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Surface modification of polymers using surfactant monomers

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SUMMARY

The film surfaces of poly(styrene) (PS) and an acrylic lacquer were modified by the addition of small amounts of three surfactant monomers. The effects of these surfactant monomers on the polymer surface were studied with respect to the nature of both the surfactant monomers and the host polymers to which they were added. By using polymerizable, monomeric surfactants, the surface modification could be made permanent. Comparison with unmodified films show that the bulk properties are not affected when the small amounts of surfactants monomers needed totally to change the surface are added.

INTRODUCTION

In many applications of polymer materials the surface properties are of vital importance. Besides appearance and finish, properties like wetting and coating characteristics, adhesion and friction, as well as biocompatibillity, are primarily dependent upon the surface. Many applications involve rather harsh environments which are first encountered by the surface of the material and in engineering applications stress cannot be applied to a material without first being transfered through the surface. It is often difficult to find a polymer material with the right combination of bulk and surface properties. Methods to alter the surface properties by changing the chemical composition of a thin surface layer without affecting the bulk characteristics have therefore been developed. Apart from coating, common methods of modifying a polymer surface include chemical methods (1), plasma treatment (2), and grafting reactions involving UV-irradiation (3-4). Common for most surface modification methods is that they all involve additional treatment of the polymer material. An exception to this is, before fabrication, to mix the polymer with surfactants (5). They will concentrate at the polymer surface, thereby changing the surface composition. Only small amounts of surface active material are needed totally to change the surface structure, leaving the bulk properties basically unchanged. It is an advantage to use low molecular weight, monomeric surfactants which will rapidly concentrate at the surface. (6) Once there, they can be made to react and become chemically bonded, making the new, modified surface permanent.

We have studied the effect of monomeric surfactants on polymer surfaces with respect to the nature of the surfactant and the functionality of their reactive, polymerizable groups.

EXPERIMENTAL

Materials. The fluorinated sulfonamide alcohols were kindly supplied by 3M. The alcohol used to synthesize I and III was used as received. The alcohol used in the synthesis of II was dissolved in THF, and the solution was passed through a column packed with 4-Å molecular sieves. Methacrylic acid, propyonic acid, pyridine, and all solvents were distilled before use. 4-pyrolidino-pyridine (Aldrich), and dicyclohexacarbodiimide (Aldrich) were used as received.

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Poly(styrene) (PS) (M_n = 53 800, M_w/M_n = 3.54) was dissolved in cyclohexanone to a concentration of 10 % by weight. The acrylic lacquer used was a 40/60 mixture of hexanedioldiacrylate and an epoxy acrylate oligomer with 3 % w/w Irgacure 184 (Ciba -Geigy), 2 % w/w methyl diethanolamine, and 0.5 % w/w isopropyl thioxanthone (Ward Blenkinsop).The viscosity of the lacquer was approximately 200 cps at 23 °C.

Apparatus and methods. Liquid chromathography was conducted on columns packed with silica gel 60 (230-400 mesh ASTM) with a hexane/ethyl acetate gradient. ESCA spectra were recorded on a Leybold Heraeus ESCA/Auger spectrometer LH 2000, with an AlKa X-ray radiation source. 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 ml 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 (7). This method was found to give results well comparable with the measurements made with the goniometer. IR analyses were performed with a Perkin Elmer 1710 infrared Fourier transform spectrometer. NMR spectra were recorded on a Bruker AC 250 mHz spectrometer. The pendulum hardness was measured with a König Pendelum.

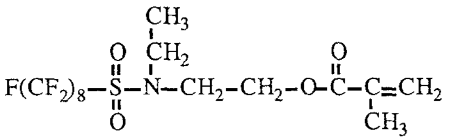
Approximately 1 µm PS films were spin-coated on single crystal silicon wafers at 3000 rpm for 60 s using a spin-coater from Headway Research Inc. and then baked at 100 °C for 15 minutes. PS films were also cast on glass plates at room temperature. Lacquer films were prepared in two different ways. The films used for the ESCA analyses were spin-coated on silicon plates at 3000 rpm for 60 s and cured by exposure to UV light from an OSRAM Ultra-Vitalux 300W Sunlamp which emits light in the near UV (>300 nm) in an inert atmosphere, yielding films of approximately 1 µm. Pendulum hardness measurements and DMTA measurements were performed on 40 µ and 100 µ lacquer films respectively which were drawn on glass plates and cured in a Minicure (Primarc Ltd. Great Britain) with two ozone-free 80 W/cm medium pressure mercury lamps. The films were passed through the Minicure for various times at a speed of 44 m/min. DMTA measurements were performed on a Polymer Laboratories DMTA. Fully cured samples with dimensions of 10 x 7 mm were subjected to a constant tensile strain of 0.45 mm between 0 and 130 °C. No differences were observed related to differences in preparing the lacquer films.

Synthesis procedures. Three surface active monomers were synthesized (Figure 1). Monomers I and II were prepared by the reaction of fluorosulfonamide alcohols with methacrylic acid chloride. This has been described in detail in a previous publication (6).

Monomer III was synthesized by the reaction of a fluorosulfonamide alcohol with propyonic acid. The alcohol (12.20 g, 21 mmol) was dissolved in dry ether (150 ml) together with dicyclohexacarbodiimide (4.95 g, 24 mmol) and 4-pyrolidino-pyridine (0.37 g, 2.5 mmol). Propyonic acid (1.6 g, 23 mmol) was then slowly added under stirring at °C in an argon atmosphere. The reaction mixture was stirred for 24 h, during which the temperature was allowed to rise to room temperature. After filtration and evaporation the product was purified using liquid chromatography and twice recrystallized from hexane. ^{13}C-NMR ($CDCl_3$) show peaks at (d) 13.9 ($\underline{C}H_3$), 45.0 ($N\underline{C}H_2CH_2$), 46.1 ($N\underline{C}H_2CH_3$), 63.5 ($\underline{C}H_2O$), 74.0 ($\underline{C}$=), 75.9 ($\underline{C}H$=), 108-116 ($\underline{C}F$), and 152.1 ($\underline{C}$=O). IR spectra show singlet peaks at 3247, 2116, and 1715 cm^{-1}.

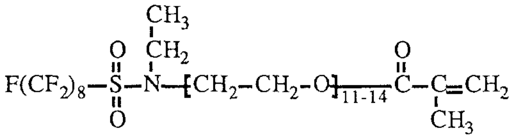
RESULTS AND DISCUSSION

We have studied surface active fluoro-compounds (figure 1), whose presence in a polymer surface are easilly detected with ESCA due to the strong F_{1s} signal and by contact angle measurements due to the highly hydrophobic nature of the flourinated moiteies.



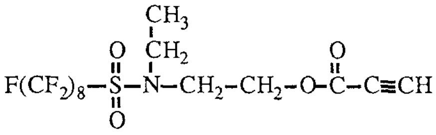
$F(CF_2)_8-\overset{O}{\underset{O}{S}}-\overset{CH_2CH_3}{N}-CH_2-CH_2-O-\overset{O}{C}-\underset{CH_3}{C}=CH_2$

I



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

II



$F(CF_2)_8-\overset{O}{\underset{O}{S}}-\overset{CH_2CH_3}{N}-CH_2-CH_2-O-\overset{O}{C}-C\equiv CH$

III

Figure 1. Chemical structure of surface active compounds studied.

Surface activity is observed with amphiphilic molecules, composed of both hydrophobic and hydrophilic groups. They concentrate at interfaces between media of different polarities orientated with the hydrophilic part towards the more polar medium and the hydrophobic part towards the less polar medium. A condition for this is that either the hydrophobic or the hydrophilic parts of the molecule are compatible with the host medium. Should this not be the case, phase separation will occur, whereas total compatibillity results in total solubility. The enrichment of surface active molecules at a polymer surface is primarily a result of diffusion caused by thermal motion. Once at the surface, the surfactant molecules have a low tendency to diffuse back into the bulk. They are, due to their dual nature, energetically favoured by orientation at the surface.

The rate of difussion through the bulk is dependent on the nature of the surfactant as well as on the host polymer. Large and bulky molecules take a longer time to diffuse to the surface. Furthermore, the lower the viscosity of the host polymer the, faster will a specific surfactant molecule migrate to the surface. (6-7)

The viscosity of a polymer material increases rapidly when spin-coated, leaving little time for the surfactant molecules to concentrate at the film surface. Although all three monomers studied are surface active in polystyrene, only monomer II gives any obvious change to the surface structure of the polystyrene film upon spin-coating. The diffusion rates of the other two, monomers I and III, are obviously too low to allow them to accumulate to any great extent at the spin-coated film surface.

The three monomers have identical hydrophobic groups and otherwise similar chemical structures. Monomer II, however, differs from the others by having a section of flexible poly(ethylene glycol) (PEG) incorporated, which probably improves the mobility of the molecule.

Given sufficient time, monomers I and III will give the same effect as monomer II to the surface properties of polystyrene. This can be achieved by casting the polystyrene films at room temperature and allowing the solvent to evaporate at a low rate. In this way, the viscosity of the film is slowly increased. The same improved effect of monomers I and III in polystyrene is achieved when films are spin-coated from pre-heated solutions, which gives a lower viscosity to the polystyrene solution and also increases the mobility of the surfactant molecules.

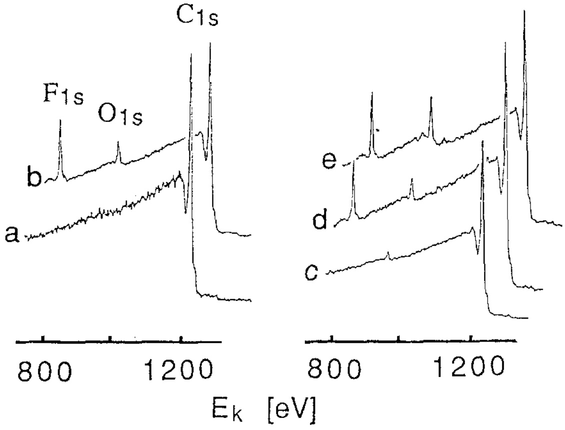


Figure 2. ESCA spectra of a) polystyrene, and polystyrene modified with b) 1 % II, c-d) 1% I, and e) 1 % III. The films were a-c) spin-coated from room temperature solutions, d) spin-coated from a preheated solution, and e) cast at room temperature.

We have found it favourable to use polymerizable, monomeric surfactants which can be made to react and become chemically bonded at the modified polymer surface. This is especially the case when the surfactant molecules are added to a rather low viscosity lacquer system, in which the surfactant molecules rapidly diffuse to the surface and upon curing react with the lacquer monomers and become part of the lacquer network.

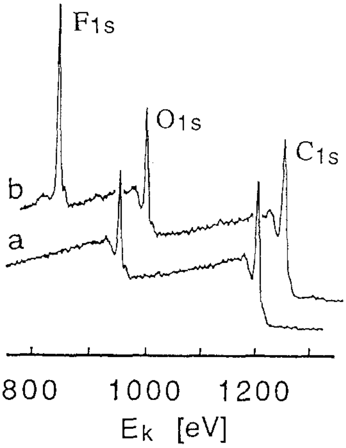


Figure 3. ESCA spectra of a) lacquer film and b) lacquer film modified with 1 % w/w I.

Only very low concentrations of surfactant monomers are needed to achieve a large and permanent change to the lacquer film surface. The bulk properties of the film then remain basically unchanged. Addition of 1 % by weight of surfactant monomers give a totally modified lacquer film surface, whereas the pendulum hardness of the film is not effected at all. In fact up to 5 % of monomer I was added without any changes being observed in the hardness of the lacquer film as measured by the König pendulum.

Nor did DMTA (dynamic mechanical thermal analysis) measurements show any differences between pure lacquer films and lacquer films modified with 1 % monomer I, further indicating that the bulk properties are hardly affected by the addition of small amounts of surface active compounds.

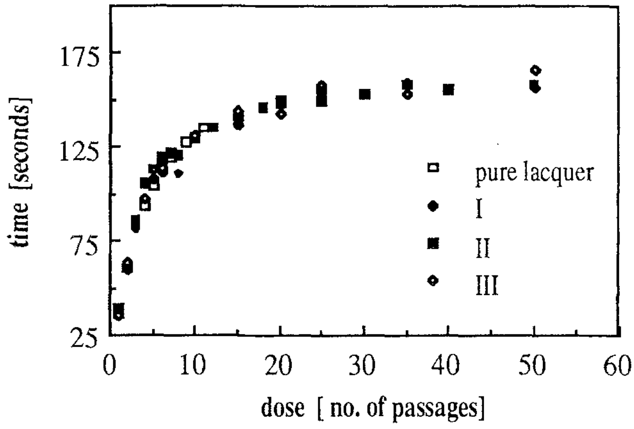


Figure 4. Pendulum hardness of a pure lacquer film, and lacquer films modified with 1 % by weight I, II, and III respectively as a function of dose used to cure the films. The dose is measured as number of passages through the minicure.

When first introduced, the surface active monomers orientate themselves more or less randomly in the lacquer film surface, resulting in a somewhat disorganized top surface. Upon further addition however, the surfactant monomers in the outermost surface become more closely packed and well organized, comparable with what happens in a Langmuir-Blodgett monolayer (9-10) as the surface area is compressed. This can be seen in contact angle hysteresis measurements. The contact angle hysteresis, being the difference between the advancing and the receding contact angles, provides a rough estimate of the surface heterogeneity (11). The hysteresis of water on lacquer films modified with monomer I increases with increasing surfactant concentration, reaching a maximum at 2 % by weight added and then decreases again when the outermost surface becomes more organized as the surfactant concentration is further increased.

The three surfactant monomers used in this study are monofunctional compounds, monomers I and II being acrylates and the third, monomer III, having an acetylenic functionality. The introduction of these monomers into the lacquer film therefore results not only result in a disorganized but also in a monofunctional top surface. This combination of disorder and monofunctionality in turn means that a longer time or higher doses are needed to cure the top surface of the modified films. Similar to the contact angle hysteresis behaviour, the dose necessary to cure the surface initially increases with increasing surfactant concentration, passes through a maximum and then decreases as the surfactant monomers in the modified surface become more organized and coherently aligned.

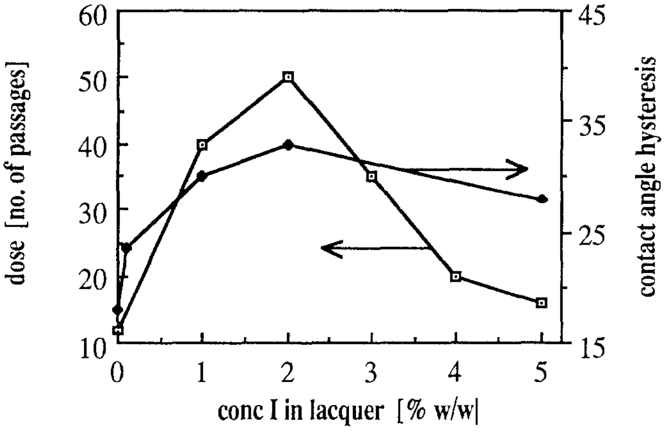


Figure 5. Dose needed fully to cure the lacquer film surface and the contact angle hysteresis of water on the lacquer films as functions of concentration of I added. The dose needed to cure the film can be seen from contact angle measurements made on modified lacquer films cured at different dosages, since the contact angle of water is larger on the uncured surface than on a dry, fully cured film surface. The dose is measured as number of passages through the minicure.

The phenomenon of surfactant modified surfaces needing longer times to cure is observed in the case of all three surface active monomers studied. Monomer III with its acetylenic functionality however cures noticeable faster than films with corresponding amounts of monomers I and II added. This is probably an effect of the acetylenic group being more reactive and more willing to polymerize in the lacquer system studied than the acrylate function of monomers I and II. Whether the film surface is fully cured or not can be seen from ESCA spectra taken on the various films before and after rinsing with water. If not fully cured, the amount of fluorine in the modified surface will decrease on rinsing since the uncured surfactant monomers at the film surface, being soluble in water, are easily washed away. Using a simple UV sun-lamp, rather long times are needed fully to cure the lacquer films and the differences in time needed to cure various films become more obvious. With this lamp, 4 minutes exposure were needed fully to cure a lacquer film with 1 % by weight monomer of I added, whereas the film with 1 % of monomer III was fully cured after only 3 minutes. Using a more reactive surfactant monomer, such as III, therefore gives a more effective surface modification to the lacquer film.

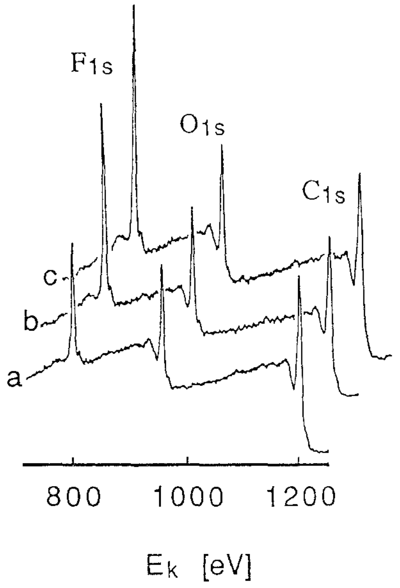


Figure 6. ESCA spectra of lacquer films modified with a-b) 1% of monomer I and c) 1% of monomer III. The films were cured for a,c) 3 minutes and b) 4 minutes respectively by a UV sun-lamp. All films were washed with water and allowed to dry before being analysed.

CONCLUSIONS

The addition of small amounts of surfactant monomers effectively modifies the surface of polymers without affecting their bulk properties. The final structure of the modified polymer surface is dependent on the nature of the surfactant molecule, the hydrophobic as well as of the hydrophilic part of the molecule, and the host, bulk polymer. Using specially designed surface active monomers it is thus possible permanently to remodel the surface properties of a polymer material simply by adding the surfactant material before processing.

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LIST OF REFERENCES

1. Ward, W. J.; McCarthy, T. J. in Kroschwitz Ed; *Encycl. Polym. Sci. Eng., Suppl. Vol.,* 674, Wiley: N.Y. (1990).
2. Yasuda, H. K. *ACS Symp. Ser.*, **287**, 89 (1985).
3. Allmér, K.; Hult, A.; Rånby, B. *J. Polym. Sci.: Part A: Polym. Chem.*, **26**, 2099 (1988).
4. Hult, A.; MacDonald, S. A.; Willson, C. G. *Macromolecules*, **18**, 1804 (1985).
5. Yamashita, Y.; Tsukahara, Y. *Polym. Sci. Technol.*, **21**, 131 (1983).
6. Torstensson, M.; Rånby, B.; Hult, A. *Macromolecules* , **23**, 126 (1990).
7. Dahlgren, C.; Sundquist, T. *J. Immonol. Methods* , **40**, 171 (1981).
8. Gaines, G. L. Jr., *Macromolecules*, **12**, 1011 (1979).
9. Blodgett, K. B. *J. Am. Chem. Soc.*, **57**, 1007 (1935).
10. Blodgett, K. B.; Langmuir, I. *Physical Review,* **51**, 964 (1937).
11. Andrade, J. D.; Smith, L. M.; Gregonis, D. E. *Surface and Interfacial Aspects of Biomedical Polymers, vol 1,* 249, Plenum Press, New York (1985).

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