Selective Surface Modification of PVC Films As Revealed by Confocal Raman Microspectroscopy

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ABSTRACT: The chemical modification of PVC films with sodium azide and 4-aminothiophenol was investigated. Using mixtures of a good and a nonsolvent for PVC, reactions took place in a controlled way, and the films remained transparent and smooth. To obtain information about the surface selectivity of the reactions, the degree of modification of the polymer across the film was determined by depth profiling carried out using confocal Raman microscopy. It is shown that the reaction with sodium azide always occurs homogeneously through the film while in the case of aminothiophenol, conditions could be found that allowed the polymer film to be preferentially modified at the surface. The gradient of the degree of modification and the surface selectivity depend on the relationship between the rate constants of the substitution reaction and the diffusion process of the reactant. They are, therefore, functions of reaction time, temperature, and the proportion of solvent/nonsolvent used for the reaction. The measured depth profiles as a function of reaction time have been fitted to a solution of the second Fickian law and combined diffusion/reaction coefficients for the transport of the reactant have been calculated.

Introduction

In most engineering applications, a polymeric material is selected because of its favorable bulk properties, processability, or thermal stability. The surface of a polymer, however, is important when aspects such as adhesion and barrier characteristics, chemical resistance, and physical corrosion are dealt with. Often it is desired to change the surface properties of a material without altering its bulk characteristics. Modification of a polymer surface can be achieved by means of various chemical or physical processes. The most common surface modification techniques include plasma-ion beam treatment, electric discharge, surface grafting, chemical reaction, vapor deposition of metals, and flame treatment.[1−3]

A second important aspect of surface modification of polymer films involves material characterization and especially the determination of the concentration profile through the film. Several techniques for surface analysis have been developed during the past decade.[3,4] The most commonly used methods include X-ray photoelectron spectroscopy (XPS)[5−9] and attenuated total reflection infrared spectroscopy (FTIR-ATR).[10−12] XPS allows one to gain information about the composition of a few atomic layers on a film surface. FTIR-ATR allows depths of the order of magnitude of a micrometer to be analyzed. In this work, we have used confocal Raman microscopy[13−17] to study the degree of modification of PVC films as a function of depth. The technique is suitable to analyze depths of about 50 μm and has, furthermore, the advantage of being nondestructive and easy to use.

We have recently initiated studies on modification reactions of polymer surfaces using the knowledge acquired in investigations of polymer bulk modification in the melt or solution performed for different purposes.[18−21] In a recent paper[22] we have reported that PVC films can be modified chemically without loss of their transparency and surface smoothness when carrying out the reactions in appropriate mixtures of a solvent and a nonsolvent for the polymer. It was shown qualitatively that the surfaces of films can be selectively modified in cases where (i) the rate constant of the substitution reaction is greater than that of the transport process of the modification reactant in the interior of the film and (ii) the reaction is stopped before the compound is homogeneously distributed within the laminate. In reactions of PVC with sodium azide this condition is not fulfilled, and consequently, homogeneously modified films are obtained. On the other hand, by substitution of chorine atoms by aminothiophenol, a gradient of the degree of modification is established. Confirmation of these qualitative findings and quantification of the gradient by depth profiling using the confocal Raman microscopy technique is the main object of the present paper.The depth profiles obtained will be used to discuss the influence of different reaction parameters on the surface selectivity of the modification process.

Experimental Part

Commercial bulk polymerized PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by GPC were M_W = 112 000 g/mol and M_N = 48 000 g/mol.

The tacticity measured by ^{13}C NMR was syndio = 30.6%, hetero = 49.8%, and iso = 19.6%.

For the modification reactions PVC films of thickness 10−60 μm were prepared by the casting of THF solutions. The films were extracted in a Soxhlet apparatus for 24 h using diethyl ether and then dried under reduced pressure for a further 2 h. Thicknesses of the films were determined optically, focusing a laser spot in turn on each surface of the film and measuring the distance the objective had moved. The accuracy of this method is about 1 μm.

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Table 1. Conditions for the Reaction of PVC with Sodium Azide

sample	H_2O/DMF comp	temp (°C)	reaction time (h)	film thickness (μm)	deg of modification (%)
A1	1:2	45	200	25, 50	no reaction
A2	1:2	60	200	25, 50	no reaction
A3	1:3	30	100	25, 50	0.1
A4	1:3	45	200	25, 50	0.5
A5	1:4	30	170	25, 50	0.5
A6	1:4	45	275	25, 30, 50, 60	1.3
A7	1:4	60	70	50	3.7
A8	1:6	30	150	50	1.2
A9	1:6	45	320	10, 25, 50	2
A10	1:6	52	220	50	6.1
A11	1:6	60	48	50	5.3
A12	1:7	45	160	50	5.2
A13	1:8	30	150	20, 50	2
A14	1:8	45	200	25, 50	6.4
A15	1:8	60	5	25, 50	film dissolves
A16	1:9	30	1	25, 50	film dissolves

Sodium azide was purchased from Fluka and used without further purification. Aminothiophenol was purchased from Acros and was distilled under reduced pressure prior to use.

Modification of the Films. To allow the film to react on both sides and avoid folding or contact with the reactor wall, PVC films of size 60 mm × 20 mm and different thickness were clamped in Teflon frames. The frames were immersed in a reactor containing a 0.5 M solution of modification reactants in a solvent/nonsolvent mixture. The temperature of the reactor was controlled by a thermostate. Oxidation of the reactants is avoided by performing the reactions under a nitrogen atmosphere. To follow the kinetics of the reaction, pieces (10 mm × 10 mm) of the film were removed at different time intervals and washed with water, extracted for 24 h in ether, and dried.

Global degrees of modification of the modified films were determined by FT-IR measurements on a Nicolet 520 FT-IR spectrometer. Calibration curves were recorded in order to quantify the modification of the films using IR spectra of PVC samples modified homogeneously in solution. The degree of modification had previously been determined by elemental analysis in the case of PVC-N_3 (PVC modified with sodium azide) and by ^{1}H NMR in the case of PVC-ϕ-NH_2 (PVC modified with aminothiophenol).

Confocal Raman Microspectroscopy. Raman spectra were recorded on a Renishaw Ramascope 2000 spectrometer using the 632.8 nm line of a He−Ne laser. This instrument was equipped with a Peltier-cooled charge-coupled device (CCD) detector and a holographic edge filter, which prevented the backscattered laser radiation from entering the spectrograph. The stigmatic single spectrograph was attached to an Olympus BH2 microscope. More details of the experimental setup are described elsewhere.[13,16] The depth resolution achievable with this setup is about 1.4 μm (half-width of the confocal profile for a silicon wafer). The spectral resolution has been determined to be 3 cm^{-1}.

A depth profile of each laminate was then obtained by focusing the microscope stepwise (1.4 μm steps) through the polymer film and recording a spectrum at each step. The position, the area, and the full width at half-height of the important bands were determined as a function of the depth by using the Renishaw curve-fitting program.

Results and Discussion

In recent work[22] we have shown that PVC films can be chemically modified while preserving their form, optical properties, and smoothness when reactions are carried out in an appropriate mixture of a solvent and a nonsolvent of the polymer. The mean degree of modification of the films is a function of the composition of the medium, reaction temperature, and time and can be determined by conventional FTIR. To obtain information about the distribution of the modified groups within the membranes, depth profiling experiments using confocal Raman microscopy were carried out.

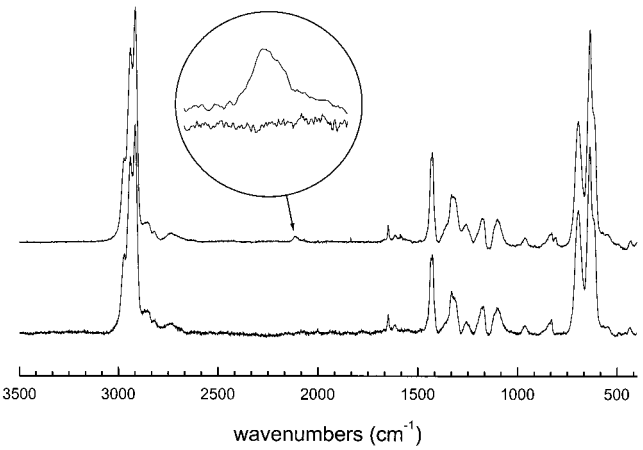

Figure 1. Raman sprectrum of a PVC film modified with sodium azide.

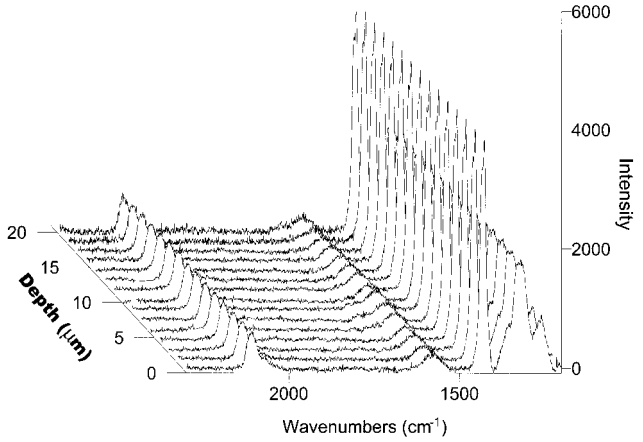

Figure 2. Series of Raman spectra as a function of depth of a PVC film (**A11)** modified with sodium azide. The spectra are normalized with respect to the intensity of the band at 1425 cm^{-1}.

PVC Modification with Azide Groups. PVC films of 10−60 μm thickness were modified with sodium azide[23] under different conditions (Table 1). The Raman spectrum of modified PVC (sample **A9**) is shown in Figure 1. It exhibits a weak band at 2150 cm^{-1}, resulting from the azide stretching vibration, $\nu(N_3^-)$, and another characteristic well-resolved band at 1425 cm^{-1} corresponding to the C−H bending vibration of the PVC chains. The relative degree of modification of the film can be calculated from the ratio of the integrals of the two signals, absolute values being obtained using a calibration curve.[22] Because of the low crystallinity of PVC, it is assumed that conformational sensitivity of Raman bands is not a significant factor here.

To obtain the depth profile of the films, a Raman microscope was focused stepwise (1.4 μm) through the polymer laminate and the 1200−2300 cm^{-1} region of the spectrum was recorded at each step. Figure 2 shows the series of spectra of **A11** recorded as a function of depth and normalized with respect to the intensity of the band at 1425 cm^{-1}. It may be seen that the intensity of the azide peak at 2150 cm^{-1} does not change with depth but is constant through the film. This result does not depend on the reaction conditions but is found in all PVC film samples modified with sodium azide (**A1**−

Table 2. Conditions for the Reaction of PVC with 4-Aminothiophenol

sample	reaction time (h)	temp (°C)	mixture H_2O/DMF	thickness d (μm)
T1a	5	30	1:5	42
T1b	14	30	1:5	42
T1c	22	30	1:5	45
T1d	29	30	1:5	36
T1e	46	30	1:5	38
T2a	2	30	1:7	60
T2b	5	30	1:7	60
T2c	7	30	1:7	59
T2d	23	30	1:7	56
T3a	5	40	1:5	55
T3b	20	40	1:5	58
T3c	29	40	1:5	55
T3d	54	40	1:5	55
T3e	74	40	1:5	56
T4	5	30	1:4	28
T5	5	30	1:6	47

A15). Shorter reaction times or lower temperatures than those in Table 1, which could be supposed to favor a surface selectivity, lead to very low degrees of modification below the detection limit for the Raman azide band.

The result indicates that the modification reaction of PVC with this reactant occurs homogeneously within the film and that no surface selectivity was achieved. This finding is in complete agreement with what has been concluded from modification reactions on films of different thickness[22] and had been attributed to the small size of the reactant which results in a high ratio of the rate constant for the diffusion process of the azide group to the reaction rate of the nucleophilic substitution reaction.

PVC Modification with Aminothiophenol. To reduce this ratio, thereby hindering the transport of the modification reactant in the interior of the PVC film and facilitating the substitution reaction, aminothiophenol was chosen. This molecule is a strong nucleophile[24] and significantly larger than the azide group.

PVC films of 28−60 μm thickness were modified with aminothiophenol. In Table 2 reaction conditions, namely the times, temperatures, and solvent/nonsolvent composition, for the modification reactions are summarized.

An example of a Raman spectrum of modified PVC is shown in Figure 3. In addition to the spectrum arising from the PVC structure, there is an intense band at 1596 cm^{-1}, resulting from the stretching vibration of the aromatic rings and a smaller one at 1658 cm^{-1} corresponding to the ν(C−N) vibration of the amino groups. The relative degree of modification of the film can be calculated from the ratio of the integrals of the deconvoluted aromatic ring signal to that of the PVC band at 1425 cm^{-1}, absolute values being obtained using a calibration curve.

The depth profiles of the films were again obtained using confocal Raman microscopy recording the 1380−1750 cm^{-1} region of the spectrum at various focal planes inside the film. Figure 4 shows the series of spectra of sample **T1c** as a function of depth. Comparison of the spectra shows that both the band at 1425 cm^{-1} and the one at 1596 cm^{-1} show changes in intensity on penetrating the interior of the film. Since the intensity of the band at 1425 cm^{-1} corresponding to the bending of CH bonds of the PVC chains can be expected to remain unaffected by the reaction, the increasing intensities measured in the first 7 μm below the surface and the decrease of the signal intensity in the last 7 μm before reaching the opposite surface must be due to the technique used. This feature may be explained simply by the fact that in the region of the film surfaces the scattering volume giving rise to the Raman spectrum is not entirely confined within the film. Indeed, this effect is utilized in estimating the depth resolution of the technique, by measuring the scattered intensity as a function of depth for a silicon wafer.[17] The half-width of the confocal profile is found to be approximately 1.4 μm, and the intensity falls rapidly in the wings of the profile.

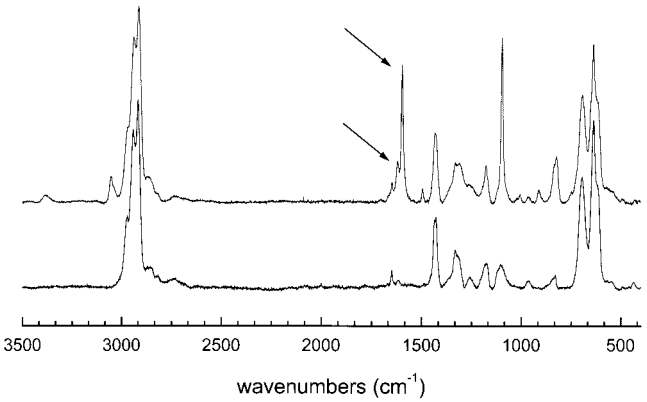

Figure 3. Raman sprectrum of a PVC film (thickness 36 μm) modified with 4-aminothiophenol.

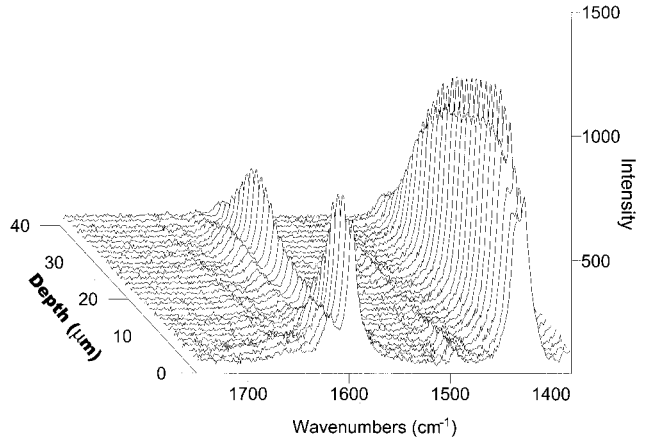

Figure 4. Series of Raman spectra as a function of depth of a PVC film modified with 4-aminothiophenol in H_2O/DMF 1:5 at 30 °C.

A similar effect can be observed for the aromatic band at 1596 cm^{-1}, which increases from the surface up to a depth of about 7 μm. The signal then decreases and nearly vanishes in the center of the film until it begins to increase again and finally falls off when approaching the opposite surface of the membrane. The degree of modification as a function of depth, as obtained from the relative area of the integrals of the signals [I(1596 cm^{-1}/I(1425 cm^{-1})], leads to a depth profile which is depicted in Figure 5. The shape of the curve demonstrates clearly that, in this case, substitution of chlorine atoms has taken place preferentially at the surface of the laminate. Mean degrees of modification ($\bar{M}$) of the films were calculated from the depth profiles according to the expression

$$\bar{M} = \frac{\int_0^{d/2} f(M)\,\mathrm{d}x}{\int_0^{d/2} \mathrm{d}x} \qquad (1)$$

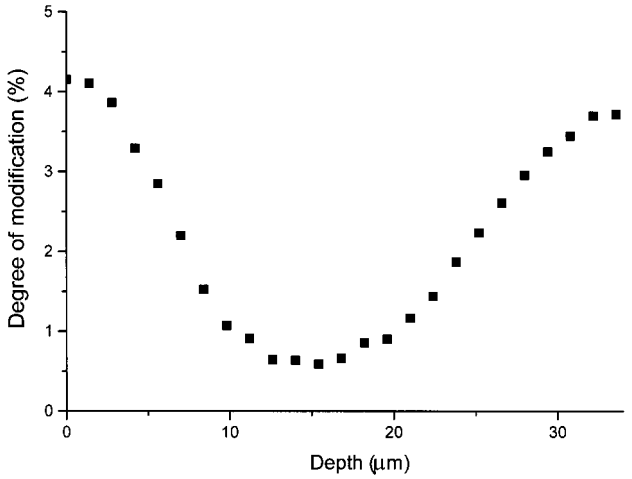

Figure 5. Depth profile of the degree of modification of a PVC film modified with 4-aminothiophenol in H_2O/DMF 1:5 at 30 °C for 29 h.

Table 3. Results for the Reaction of PVC with 4-Aminothiophenol

sample	$\bar{M}$ (%) (IR)	$\bar{M}$ (%) (depth profile)	M_{surf} (%)	$\int_0^{d/2} f(M)\,dx$	SS
T1a	0.2	0.1	0.5	2.5	0.77
T1b	0.7	0.6	1.8	12.1	0.68
T1c	1.3	1.1	2.8	24.3	0.62
T1d	1.7	1.4	3.0	24.7	0.55
T1e	2.2	2.0	4.3	37.9	0.53
T2a	0.9	0.6	1.1	17.4	0.47
T2b	0.9	0.6	1.2	17.6	0.51
T2c	3.1	2.8	4.3	83.5	0.34
T2d	9.4	9.1	11.1	255.2	0.18
T3a	0.7	0.4	1.3	11.4	0.68
T3b	3.5	3.5	6.4	99.5	0.46
T3c	5.6	5.9	8.1	161	0.27
T3d	12.3	11.5	14.6	313.4	0.21
T3e	16.3	17.1	19.0	478.2	0.1
T4	1.4	1.1	2.1	14.8	0.5
T5	<0.1	<0.1	<0.1		

where d is the thickness of the film and $f(M)$ is the function which describes the evolution of the degree of modification with depth x. $\bar{M}$ values obtained for PVC films modified using different reaction conditions are listed in Table 3 together with data obtained by conventional FTIR−IR spectroscopy. Comparison of both values shows that they agree satisfactorily, within the experimental error indicating the accuracy of the confocal Raman microscopic technique.

Diffusion Coefficients. To understand the modification reaction of the film and to describe the observed concentration gradient, it is supposed that the entire process is composed of three steps, each of them with its own reaction rate constant. The first step after immersing the film into the reaction solution is the swelling of the polymer film by the reaction medium, i.e., the diffusion of the solvent into the membrane (k_1). The second step is the transport of the modification reactant to the functional groups of the polymer (k_2), and the third step is the reaction itself (k_3). The existence of a gradient of the degree of modification across the film indicates clearly that the entire process is diffusion-controlled in the sense that the transport of the solvent and the reactant through the membrane must be slow in comparison to the nucleophilic substitution reaction ($k_3 > k_2, k_1$). As has been shown elsewhere,[22] diffusion of the relatively small solvent molecules proceeds very fast in comparison to the transport of the reactant ($k_1 > k_2$). Thus, k_2 is the rate constant which mainly controls the modification reaction. The depth profiles of reacted polymer shown above therefore also provide information on the diffusion at the appropriate reaction times. We will show here that an "effective diffusion constant", D, for the reacting species can be determined. Consider a plane film of thickness d with surfaces in contact with an excess of the reactant species at all times. Since there is no net transport of reacted species across the central plane of the film, the boundary conditions for the concentration, C, of the reacted species as a function of distance from the central plane can be written

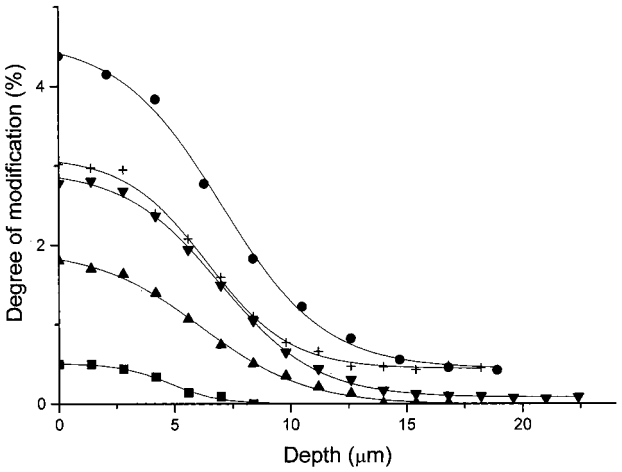

Figure 6. Evolution of depth profiles with time as recorded for a PVC film 41 μm) modified in H_2O/DMF 1:5 at 30 °C for 4 (■), 14 (▲), 22 (▼), 29 (+), and 46 h (●). Lines correspond to the fitting results using eq 4.

$$C = C_0 \qquad x = \frac{d}{2},\ t \geq 0 \tag{2}$$

$$\partial C/\partial x = 0 \qquad x = 0,\ t \geq 0 \tag{3}$$

For Fickian diffusion, a solution is obtained[25] as

$$C/C_0 = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{d^2}\right\} \times \cos\left[\frac{(2n+1)\pi x}{d}\right] \tag{4}$$

This series converges rapidly for large times t. Fits were performed on selected data for aminothiophenol-modified PVC, and these showed fair agreement with the data in favorable cases. However, considerably better agreement could be obtained with the coefficients of $\cos[(2n+1)\pi x/d]$ in eq 4 allowed to vary freely. As an example, Figure 6 shows the fits obtained for the system **T1**. Table 4 shows the difference between the coefficients as predicted by eq 4 and those obtained as fitting parameters in a typical case.

Although the agreement is good for the $n = 0$ coefficients, the latter ones obtained as fitting parameters are significantly larger than those predicted from eq 4. Possible reasons include the inadequacy of a single diffusion/reaction constant in a medium which is known to be inhomogeneous in terms of chemical composition. Nevertheless, the technique provides an estimate of the combined diffusion/reaction constant from the dominant

Table 4. Values for the First Four Coefficients of cos [(2*n* + 1)*πx*/*d*] Obtained from Eq 4 and as Fitting Parameters (Sample T1d)[a]

n	coeffs from eq 4	coeffs from fit to data
0	0.7922	0.7781
1	0.0059	0.1788
2	1.8×10^{-6}	0.1404
3	0	0.0186

[a] Values used for the variables were $t = 10^5$ s, $D = 6.5 \times 10^{-12}$ cm^2/s, and $d = 3.6 \times 10^{-3}$ cm.

Table 5. Average Diffusion/Reaction Constants Obtained from Fits to Film Modification Depth Profiles as a Function of Reaction Conditions

sample	temp (°C)	proportion H_2O/DMF	av diffusion/reaction constant D (cm^2/s)
T1	30	1:5	6.5×10^{-12}
T2	30	1:7	17.0×10^{-11}
T3	40	1:5	4.1×10^{-11}

$n = 0$ term. Values obtained from individual fits for different reaction times were averaged, and the results are shown in Table 5, with the different reaction parameters. As expected, the constant D is increased by raising the reaction temperature, but the influence of solvent proportion in the reaction mixture is far more pronounced. Values obtained here for D are similar to diffusion constants determined for molecules of similar size in PVC.[26] Furthermore, the values are significantly smaller that those reported for small molecules such as water.[27] This tends to confirm that diffusion of reactant, rather than the reaction itself or the progress of solvent, is the rate-limiting step.

In summary, we note here the potential for using depth profiles of modified polymers to obtain quantitative information on the combined diffusion/reaction rates.

Surface Selectivity. It is of general interest to find reaction conditions that entail a high surface selectivity, that is, high degrees of modification at the surface while the bulk inside the film remains unreacted. We propose to define the surface selectivity SS as follows

$$\mathrm{SS} = 1 - \frac{\int_0^{d/2} f(M)\,\mathrm{d}x}{{}^1/_2 d M_{\mathrm{surf}}} \qquad (5)$$

where M_{surf} is the degree of modification at the surface of the film.

To study the chemical modification of the film and controll the surface selectivity, PVC films were modified in different conditions with 4-aminothiophenol, varying reaction time, temperature, and composition of the solvent. The evolution of the depth profiles with time as recorded for a PVC film (41 μm) modified in H_2O/DMF 1:5 at 30 °C is presented in Figure 6. It can be seen that longer reaction times favor both higher degrees of modification at the film surface and a deeper penetration of reactant. Surface selectivities were calculated from the depth profiles according to eq 5 and are summarized in Table 3. As expected, the values decrease with increasing conversion of the film.

A second parameter that strongly influences the shape of the depth profile is the composition of the solvent/nonsolvent mixture. As can be seen in Figure 7, which represents the results for the reaction in H_2O/DMF 1:7 at 30 °C, the curves are considerably flatter than those in Figure 6 (solvent composition 1:5). This is explained by the enhanced swelling of the film which facilitates both the contact between polymer and reactant leading to higher degrees of modification at the surface (at the same reaction times) and a faster distribution of the reactant within the film. This last point had also been deduced from the higher diffusion coefficients calculated from the corresponding depth profiles (Table 5). As a consequence, we observe lower surface selectivities, which decrease more rapidly with reaction time (Figure 8).

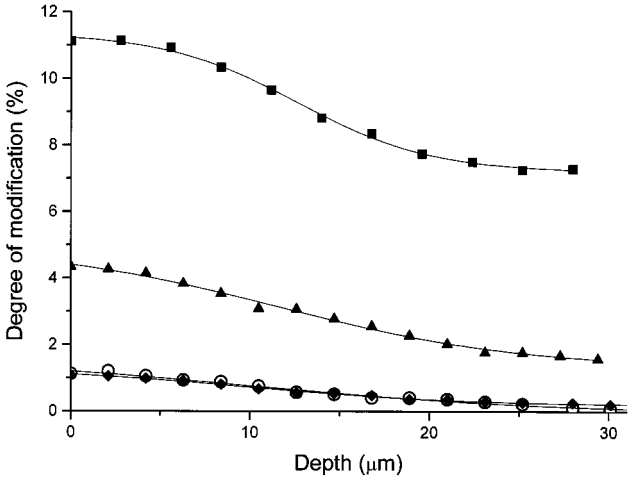

Figure 7. Evolution of depth profiles with time as recorded for a PVC film (58 μm) modified in H_2O/DMF 1:7 at 30 °C for 2 (◆), 5 (○), 7 (▲), and 23 h (■).

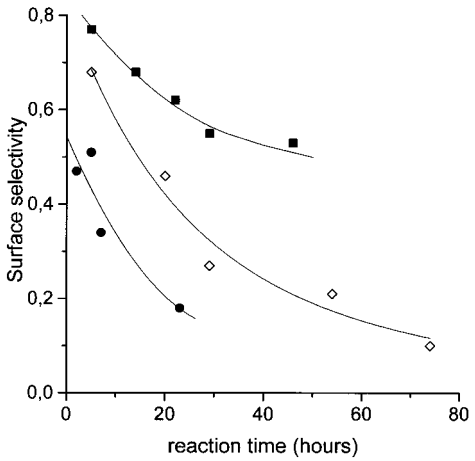

Figure 8. Evolution of surface selectivities with reaction time for modification of a PVC film in 4-aminothiophenol in H_2O/DMF 1:5 at 30 °C (■), H_2O/DMF 1:7 at 30 °C (●), and H_2O/DMF 1:5 at 40 °C (◇). Lines are guides for the eyes.

The strong influence of the solvent quality on the degree of modification of the films is also shown in Figure 9, where M_{surf} is represented as a function of the volume fraction of the nonsolvent (H_2O) for a PVC film exposed to the reaction solution for 5 h at 30 °C. On one hand, H_2O volume fractions cannot be smaller than 0.12, to avoid that films dissolving during the reaction. On the other hand, values larger than 0.2 impede the reaction by hindering the transport of the reactant. However, the appropriate choice within this small region between 0.12 and 0.2 allows one to achieve a wide range of degrees of modification.

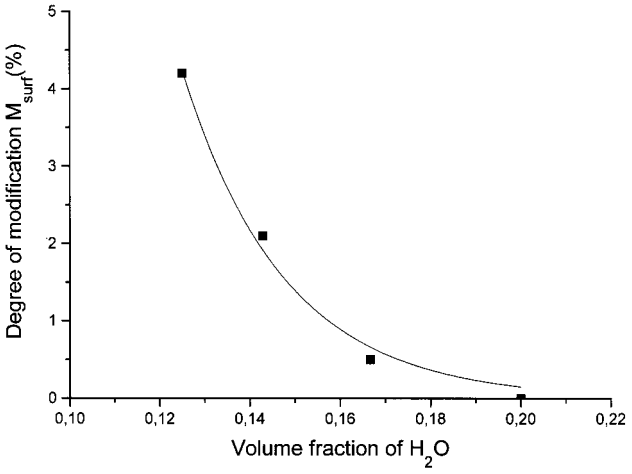

Figure 9. Influence of solvent quality on the degree of modification at the surface of PVC films modified for 5 h at 30 °C.

Conclusions

It was shown that the confocal Raman microscopy technique is an excellent means for analyzing the distribution of modified groups within transparent polymer films. By depth profiling of PVC laminates with aminothiophenol using this technique, it was shown that a gradient in the degree of modification is established. The surface selectivity of the reaction depends on solvent quality, temperature, and reaction time. High surface selectivities are generally favored by short reaction times, low temperatures, and low solvent quality while using a good solvent, higher overall degrees of modification with lower surface selectivity are achieved.

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