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Registry No. Decane, 124-18-5; dodecane, 112-40-3; tridecane, 629-50-5; tetradecane, 629-59-4; hexadecane, 544-76-3.

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Formation of Hydroxyl Groups in Plasma-Polymerized *N*-Vinyl-2-pyrrolidone by Reduction with Sodium Borohydride

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ABSTRACT: Reduction of carbonyl to hydroxyl groups in plasma-polymerized *N*-vinyl-2-pyrrolidone (PPNVP) has been accomplished by using an aqueous sodium borohydride solution. Quantitative estimates of the hydroxyl content, determined from IR spectroscopy, indicated that the interfacial reduction of PPNVP films (approximately 1.5 μm thick) increased the hydroxyl content in the bulk polymer by up to 2.3 mmol/g. This was increased further by reducing PPNVP in the form of a suspension rather than as a film. The IR analysis, based on poly(vinyl alcohol) and 1-hexadecanol reference compounds, indicated that secondary alcohol was greater than 90% of the total hydroxyl in the reduced polymer films.

Introduction

The composition and structure of solid polymer surfaces dominate such properties as wettability,[2-4] adhesion,[3-5] friction,[3,4] permeability,[6] and biocompatibility.[7,8] Consequently, procedures for the surface modification of materials to improve interfacial properties are of considerable technological importance. One approach has been the use of plasma polymerization,[9,10] also referred to as glow discharge polymerization.

Plasma-polymerized films can be prepared with a wide range of compositions[10] and surface energies[10,11] through the choice of monomer and discharge reaction conditions. The deposition is largely independent of the substrate materials and is surface specific, so that a polymer (or other material) can be modified with little effect to its bulk properties. While plasma polymerization does have several attractive advantages over other methods of surface modification, there is a significant lack of chemical control over the polymer product. Reactions in the low-temperature plasmas are dominated by electron impact events such as ionization and dissociation, with active species reacting and recombining in the plasma and at the substrate surface. Because of the high energies involved in the process, this technique does not provide films with well-defined structures and specific functional groups.[12] Plasma-polymerized films prepared from monomers with oxygen or nitrogen functional groups invariably are polyfunctional, cross-linked, heterogeneous polymers.

Nevertheless, the objective of our studies has been to prepare plasma-polymerized films with a well-defined functional group that could serve as a reactive site for further modification. The common approaches for introducing specific functional groups into plasma polymers have been to vary the monomer and discharge conditions[13] or to use or include a gas such as CO_2[14] or NH_3,[15] which tend to increase carboxyl and amine groups, respectively. However, these reactions do not normally proceed to high yield with respect to a specific functional group. Nakayama et al.[15] have reported that primary amine in NH_3 plasma treated[16] polystyrene was 15–20% of total nitrogen content.

A novel alternative approach to functionalize a plasma-polymerized material is to take advantage of the functional group that is easily generated in the process: carbonyl groups. Plasma polymers derived from oxygen-containing monomers are invariably rich in carbonyl, regardless of the initial monomer structure. Thus, if a polymer or nonorganic was surface modified by plasma polymerization, carbonyl groups in the modified layer could then be derivitized to introduce a desired functional group. The major difficulty of this approach is associated with the very poor solubility of cross-linked plasma polymers in organic solvents. Derivitization has to be accom-

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plished across an ill-defined interface between a constrained solid polymer and the liquid reaction medium. However, Whitesides et al.[17,18] carried out several derivitization procedures on chromic acid oxidized polyethylene. These included the surface reduction of carboxyl to hydroxyl by using diborane in THF and by using an etheral solution of lithium aluminum hydride.[17] More recently, Dias and McCarthy[19] reported a series of surface-specific (i.e., <300-Å depth) derivitization reactions performed on fluorocarbon and fluorchlorocarbon polymers. In each of these previous studies the objective was to introduce specific functional groups into the surface of relatively unreactive solid polymers. Their results indicate that derivitization of a plasma-polymerized polymer should be feasible, depending on the effect of the additional geometric constraint imposed by the cross-links in a plasma polymer.

In this report, we have focused on the formation of hydroxyl groups by reduction of carbonyl in plasma-polymerized *N*-vinyl-2-pyrrolidone (PPNVP), a polymer which is rich in carbonyl.[20] To our knowledge, bulk reduction or chemical modification of a cross-linked plasma-polymerized polymer has not been reported previously. It was of interest, therefore, to appreciate how much hydroxyl could be formed in the plasma polymer. Thus, we conducted our experiments on relatively thick films (ca. 1.5 μm) deposited on glass followed by bulk rather than surface characterization. Reactions were carried out by using aqueous solutions of sodium borohydride. The increase in hydroxyl content in PPNVP after reduction was estimated from infrared measurements.

Experimental Section

Materials. *N*-Vinyl-2-pyrrolidone (NVP, from Aldrich) was distilled under vacuum, degassed three times by the freeze (dry ice/acetone)–thaw technique under vacuum, and stored under argon at −4 °C. Poly(vinyl alcohol) (PVA, 100% hydrolyzed, MW 14 000, from Aldrich) was finely ground, dried under vacuum at 50 °C for 12 h, and stored in a desiccator over fresh phosphorus pentoxide. 1-Hexadecanol (Aldrich) was recrystallized (mp, 55 °C) from hot ethanol and stored under argon in the refrigerator. Acetic anhydride (99+% grade, Aldrich) was distilled and stored over 3A sieves and under argon. Potassium thiocyanate (99+%, ACS grade, Aldrich) was finely ground and stored in the desiccator. Potassium bromide (IR grade, Fisher) was finely ground, dried overnight at 140 °C, and stored in the desiccator. Metal hydride reducing agents, sodium borohydride (99%, Aldrich), lithium aluminum hydride (1.0 mol, solution in THF, Aldrich), and other chemicals were used as received.

Cleaned glass microslides (75 × 25 mm^2) were used as substrates for the plasma polymerization. The glass slides were cleaned by using a freshly prepared solution of H_2SO_4 and Nochromix (Godax Laboratories Inc.), thoroughly washed with distilled water and then with refluxing acetone vapor in a Soxhlet extraction system for 24 h, and dried at 80 °C under vacuum.

Plasma Polymerization of NVP. Thin films of plasma-polymerized *N*-vinyl-2-pyrrolidone (PPNVP) were prepared by using an inductively coupled radiofrequency (13.56 MHz) glow discharge in a flow-through Pyrex reactor system.[20] NVP monomer was plasma polymerized for 2 h at 30 W net discharge power, a reaction pressure of 3×10^{-2} Torr, and a monomer flow rate of 0.28 cm^3 (STP) min^{-1}. Under these conditions, hydrophilic polymer films of PPNVP approximately 1.5 μm thick were obtained on glass slides. At the end of the reaction period, the base pressure (ca. 5×10^{-3} Torr) was restored and maintained for 1 h. The chamber pressure was then raised to atmospheric with argon. PPNVP films on glass slides were removed from the reactor and stored in a desiccator over phosphorus pentoxide.

Reduction of PPNVP. An aqueous solution (200 mL, 0.26 mol) of sodium borohydride was freshly prepared and stirred slowly at room temperature. A PPNVP film sample supported on a glass slide was immersed in the solution and left stirring for the selected reaction time (0.5–48 h). Reactions were performed at room temperature under a constant argon purge.

After reaction, the polymer was sonicated in distilled water, washed three times in distilled water, and then left in stirring water for 12 h. Polymer was then washed twice in acetone and vacuum dried at 80 °C for 12 h. Dry polymer was stored in a desiccator over phosphorus pentoxide. The reduction was repeated with a suspension of PPNVP. A PPNVP film was removed from the glass slide by sonication in distilled water and then dried under vacuum at 80 °C for 12 h. The dry polymer was finely ground and added to the reducing solution. The reaction was carried out for 30 h. After reaction, the polymer was filtered from solution and then washed and dried as before.

Infrared Spectroscopy. Spectra of polymer samples were obtained by using the KBr pellet method with a Digilab FTS-14 Fourier transform infrared spectrometer equipped with a TGS detector. Over 100 sample scans and reference scans at a resolution of 8 cm^{-1} were averaged and subtracted. IR spectra were then transferred to a DEC VAX 11/780 for data processing.

Materials used in the preparation of KBr pellets were preground, dried, mixed, and ground together before being pressed into a pellet under vacuum. In the case of PVA samples, repeated grinding and molding were required to obtain a satisfactory pellet.

Quantitative estimation of the increased hydroxyl content in reduced PPNVP samples was accomplished by using the relative (integrated) absorbance ratio method with added internal standard (potassium thiocyanate). 1-Hexadecanol and PVA were used as reference compounds for primary and secondary alcohol groups, respectively. The percent primary and secondar alcohol contents in plasma-polymerized samples was estimated by using a curve-fitting procedure based on linear combinations of the two reference compounds.[21] Using this result, the increased hydroxyl content could then be estimated from the standard calibration curves of the two model compounds, subtracting the result obtained for the original PPNVP control.

The calibration curves for the model compounds were obtained from the ratio of the integrated absorbance at 1180–980 cm^{-1} (from ν(C–O) in COH) to the integrated absorbance at 2150–2000 (from KSCN), plotted against the concentration ratio of model compound to KSCN. The standard calibration curve for 1-hexadecanol was linear and passed through the origin (correlation coefficient = 1.000). The calibration curve for PVA showed a slight deviation from linearity, with an intercept close to zero for the concentration range employed (correlation coefficient = 0.98).

Hydroxyl contents (mmol/g) in PVA and 1-hexadecanol reference compounds were quantified by using the analytical method of Stetzler and Smullin.[22] This method involves the acid-catalyzed esterification of alcohol groups with excess acetic anhydride, followed by the addition of aqueous pyridine solution to hydrolyze unreacted reagent. Hydroxyl content was calculated from the titration of test solutions and blank reference against standardized potassium hydroxide solution. This analysis gave 21.46 mmol/g (calculated value = 22.7) for PVA and 4.05 mmol/g (calculated value = 4.13) for 1-hexadecanol.

Results and Discussion

Reduction Reaction. Nucleophilic metal hydrides have been widely used for organic reductions in solution. However, in our preliminary experiments on PPNVP, using $LiAlH_4$ in anhydrous THF, no reaction was detected. A large excesses of $LiAlH_4$ and long reaction times provided no change to the infrared spectrum of PPNVP (see Figure 1a,b). The absence of detectable reaction in this heterogeneous system was attributed to the lack of polymer solvation.

PPNVP, like any plasma-polymerized organic material, is a cross-linked polymer with an irregular complex structure; however, PPNVP is hydrophilic and will absorb 51.7% water by weight.[23] This suggested that the reduction of carbonyl groups in the polymer should be feasible in aqueous or other polar media. Sodium borohydride is a metal hydride that can be used in polar solvents for the selective reduction of aldehydes and ketones.[24,25] Indeed, the reduction by $NaBH_4$, unlike $LiAlH_4$, requires the presence of an electrophilic catalyst such as a protic sol-

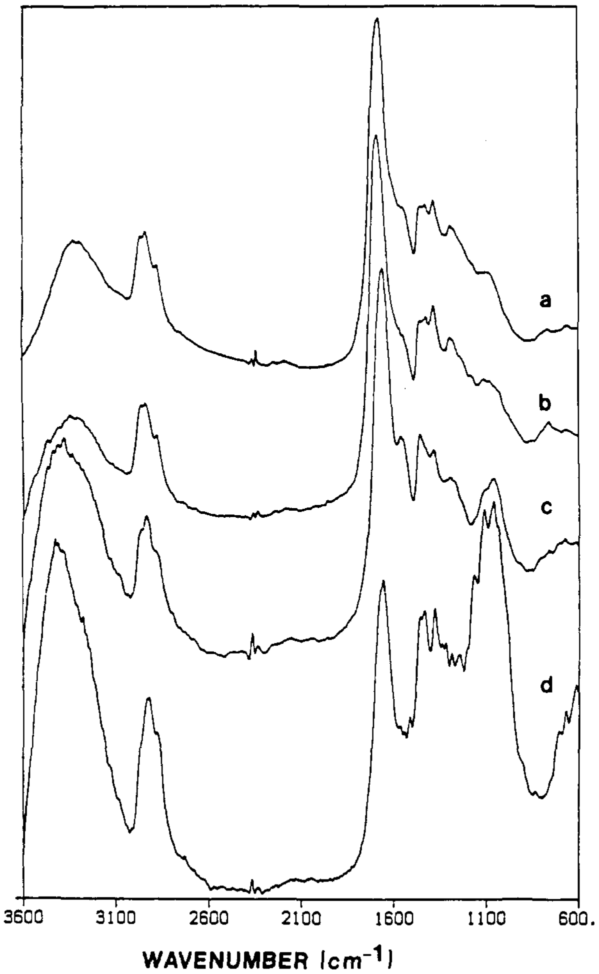

Figure 1. FT-IR spectra, 3600–600-cm^{-1} region, of PPNVP and reduced PPNVP samples. (a) Spectrum of PPNVP prepared at 30-W discharge power, 0.03-Torr reaction pressure, and 0.28 cm^3 (STP) min^{-1} monomer flow rate. (b) Spectrum of PPNVP reduced in the film form by 1 mol of $LiAlH_4$ in THF at room temperature for 68 h. (c) Spectrum of PPNVP reduced in the film form by 0.26 mol of aqueous $NaBH_4$ at room temperature for 30 h. (d) Spectrum of PPNVP reduced in suspension form by 0.26 mol of aqueous $NaBH_4$ at room temperature for 30 h.

vent. The reaction with carbonyl groups is believed to occur by hydride ion transfer to the carbonyl carbon with prior protonation of the carbonyl oxygen.[26] $NaBH_4$ will react directly with water but very slowly.[27] In contrast, our attempts to conduct the reaction in either anhydrous methanol or 2-propanol were unsuccessful, since both alcohols reacted with $NaBH_4$ at room temperature to form white precipitate within 1 and 6 h, respectively.

The effect of using $NaBH_4$/water rather than $LiAlH_4$/THF to reduce carbonyl to hydroxyl can be seen by comparing parts a–d of Figure 1. Prominent features of these spectra are the strong carbonyl (ν(C=O), ca. 1670 cm^{-1}) and hydroxyl stretching absorptions (ν(O—H), ca. 3500–3200 cm^{-1}). This latter band is complicated by contributions from ν(N—H) absorptions derived from any amide or amine groups present in the polymer.

In the reduced PPNVP samples (Figure 1c,d), the "hydroxyl peak" (3500–3200 cm^{-1}) has increased, while the intensity of the carbonyl absorption has decreased compared with that of underivitized PPNVP. However, the most obvious change was the concomitant appearance of a strong absorption at 1180–980 cm^{-1} attributed to ν(C–O) in COH, indicating the formation of hydroxyl groups. Other notable spectral features of the reduced polymer were in the 1500–1300-cm^{-1} region, which contains overlapping bands derived from C–H deformation absorptions such as methylene C–H deformation at 1455 cm^{-1} and δ(C–H) in CH_2 adjacent to a carbonyl group at 1415 cm^{-1}.

Figure 1c shows that hydroxyl groups were formed by reduction of the PPNVP film, but the figure also shows that the reaction did not go to completion, with the carbonyl absorption still the most prominent. The cause of the observed inhibition was not clear, with several possible contributing factors such as geometric constraints, product inhibition, surface area, and mixing efficiency. In these film experiments, stirring was kept relatively slow to avoid sweeping the film off the glass. To evaluate qualitatively the nature of the observed inhibition, the reduction was repeated using a suspension of finely ground PPNVP, rather than films. The result is shown in Figure 1d. The increased conversion thus reflects improved mixing and interfacial contact between polymer and reaction medium. The few remaining unreacted carbonyls may then be attributed to inaccessible groups, presumably constrained below the polymer surface. An implication of this result is that a thinner PPNVP film (<0.5 μm is more typical for a surface modification procedure) covalently bound to a polymer substrate could be reduced almost to completion. The hydroxyl groups could then be used in a subsequent modification procedure such as immobilization, which is of considerable importance for a wide range of biomedical applications.

In solution, reduction of carbonyl can be inhibited by steric factors or the presence of conjugated substituents.[26] In a biphasic system, the extent of reaction will be largely determined by the availability of reactive functional groups at the solid/liquid interface. The initial interfacial concentration of reactants is strongly influenced by the nature and extent of the polymer–solvent interactions. Thus, reduction of carbonyl in PPNVP by $LiAlH_4$ was not observed because THF is a nonsolvent for the polymer. The work of Whitesides et al.[17,18] and Dias and McCarthy[19] infers that carbonyl groups located at the polymer surface (i.e., <10-Å depth)[28] should have been reduced by $LiAlH_4$. However, for a 1.5-μm-thick PPNVP film and with assumption of a uniform spatial distribution of carbonyl groups, less than 0.1% of the total carbonyl were available for reaction. Such low conversion would not be detected by IR analysis of the bulk polymer. For significant reaction to occur, the carbonyl groups require sufficient mobility to approach the polymer surface and undergo solvation. In this way, an initial three-dimensional distribution of carbonyl is established in the liquid phase.

The phenomenon of functional group mobility in plasma-treated polymers has been the subject of several publications;[29,30] while the effects of the same phenomenon in cross-linked plasma-polymerized materials has not been studied in detail. However, PPNVP shows considerable contact angle hysteresis with a water probe.[20] This we attributed to reorientation effects that occur in the polymer surface in order to minimize the polymer–water interfacial free energy. As a good solvent for PPNVP, water is able to penetrate into the film, disrupt intermolecular associations such as hydrogen bonding, and swell the cross-linked polymer. Swelling of PPNVP increases interchain spacing and segmental mobility, exposing additional carbonyl groups initially in the bulk polymer to the aqueous phase. Solvation of the carbonyl then enables the protonation and hydride ion transfer to occur.

Quantitative Estimation of Hydroxyl Groups. Determination of hydroxyl content in polymers using IR spectroscopy is usually accomplished by using the hydroxyl stretching absorption ν(O-H)[31] at 3600–3200 cm^{-1}. In our studies, the choice was complicated by the presence of

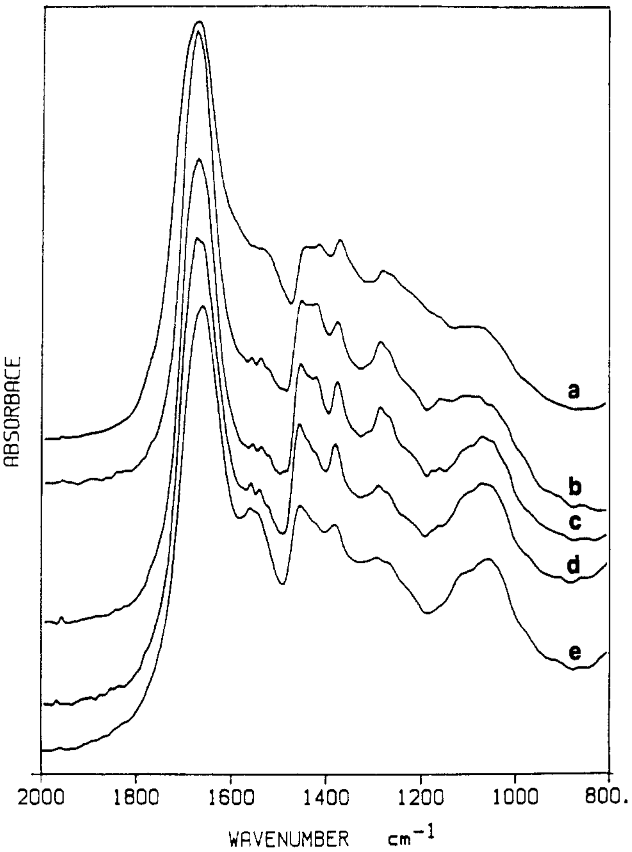

Figure 2. FT-IR spectra, 2000–800-cm^{-1} region, of PPNVP reduced in the film form by 0.26 mol of $NaBH_4$ at room temperature for (a) 0 h (original PPNVP), (b) 1 h, (c) 5 h, (d) 20 h, and (e) 30 h.

Table I
Variation in Absorption Ratio (ν(C=O)/ν(C—O)) in PPNVP with Reaction Time[a]

reactn time, h	$A(\nu(C{=}O))/A(\nu(C{-}O))$	reactn time, h	$A(\nu(C{=}O))/A(\nu(C{-}O))$
0 (i.e., PPNVP)	14.50	12.0	3.32
0.5	9.53	20.0	3.04
1.0	8.98	30.0	2.65
4.0	4.19	48.0	3.11
5.0	4.33	30.0 (suspension)	0.51
8.0	3.84		

[a] Reductions were carried out on PPNVP films in 0.25 mol of aqueous $NaBH_4$.

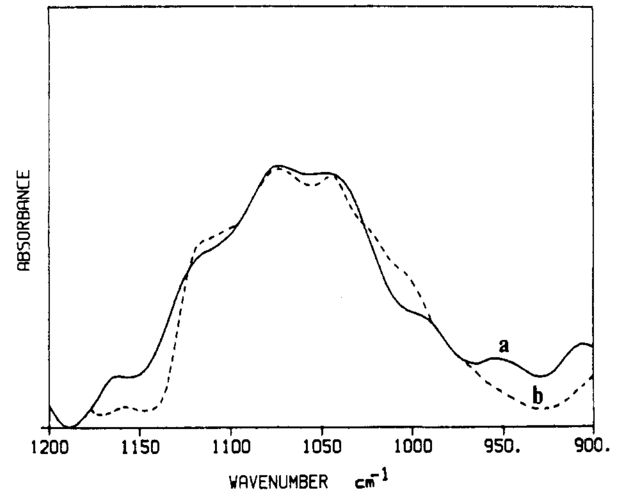

Figure 3. FT-IR spectra, 1200–900 cm^{-1}, of (a) PPNVP reduced in the film form by 0.26 mol of $NaBH_4$ for 5 h (solid line) and of (b) a linear combination of PVA (scale factor = 1.00) and 1-hexadecanol (scale factor = 0.075) after shifting to lower wavenumbers by 25 cm^{-1}.

nitrogen functional groups and the concomitant spectral interference from N–H absorptions in the 3500–3200-cm^{-1} range. It became evident in our preliminary studies that the ν(C–O) of COH[31-34] at 1180–980 cm^{-1} was very sensitive to the progress of the reaction. Figure 2 and Table I show the effect of reaction time on the intensity of the C–O stretching absorption. The relative intensity of this band increased with reaction time (up to about 20–30 h). Hence this absorption band was used in the determination of hydroxyl content.

Figure 3 provides the result of a typical curve-fitting procedure for the 1180–900-cm^{-1} range, based on linear combinations of the reference spectra for PVA and 1-hexadecanol. The dashed spectrum in Figure 3 is a linear combination of PVA and 1-hexadecanol in the ratio 1:0.075. The curve-fitting analysis for all reduced PPNVP indicated that the hydroxyl contents consisted of greater than 90% secondary alcohol (see Table II). Best fit was obtained by shifting the composite reference spectrum to 25 cm^{-1} lower wavenumbers. Based on this analysis, the absorptions at 1075 and 1045 cm^{-1} in reduced PPNVP were assigned to secondary and primary alcohol, respectively. This latter assignment is consistent with that recently observed for primary alcohol in a polyocten-8-ol.[34] The ν(C–O) frequency in alcohols is sensitive to the molecular environment; hydrogen bonding, unsaturation, and chain branching all decrease the vibrational frequency.[33] Consequently, the required shift appears consistent with the different molecular environments between the reference compounds and the reduced PPNVP. In the absence of appropriate branched model compounds for the cross-linked PPNVP, we used the two linear alcohols as reference compounds. The differences in hydrogen-bonding behavior and the effect of branching in PPNVP introduced a systematic error which diminished the accuracy of our quantitative determinations. The results are therefore considered quantitative estimates only.

The estimated increase in hydroxyl content in reduced PPNVP derived from the calibration curves for PVA and

Table II
Formation of Hydroxyl Groups in PPNVP Films by Reduction with 0.26 mol of Aqueous $NaBH_4$

reactn time, h	% 2° hydroxyl of total hydroxyl	increased hydroxyl content in reduced PPNVP, mmol/g	max hydroxyl in reduced PPNVP, mmol/g
0 (i.e., PPNVP)			1.87
0.5	96.9	0.58	2.45
1.0	94.5	0.71	2.58
4.0	93.4	1.62	3.49
5.0	95.4	1.71	3.58
12.0	93.4	1.99	3.86
20.0	92.3	1.92	3.79
30.0	91.2	2.27	4.14
48.0	92.3	2.22	4.09

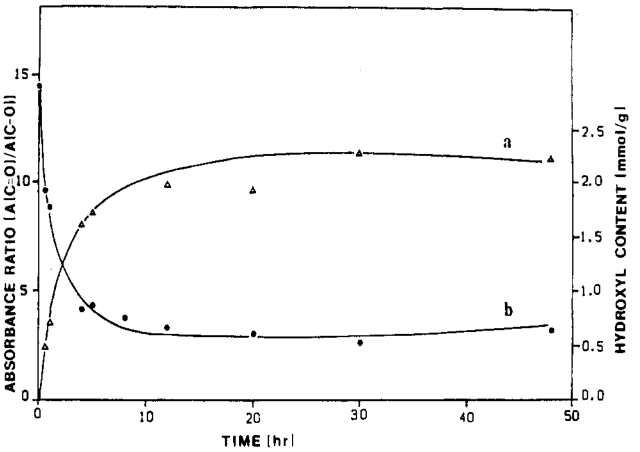

Figure 4. Variation in IR (integrated) absorbance ratio, $A(\nu(\mathrm{C{=}O}))/A(\nu(\mathrm{C{-}O}))$ (●), and increased hydroxyl content (mmol/g) (△) in PPNVP films reduced by 0.26 mol of $NaBH_4$ with reaction time.

1-hexadecanol are shown in Figure 4 and Table II. The results reflect quantitatively the effectiveness of the reduction and its progress with reaction time. Figure 4 includes the absorption ratio of ν(C=O) at 1670 cm^{-1} to ν(C—O) at 1180–980 cm^{-1}, which reflects the relative progress of the reaction.

We can attribute the increase in the ν(C—O) peak to increasing hydroxyl content in the polymers, since the same absorption in the PPNVP control is subtracted out in the calculations. This procedure minimizes errors caused by spectral overlap (e.g., from ν(C—C) vibrations). Consequently, the total hydroxyl content in the reduced polymers is probably somewhat higher than that reported in Figure 4, since the hydroxyl content in the original PPNVP can be assumed to be greater than zero. To reflect this, the maximum total hydroxyl content has been included in Table II. These values assume that IR band at 1180–980 cm^{-1} in the original PPNVP consists entirely of ν(C–O) in COH and thus ignores other spectral contributions.

In summary, this study on the reduction of PPNVP has shown that reproducible hydroxylated plasma-polymerized films can be obtained by using aqueous $NaBH_4$ as reducing agent at room temperature. Water plays an important role in solvating the cross-linked polymer and increasing the mobility of the carbonyl groups. Infrared analysis indicated that secondary alcohol was greater than 90% of the total hydroxyl content. Reduction increased the hydroxyl content in PPNVP films by up to 2.3 mmol/g. By reducing a suspension of PPNVP rather than films, the hydroxyl content was further increased.

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