Contact angle hysteresis, as a function of surfactant concentration, of glycol and water on lacquer films modified with monomeric surfactant II and of water on lacquer films modified with monomeric surfactant III.

When surface-active molecules are first introduced into the spin-coated and rather smooth, homogeneous lacquer films, the surface structure becomes less homogeneous and easier to penetrate (Figure 9). The contact angle hysteresis of ethylene glycol on lacquer films modified with monomeric surfactant II passes through a maximum at a total surfactant concentration of 2% w/w. An increase in the surfactant concentration gives a more closely packed top surface layer, and above 2% the surface becomes so dense that additional surface-active molecules result in a more homogeneous surface that is not as easily penetrated by the ethylene glycol droplet molecules. The contact angle hysteresis of water on lacquer films modified with monomeric surfactant II shows the same phenomenon but with a more pronounced maximum at 2% w/w surfactant and higher hysteresis values. This is an effect of penetration, since the smaller water molecules more easily penetrate the surface region of the modified lacquer films.

The contact angle hysteresis of water on lacquer films with monomeric surfactant III also shows a maximum at 2% w/w surfactant concentration (Figure 9), but the maximum is even higher and the hysteresis curve does not decline as much with further increasing surfactant concentration due to the larger hydrophilic group.

The changes introduced into the structure of the uppermost surface layer of a lacquer film by adding successively increasing amounts of monomeric surfactant can be compared with the behavior of surfactant molecules spread on a water surface in a Langmuir–Blodgett balance. At first, the surfactant molecules are separate and move about independently in the surface layer, but a decrease in the surface area finally results in the formation of an insoluble two-dimensional monolayer of surfactant molecules. If the surface area is further compressed, the surfactant molecules in the monolayer become

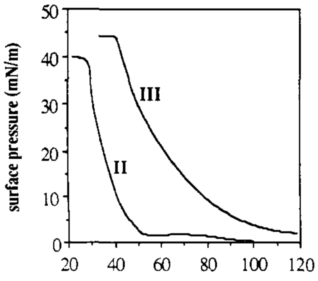


Figure 10. Compression isotherms of monomeric surfactants II and III on water.

more closely packed together and coherently orientated toward the surface. Finally, no additional compression is possible and the monolayer collapses.

Compression isotherms were recorded for monolayers of the two monomeric surfactants II and III (Figure 10). The monomeric surfactant II, being the smaller molecule with a shorter hydrophilic group, occupies less area per molecule at a specific surface pressure than the monomeric surfactant III, so that the LB monolayer of II can be compressed more before collapse. Monomeric surfactant III has a longer hydrophilic group that enables it to lay down and penetrate the water surface to a somewhat larger extent. This probably results in a less organized monolayer, so that the area occupied by each molecule is larger and a higher surface pressure is needed in order to force the monolayer of III to collapse.

Monolayers of the two monomeric surfactants II and III were prepared and deposited on films of the acrylic lacquer. The surfactants were deposited at a lower surface pressure, 30 mN/m, than that which gives maximum orientation and packing, and this resulted in a tilted and not fully coherently orientated monolayers on the solid lacquer surface. There is a small, but pronounced, difference with regard to the hysteresis of water between deposited monolayers of II and III, 33 and 36, respectively, which is well in agreement with the variations in area per molecule in the isotherms discussed above.

The two monomeric surfactants have the same hydrophobic groups, but differences in hydrophilic groups result in that the monolayer of III is less tightly packed and less orientated at the specific surface pressure of deposition. This difference is even more pronounced in the case of modified lacquer films (Figure 9). The phenomenon of surface activity is the result of an equilibrium process between the tendency for surfactant molecules to adsorb at interfaces and the tendency for complete mixing. The surfactant molecules concentrating at the outmost surface layers of a modified lacquer film are not perfectly vertically orientated in the surface. The hydrophilic part, being compatible with the lacquer, is likely to orientate in a variety of ways, the less likely being vertical orientation. Monomeric surfactant III is a larger molecule and is to a greater extent compatible with a polar host medium, and this probably increases the tendency for mixing and results in a lower degree of order and alignment of the surfactant molecules concentrating at the surface. As indicated by contact angle hysteresis, the tendency is more apparent in a viscous host medium like the acrylic lacquer system than on the water surface in an LB balance. Furthermore, the larger surfactant molecules, III, have a lower diffusion rate through the bulk of the lacquer films, and the equilibrium of surface activity is reached more slowly, which is also important for the final structure of the modified film surfaces.

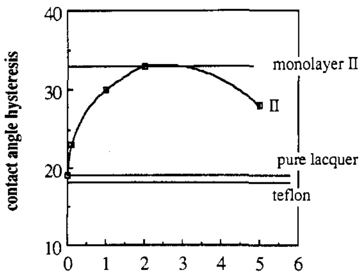


Figure 11. Contact angle hysteresis of water on lacquer films modified with monomeric surfactant II as a function of surfactant concentration. Also marked are contact angle hysteresis of water on a monolayer of monomeric surfactant II deposited on lacquer and on pure lacquer and Teflon.[21]

Ideally, as the amount of fluorinated surface-active monomer is continuously increased, the top surface layer of a modified lacquer film should change from being a pure, homogeneous lacquer surface to that of a homogeneous Teflon-like surface, the latter being reached through various stages of heterogeneity as the surfactant molecules become more and more tightly packed together. In reality, there is a tendency for this to happen (Figure 11). The contact angle hysteresis of water on lacquer films increases as monomeric surfactant II is introduced to the system, reaches a maximum, and then decreases with increasing surfactant concentration, approaching the value of water on Teflon. This was measured by Good and Koo[21] to be 18. The overall higher values of contact angle hysteresis compared with those on Teflon are explained by the presence of hydrophilic groups that enable water to penetrate these surfaces more easily, although the advancing contact angle of water on modified lacquer films becomes comparable with that of Teflon at higher surfactant concentrations.

Conclusions

Surface modification of polymers is effectively achieved by surface-active compounds. It is favorable to use a low molecular weight, monomeric surfactant. Such surfactants diffuse rapidly through the bulk material and can be made to react and become chemically bonded to the material at the surface. The surface activity of these monomers is intimately dependent upon the nature of the surrounding media, and this makes it possible selectively to design and modify polymer surfaces by varying the environmental conditions. When surface-active monomers are introduced to the lacquer system, the surface structure first becomes more heterogeneous and easier to penetrate, but as the surfactant concentration is increased, the amount of surface active molecules in the surface also increases until finally the surface once again becomes more homogeneous. Comparison with LB monolayers show that the modified surface layer of a lacquer film is thicker than one monolayer. There is probably a gradient in surfactant concentration increasing rapidly from the bulk toward the surface.

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Molecular Weight and Polydispersity Effects at Polymer–Polymer Interfaces

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ABSTRACT: We study the interfacial properties of immiscible polymers, going beyond the usual approximation of infinite molecular weight, complete immiscibility. For finite molecular weights, the interfaces are broader and the interfacial tensions smaller than predicted by this approximation. These corrections are entropic effects and are significant for typical experimental situations: they are in fact inversely proportional to the incompatibility $\chi_{AB}N$, where χ_{AB} is the Flory interaction parameter between unlike (A and B) monomers and N the number of monomers per chain. In polydisperse systems, small chains accumulate slightly at the interface, lowering the interfacial tension. Our analysis seems consistent with recent interfacial tension measurements.

I. Introduction

An understanding of the physics of polymer–polymer interfaces is essential for many practical applications, such as adhesion or coextrusion. Most polymer pairs are in fact immiscible at ambient temperatures and form multiphase systems whose bulk physicochemical behavior depends strongly on the properties of the interfaces between the different phases.[1,2]

The most accessible interfacial quantity in a two-phase system is the interfacial tension, which can be experimentally determined from the profile of a drop of one phase immersed in the other phase.[3] Measurements of this kind are performed specifically to gain insight into interactions at the molecular level. With the help of an adequate theory, they allow one to infer a measure of the incompatibility between unlike monomers.[4]

There are various theories that relate the interfacial properties of two immiscible polymers, e.g., A and B, to the microscopic interactions described by the (Flory) interaction parameter χ_{AB} between the corresponding monomers. In the early 1970s, Helfand and co-workers constructed a self-consistent field theory of polymer–polymer interfaces.[4,5] They found, in the limit of *infinite* molecular weight, very simple expressions relating the interfacial tension, γ_∞, and the interfacial thickness, D_∞, to the interaction parameter:

$$\gamma_\infty = \frac{kT}{a^2}(\chi_{AB}/6)^{1/2} \tag{I.1}$$

$$D_\infty = 2a/(6\chi_{AB})^{1/2} \tag{I.2}$$

where a is the statistical segment (monomer) length. These results were eventually extended to asymmetric poly-

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