Hydrogen Bonding and Wettability of Surface-Grafted Organophosphate Polymer

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ABSTRACT: Thin layers of grafted polymer chains were produced by ultraviolet light-induced graft polymerization of a hydrophilic monomer, methacryloxyethyl phosphate, onto the Ar plasma-pretreated film surface of high-density polyethylene. The hydrogen-bonding interactions in the grafted polymer and the wettability of the grafted layers were studied by Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopy and water contact angle measurements, respectively. The grafted layers exhibited a distinct wetting transition with an increase in the graft density, which closely correlated with a clearly observable change in the hydrogen-bonding extent of the grafted chains.

Introduction

Thin layers of polymer chains grafted at one of the ends on solid surfaces have widespread applications for surface modifications of materials[1] and have been the subject of intensive theoretical and experimental investigations during the last decade. A variety of technological problems such as colloidal stability, adhesion, wettability, biocompatibility, etc., are strongly related to the properties of the polymer layer and, consequently, to the structure and interactions of the grafted chains. In addition, a large number of technological applications of grafted layers are based on the use of hydrophilic polymers that contain chemical functionalities (e.g., carboxylic acid, amide, phosphate, or hydroxyl groups)[2−5] possessing strong mutual attractions, particularly hydrogen bonds. It is then of considerable practical importance to understand how the attractive interactions in grafted polymers affect the structure and properties of the grafted layers.

Most theoretical studies of these systems have been devoted to determination of the chain configuration in good solvent conditions.[6−11] The structure of surface-grafted chains depends strongly on the grafting density: the loosely grafted chains adopt nearly random-walk configurations (the so called "mushroom" structure), while at significantly high grafting densities they stretch normal to the surface, forming polymer "brushes". In a good solvent, the equilibrium brush structure is determined by the balance between the repulsive (excluded-volume) interaction between grafted chains acting to stretch them and the decrease in entropy due to the stretching. However, as the solvent conditions become worse, attractive interchain interactions may become the dominant factor. Recent theoretical works by Lai and Binder,[12] Grest and Murat,[13] and Balasz et al.[14,15] have revealed that, in a sufficiently poor solvent, intermolecular attractions drive grafted chains to associate into local bundles or "dimples" and, thereby, alter the structure of grafted layers. Balasz et al.[16] have extended their studies to grafted polymers containing attractive functional groups ("stickers"). They found that mutual attraction between these stickers causes the chains to aggregate into clusters, with the separation and depth of the clusters depending on the block length of stickers and the grafting density.

Experimental studies of surface-grafted polymers have so far almost exclusively been concerned with the determination of *quasi-macroscopic* characteristics such as the layer thickness, segment density distributions and the force−distance profile between two interacting monolayers, using neutron reflectivity, small-angle neutron scatterings and direct surface force measurements.[17−23] There remains a need for novel experimental approaches that would allow one to determine the physicochemistry of grafted polymers on the *microscopic* level. Infrared spectroscopy has been proved to be a technique which can provide information on the microscopic structure (as characterized by orientation, conformational sequences, and intermolecular interactions) of polymer chains. It has been extensively applied as a probe of molecular structure in self-assembled monolayers and Langmuir−Blodgett films of polymers on solid substrates,[24,25] but, to our knowledge, there has been no discussion on its use in the microstructure characterization of surface grafted polymers.

In this paper, we report vibrational spectroscopic and contact angle measurements made on surface-grafted layers of a hydrophilic polymer, poly(methacryloxyethyl phosphate) (PMOEP). As the polymer employed contains phosphate functional groups, the grafted polymer chains are capable of hydrogen-bonding interactions. We use FTIR-ATR spectroscopy to investigate the hydrogen bonding as a function of the graft density. We also follow the wettability behavior of the grafted polymer by measurement of the water contact angle. Comparing results from these two techniques helps us to relate the macroscopic wettability to the microscopic nature of the grafted layers. We observe, for the first time, unique transitions in the extent of hydrogen bonding of the grafted chains and the wettability of the grafted layer, which occur simultaneously by less than 2-fold changes in the graft density.

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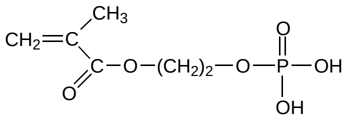
Experimental Section

Materials. A high-density polyethylene (PE) film of 35 μm thickness, supplied by Aicello Inc., Japan, was used as a substrate polymer. The film surface was macroscopically smooth when inspected by a roughness meter. The PE film was purified by Soxhlet extraction with methanol for 20 h prior to use. The monomer used for surface graft polymerization is methacryloxyethyl phosphate (MOEP)



from Unichemical Co. Ltd., Japan. The MOEP monomer was of chemical grade and used as obtained. All other reagents were of extrapure grade.

Glow Discharge. The PE film was first pretreated with Ar plasma in a low-temperature glow discharge reactor (Model LCVD 12, Shimadzu Inc., Kyoto, Japan) equipped with a bell-jar-type reaction cell. The distance between two electrodes with an area of 14×14 cm^2 was kept at 7 cm. The frequency and voltage applied were 5 kHz and 270 V, respectively. Strips of PE film were fixed on a stainless steel holder placed between the two electrodes. The holder was rotated at 68 rpm by a motor to ensure homogeneous plasma treatment over the whole film surface. The pressure in the bell jar was reduced to 10^{-3} Torr, followed by introduction of Ar gas in the bell jar at a flow rate of 20 mL/min. The pressure in the bell jar was kept at 0.03 Torr after gas introduction. After that, plasma was generated at an electric power of 24 W and the film was exposed to plasma for 10 s. After the plasma treatment, the film was removed from the reactor and exposed to air for 30 min at room temperature, so that the polymer radicals produced by the plasma treatment could be converted to polymer peroxides which are capable of initiating graft polymerization.[26]

Graft Polymerization. The plasma-treated polymer film was placed in a Pyrex tube containing 6 wt % water/acetic acid (4/1, by vol) solution of MOEP, to which riboflavin was added at 1×10^{-5} M. Following nitrogen bubbling into the monomer solution for 1 min, the tube was exposed to UV radiation at 30 °C to effect graft polymerization. The light source used was a high-pressure Hg lamp (Riko Rotary RH400-10W type, Riko Co. Ltd., Tokyo, Japan) provided with equipment to ensure uniform UV irradiation over the whole film surface from both sides of the film. Riboflavin was added to the monomer solution because riboflavin could effectively consume the oxygen dissolved in the monomer solution upon UV irradiation.[27] In order to remove the formed homopolymer, the grafted PE film was washed first in running water and then in a water/acetic acid mixture at 60 °C for 12 h, followed by rinsing with deionized water at 25 °C for 12 h.

Surface Analysis. The weight graft density of PMOEP was measured colorimetrically in a UV–vis spectrophotometer (UV-1200 type, Shimadzu Corp.) with a molybdenum blue method.[28]

The FTIR-ATR analysis was performed with a Shimadzu FTIR-8100 spectrophotometer equipped with a Shimadzu 8000 ATR attachment. The internal reflection elements (IRE) used were Ge and KRS-5 with 45° incident angle. For each spectrum at least 400 scans were signal averaged at a resolution of 4 cm^{-1}.

Static contact angles of grafted films against water were measured on a telescopic goniometer (M2010A-6II type, Elma Inc., Tokyo, Japan) at room temperature and at about 65% relative humidity. The volume of the water drops used was always 3 μL. The drops had spherical shape and their contact angle did not change significantly in 3 min. All reported values are average of at least five measurements taken at different locations of the film surface and have a maximum error of the mean of ±2°.

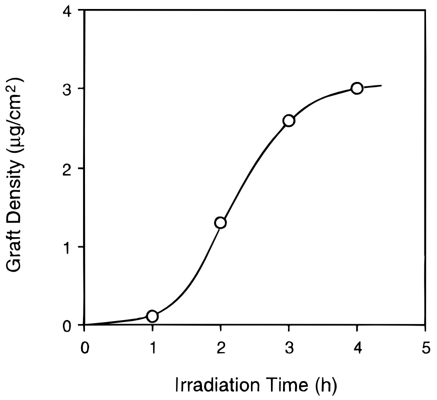


Figure 1. Effect of UV irradiation time on graft polymerization of MOEP onto PE film surface.

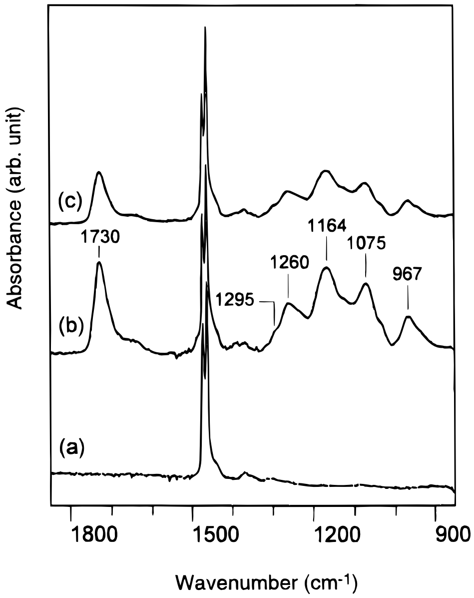


Figure 2. FTIR-ATR spectra of the virgin (a) and MOEP-grafted PE film (b and c) obtained using Ge (a and b) and KRS-5 IRE (c); the graft density of MOEP polymer was 1.1 μg/cm^2.

Results and Discussion

Surface Graft Polymerization. The grafting technique employed here uses peroxides generated on the polymer substrate by the glow discharge. The formed peroxides act as active sites for the subsequent graft polymerization. This method has already been applied to chemical immobilization of several hydrophilic polymers onto PE surfaces.[29] In the present study, graft polymerization of MOEP onto plasma-treated PE films was carried out at 30 °C in water/acetic acid (4/1, by vol) monomer solution under UV irradiation. The water/acetic acid mixture was used as a solvent for the MOEP monomer due to its poor solubility in water. Figure 1 shows the effect of the UV irradiation time on the graft polymerization of MOEP. The graft density increased with the UV irradiation time during the first hours of irradiation. Then the graft density leveled off.

Films with grafted polymer densities ranging from 0.1 to 3 μg/cm^2 were obtained by varying the time of UV irradiation and examined by means of FTIR-ATR and contact angle measurements.

FTIR-ATR Measurements. The FTIR-ATR spectra of the virgin and MOEP-grafted PE film obtained using Ge IRE are shown in Figure 2a and b, respectively. The graft density of MOEP polymer was 1.1 μg/cm^2. The spectrum of the virgin film contains two main peaks at 1462 and 1473 cm^{-1} assigned to C−H bending vibrations. After subsequent graft polymerization, the spectrum of the film surface reveals presence of PMOEP by new strong bands at 967, 1075, 1164, 1260, and 1730 cm^{-1}. The spectral features of the grafted film can be assigned by comparison to the characteristic strong infrared bands of esters and organophosphates.[30−34] The bands at 967 and 1075 cm^{-1} are due solely to P—O—(H) and P—O—(C) stretching vibrations, respectively. The band at 1730 cm^{-1} can be only assigned to carbonyl stretch mode, ν(C=O). The 1164 and 1260 cm^{-1} bands result from both ester and phosphate groups. The first can be attributed to C—O—(C) and C—O—(P) stretching vibrations and the second to the hydrogen-bonded P=O stretch overlapped with (C)—C—O stretching mode. It should be noted that in addition to the main peak at 1260 cm^{-1} a shoulder is observed at 1295 cm^{-1}, which deserves close discussion. The nearest PE band located at 1303 cm^{-1} is not close enough in frequency and is too weak in intensity to account for the feature at 1295 cm^{-1}. On the other hand, it has been well documented that IR spectra of organophosphates often contain a characteristic band at 1295 cm^{-1}, which arises from the non-hydrogen-bonded P=O groups.[31−34] Therefore, we assign the absorbance at 1295 cm^{-1} in the spectrum of the MOEP-grafted film to the P=O stretch mode in the absence of hydrogen bonding.

The FTIR-ATR spectra shown in Figure 2a and b reflect the structure of a thin (0.4−0.7 μm at the wavenumber of 1850−850 cm^{-1}) film layer adjacent to the surface. A deeper surface region of the grafted film was examined by the use of a KRS-5 IRE instead of Ge element and the observed FTIR-ATR spectrum is shown in Figure 2c. The probing depth was in the range of 0.8−1.4 μm, i.e., as twice as higher than in the case of Ge IRE. It can be seen that the relative intensity of the absorption bands of the grafted polymer to those of substrate polymer decreases, as one goes from Ge IRE to KRS-5 IRE, displaying the surface localization of the grafted layer.

Figure 3a and b shows the 800−1350 cm^{-1} region of the FTIR-ATR spectra of the MOEP-grafted films with the graft density of 0.6 and 2.3 μg/cm^2. Attention is attracted by the sharp, well-resolved band at 1295 cm^{-1} observed for the low graft density of 0.6 μg/cm^2 (Figure 3a). This band ascribed to the non-hydrogen-bonded P=O group is barely identifiable in the case of relatively high graft density of 2.3 μg/cm^2 (Figure 3b) and, returning to Figure 2, it appears as a distinct shoulder in the spectra of the film with a middle graft level of 1.1 μg/cm^2. These data indicate the presence of free (non-hydrogen-bonded) P=O in the grafted PMOEP layer at low graft densities ranging between 0.6 and 1.1 μg/cm^2. The content of free P=O groups progressively decreases with increasing graft density, and they are practically absent in the grafted polymer at the graft levels above 2.3 μg/cm^2.[35]

In addition to the above-considered P=O···HO—P hydrogen bonding, the C=O···HO—P hydrogen bonds can also occur in the MOEP polymer. Therefore, we have closely observed the carbonyl stretching region (1660−1800 cm^{-1}). The corresponding FTIR-ATR spectra are given in Figure 4. The spectra obtained on 0.6 and 1.1 μg/cm^2 grafted films exhibit a nearly symmetric band centered at 1730 cm^{-1} (Figure 4a and b). In the case of 1.8 and 2.3 μg/cm^2 graft density, the C=O band is broader and more complex (Figure 4c and d). It extends in the low-frequency region and shows a shoulder at 1710 cm^{-1}. Referring to infrared spectroscopic studies of alkyl methacrylate monomers and polymers,[36−38] we can attribute the 1730 and 1710 cm^{-1} bands in the spectra of MOEP polymer to free and hydrogen-bonded carbonyl groups, respectively. Accordingly, the evolution of carbonyl bands in Figure 4 demonstrates that at low graft densities there is no hydrogen-bonded C=O in the grafted polymer (absence of the shoulder at low wavenumber in Figure 4a and b), while at the graft levels above 1.8 μg/cm^2 a part of carbonyl groups are associated by hydrogen bonding (Figure 4c and d).

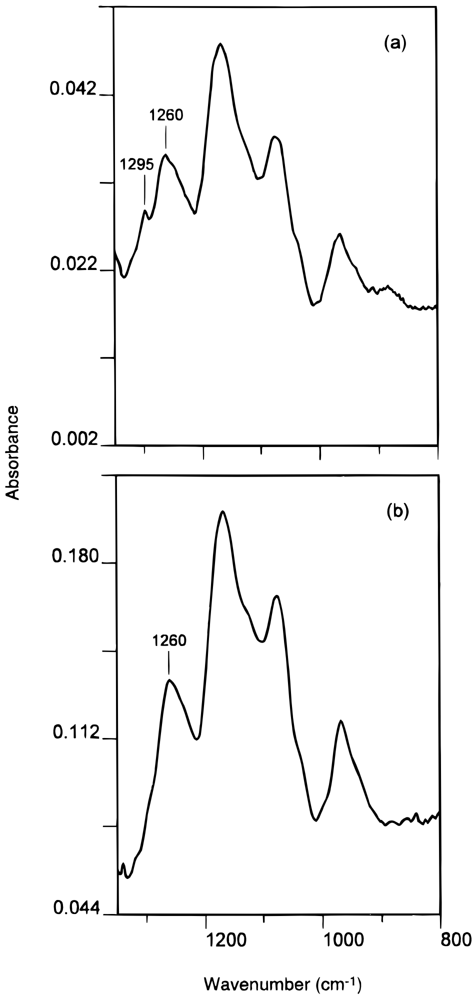


Figure 3. The 800−1350 cm^{-1} region of the FTIR-ATR (Ge IRE) spectra of the MOEP-grafted PE films with the graft density of 0.6 (a) and 2.3 μg/cm^2 (b).

At this point it might be interesting to perform a quantitative analysis of the evolution of the free and associated carbonyl groups with the graft density. For this purpose a least-squares curve-fitting method must be applied to the carbonyl stretching region. Since our FTIR instrument is not supported by any curve-fitting software, no quantitative analysis was attempted in this study. We employed a simple graphical method[39] to separate the overlapping C=O bands and found the ratio of the areas under the two peaks, A_{1710}/A_{1730}, to be 0.08 and 0.76 for the graft density of 0.6 and 2.3 μg/cm^2, respectively. It is apparent that if the quantitative data were obtained, they might demonstrate the spectral features more clearly; but they would not change the entire concept of the interpretation.[40]

Contact Angle Measurements. The virgin PE film is highly hydrophobic with water contact angle of 91°.

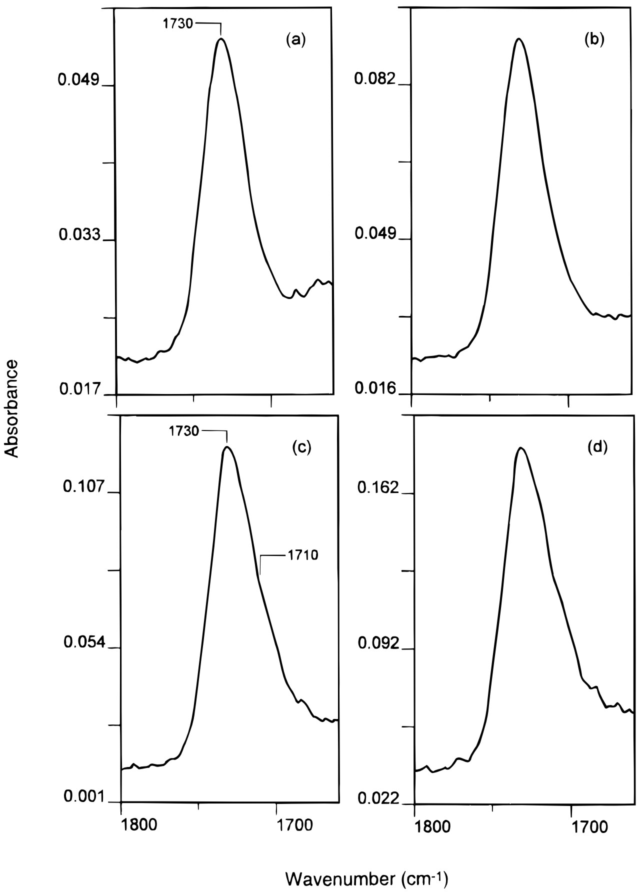


Figure 4. The carbonyl stretching region of the FTIR-ATR (Ge IRE) spectra of the MOEP-grafted PE films with the graft density of 0.6 (a), 1.1 (b), 1.8 (c), and 2.3 μg/cm^2 (d).

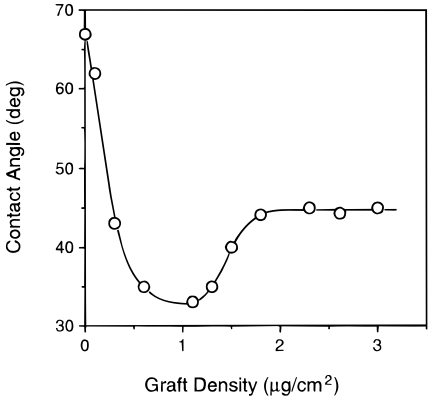


Figure 5. The contact angle of water on MOEP-grafted PE films.

The Ar plasma treatment resulted in a decrease of the contact angle of the PE film to 67°. The contact angle further decreased by the graft polymerization, as can be seen in Figure 5, which shows the result of contact angle measurements for the MOEP-grafted PE films. The graft density of 0.6 μg/cm^2 was sufficient to reduce the contact angle from 67° to 35°. The decrease in the contact angle demonstrated that the substrate surface was changed in its composition by the grafted chains rendering the hydrophobic surface more and more hydrophilic as the graft density increased. The initially sharp decrease in the contact angle slowed down drastically as the graft density approached the value of 1.1 μg/cm^2, indicating that the substrate surface got fully covered with the overlayer of the grafted chains and could no longer influence the wettability of the grafted film. One would have expected a plateau of the contact angle starting from the graft level of 1.1 μg/cm^2. However, such a behavior of contact angle was not observed. On the contrary, a further increase in the graft density resulted in a sharp increase in the contact angle (from 33° to 45°) up to the graft level of 1.8 μg/cm^2, above which the contact angle finally leveled off.

The central property of importance in the present study is the wetting behavior of the grafted polymer. However, at the graft densities below 0.6 μg/cm^2 one must be aware that the observed contact angles are out of direct relation to the wettability of the grafted layer alone because, as already stated above, the substrate is not in full cover with the grafted chains and, consequently, the substrate macromolecules exposed at the wetted surface contribute to the measured contact angle. Therefore, we deliberately exclude the region of loose grafting from consideration and focus on only the data obtained at 0.6–3 μg/cm^2 graft densities. In the region of interest, the contact angle behavior shown in Figure 5 clearly forms two well-defined regimes separated by an 12° increase in the contact angle between 1.1 and 1.8 μg/cm^2. We call these regimes the "high wetting regime" and "low wetting regime" of the grafted layer, respectively.

The findings of the macroscopic contact angle measurements are in a good accordance with the microscopic picture of the grafted layers derived from the FTIR-ATR observations. The infrared spectra have revealed two types of P═O and C═O groups in the grafted polymer: those associated by hydrogen bonding with hydroxyl groups and the free ones. The relative content of these two types of P═O and C═O groups depends on the graft density. Below 1.1 μg/cm^2 (the high wetting regime) all C═O groups and a part of P═O groups are non-hydrogen bonded, whereas almost no free P═O groups remain in the grafted layer and a part of C═O groups are associated by hydrogen bonding at the graft densities above 1.8 μg/cm^2 (the low wetting regime). Moreover, the free carbonyl to hydrogen-bonded carbonyl transition occurs within the same range of the graft densities as the high wetting to low wetting transition does. These correlations give definitive support that the wettability behaviour of the grafted layer is controlled by the hydrogen bonding extent of the polymer chains.

It is worthwhile to note that, in the case of loose grafting, only P═O groups contribute to the development of hydrogen-bond network in the grafted polymer, whereas C═O groups remain free. This indicates that at low graft densities the carbonyl groups are inaccessible for interaction with the phosphate hydroxyls (probably for steric reasons). In order for this interaction to occur, it is necessary for the grafted layer to change its structure in the way that the carbonyl–hydroxyl interaction may become favorable. In this context, the free carbonyl to hydrogen-bonded carbonyl transition can be related to the structure transformation of the grafted chains.

Conclusion

The macroscopic wettability and the microscopic structure (as characterized by hydrogen-bonding interactions) of surface-grafted organophosphate polymer have been studied at varying graft densities. The grafted polymer exhibited a distinct wetting transition with the increase in the graft density, which closely correlated with a clearly observable change in the extent of hydrogen bonding of the grafted chains. These observations provide definitive experimental evidence that the macroscopic wettability of the grafted layer is controlled by the microscopic structure of the polymer chains which, in turn, is governed by the graft density.

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(40) More specific information on the extent of hydrogen bonding in these systems could be probably obtained if it was possible to use a spectrum of a film of PMOEP homopolymer as a reference. All our attempts to prepare such a film ended in failure because of very low solubility of the homopolymer in common solvents. The FTIR spectrum of PMOEP homopolymer measured using the KBr disk sampling method was qualitatively similar to the FTIR-ATR spectrum of grafted PMOEP layer with the graft density of 2.3 $\mu g/cm^2$.

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