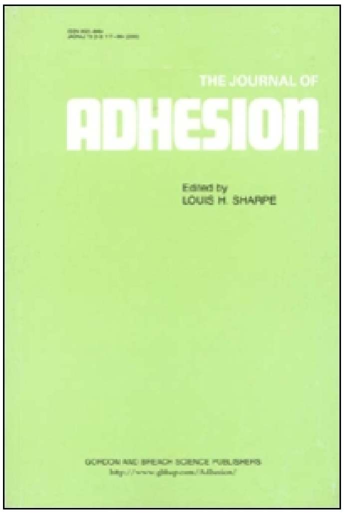

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Adhesion Improvement by UV Grafting onto Polyolefin Surfaces*

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High Density Poly(ethylene) (HDPE) and Poly(propylene) (PP) were subjected to several surface treatments, namely UV grafting of hydroxyethylmethacrylate (HEMA), plasma deposition of HEMA and oxygen plasma treatment. Treated surfaces were subjected to two post-treatment routines (extraction with ethanol and high temperature aging). The effect of these treatments on the adhesion of HDPE and PP to epoxy coated studs was evaluated by a pull test. No adhesion at all was recorded on untreated samples. On the other hand, all the treatments yield high bond strength in the case of HDPE: an average bond strength of about 290 kg/cm^2 and of about 200 kg/cm^2 was observed after UV grafting and plasma treatments. The treated samples were practically insensitive to post-treatments. As to PP, which undergoes chain scission in plasma, it is best treated by the comparatively milder conditions of UV grafting, which yields an average bond strength similar to that observed on HDPE. O_2 and HEMA-plasma-treated PP show a mean bond strength close to 50 kg/cm^2, and are deeply affected by the post-treatment routines.

KEY WORDS adhesion; polyolefin surfaces; plasma; plasma deposition; UV grafting; aging; HEMA; surface treatment; XPS.

INTRODUCTION

Several surface modification techniques are currently available to improve adhesive properties of polymer surfaces.[1] Most of them involve the introduction of polar groups on the surface, in order to increase both the solid surface tension (which affects adhesion by increasing the wettability of the solid by the liquid adhesive) and the physico-chemical interactions between the adhesive and the adherend.

The overall performance of a glued joint is, however, affected by several other mechanisms, namely the strength of the boundary layer and the extent of dynamic phenomena going on at the interface at the curing temperature.[2] Among them, overturning of introduced polar groups and outdiffusion of low molecular weight untreated chains are the most important.[2,3] The effect of the dynamic behavior on adhesive strength can be quite dramatic,[2,4] especially in the case of those polymers

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(such as poly(propylene) (PP)) which undergo chain scission in plasma.[1] Even if improved adhesion can be obtained in plasma-treated PP joints[5,6,7] (especially when the adhesive phase is applied/cured at low temperature, where the kinetics of macromolecular rearrangement slows down),[8] it is of some interest to evaluate the performances of other surface modification techniques, especially those which require less energetic treatments.

Among the different options available for the surface modification of polyolefins, surface grafting promoted by UV light is a very interesting technique:[9–12] polar monomers can be easily grafted on polyolefins by the radical chemistry of methacrylate monomers. Grafting on semicrystalline polymers yields a bumped surface texture, likely due to the difference in the activation reaction in amorphous and crystalline domains,[13,14] and creates sites for mechanical interlocking. Hydroxyethylmethacrylate (HEMA) is a good candidate monomer for UV grafting: it is rather cheap, it contains a polar hydroxyl group and can be easily grafted to polymeric substrates by UV light.[13,14]

In this paper we discuss the effect of surface UV-promoted photografting of hydroxyethylmethacrylate (HEMA) on the adhesive properties of polyolefin-epoxy joints (evaluated by a pull-off test).

Results are compared with those obtained with polyolefin surfaces oxidized by O_2 plasma, and with polyolefins coated by a plasma-deposited PHEMA film (in the latter cases the treated surfaces are smooth). Samples are evaluated after treatment and after two different post-treatment routines: extraction in refluxing ethanol for 24 h and heat-aging at 100°C for the same time. These post-treatment routines are expected to give interesting information on the stability (thermodynamic and kinetic) of the interfaces created by the treatment.

EXPERIMENTAL

Materials

Samples were prepared from High Density Poly(ethylene) (HDPE) (Eraclene H, EniChem Polimeri) and PP (SP179, HIMONT) plaques ($10 \times 10 \times 0.2$ cm). Before treatment, they were extracted for several hours in boiling ethanol, to remove additives. After this treatment, the oxygen signal from XPS was greatly reduced as compared with the unextracted sample. HEMA (97% purity) and benzophenone (BP, 99%) were purchased from Aldrich Chemie, and used without further purification. Oxygen from lecture bottles (Carlo Erba) was used in plasma treatments.

Plasma Treatments

Oxygen plasma treatments were performed in a capacitively-coupled parallel-plate, aluminum reactor, with the samples located on the water-cooled grounded electrode. The volume of the reactor is about 20 dm^3, and the distance between the electrodes is 15 cm. The diameter of the lower, grounded, electrode is 35 cm, while the diameter of the upper electrode is 15 cm. The base pressure of the reactor is 1×10^{-4} Pa. The plasma parameters were the following: excitation frequency 13.56 MHz, flow rate 8 standard cubic centimeter per minute (sccm), treatment time 30 s, pressure 2 Pa. The gas flow is controlled by MKS mass flowmeters and flow controllers.

Deposition of PHEMA coatings from plasma was performed in the same reactor. HEMA was kept in a glass vessel, connected to the reactor *via* a glass valve and a glass-metal joint. The temperature of the monomer in the vessel was maintained at 25°C throughout the cycle by means of a water bath. The flow rate, calculated by the initial increase in the system's pressure with time after cutting the vacuum pump off, was about 100 cc(STP)/min.

The deposition rate was monitored by a Quartz Crystal Microbalance (Intellemetrics) assuming a density of 1 g/cm^3. A coating of 100 nm thickness was deposited.

Treated samples were rinsed three times with hot ethanol (*ca.* 50°C).

UV Grafting

To perform photografting, samples were dipped for 30 min in 2% w/v BP in n-heptane. After this step, the photosensitized samples were put into a Pyrex® glass tube containing a 20% solution of HEMA in water. Oxygen was removed from the solution by fluxing N_2 for 30 min. The tube was then placed in an APQ 40 annular photoreactor (Applied Photophysics Ltd., London) and irradiated by a 400 W medium-pressure mercury lamp for 30 min. Treated samples were washed with hot ethanol. This experimental routine produces a coating which is about 20 μm thick, as evaluated by optical microscopy.[14]

Adhesion Tests

Adhesion tests were performed on samples subjected to two different post-treatment routines, namely extraction in refluxing ethanol for 24 h and aging at 100°C for 24 h in an oven in laboratory atmosphere. Another set of samples was subjected to the adhesion test without any further treatment other than plasma or UV.

The adhesion between the treated polyolefins and an epoxy adhesive was evaluated by a pull-off test, performed using a Sebastian II instrument (Quad Group). Epoxy-coated pull studs were provided by the manufacturer. They were adhered to PP and HDPE samples, subjected to a cure cycle of 2 h at 110°C and then tested. Reported values are averaged over 10 measurements.

Surface Composition and Surface Morphology

XPS analysis was performed with a Perkin-Elmer PHI 5500 ESCA system. The instrument is equipped with a monochromated X-ray source (Al anode), operating at 14 kV and 250 W. The diameter of the analyzed spot was 400 μm. The base pressure was 10^{-8} Pa. Peak deconvolution and quantification of the elements were accomplished using the software and sensitivity factors supplied by the manufacturer. In fixed-angle measurements the electron take-off angle was maintained at 45°, while in angle-resolved measurements it ranged from 10° to 70°. Assuming a mean free path of 3.5 nm for the C_{1s} photoelectrons,[15] the resulting sampling depth is 1.8, 7.4, and 9.9 nm, respectively, for 10°, 45°, and 70° take-off angles.

Surface morphology was observed by a Cambridge Stereoscan 360 scanning electron microscope (SEM), equipped with a LaB_6 filament.

RESULTS

Surface Composition and Morphology of Treated Samples

Surface analysis of untreated, extracted samples reveals a composition close to 100% C (Table I). The small amount of oxygen observed on these samples is probably the result of surface oxidation occurring during the molding step.[1]

After treatment, the surface composition of HEMA UV-grafted PP and HDPE is close to the theoretical composition of PHEMA (Table I). Albeit very similar, the O/C ratio is systematically lower in PHEMA samples, likely the result of oxygen loss during polymerization in plasma.[16]

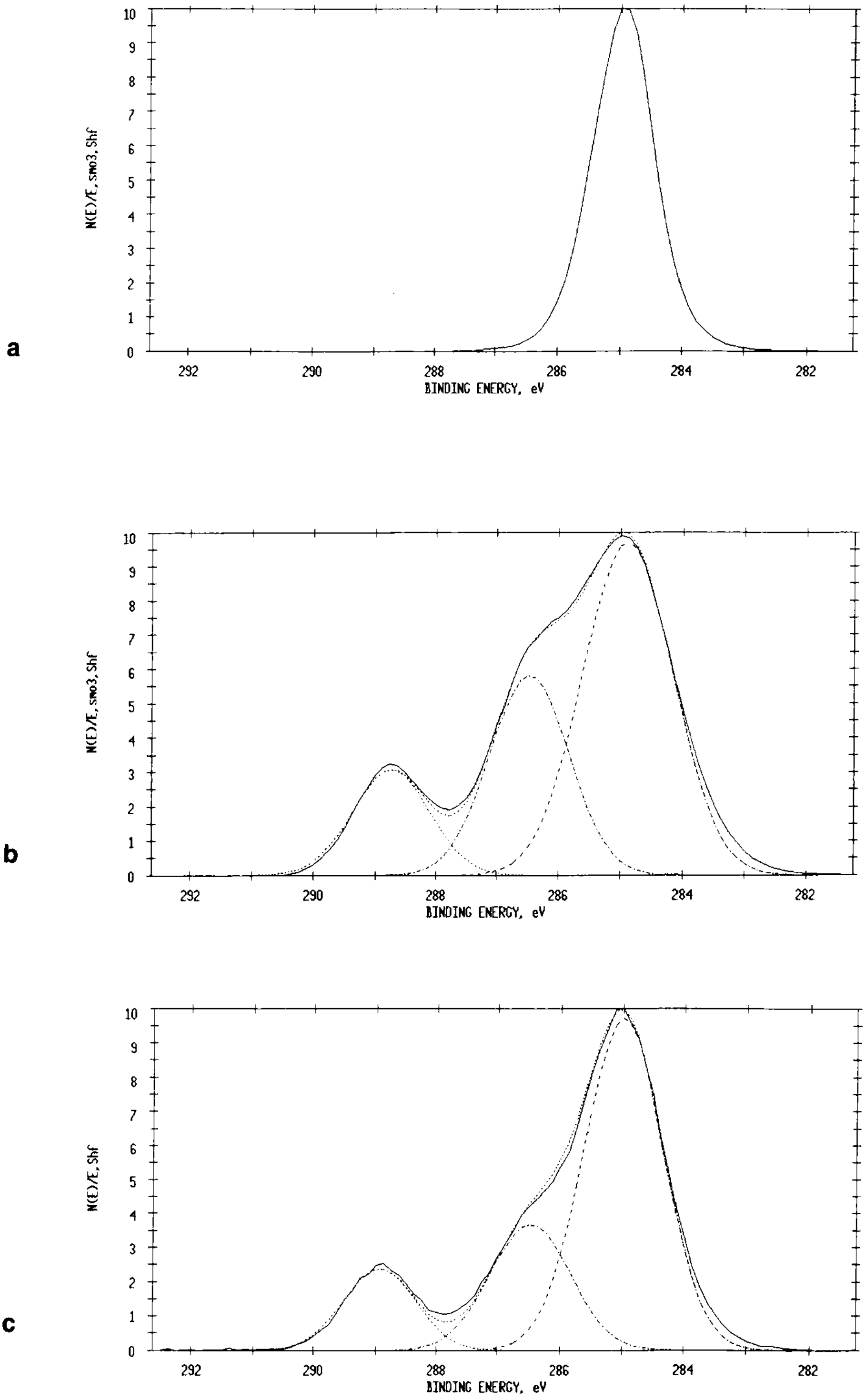
Angle-resolved XPS shows that both coatings are homogeneous within the XPS sampling depth. As to the C_{1s} peak, Figure 1 shows the effect of the treatments (here, as in the following, the take-off angle is 45°). The C_{1s} peak of untreated HDPE is shown in Figure 1a. The deconvolution of the C_{1s} peak of UV-grafted samples (Fig. 1b) yielded the typical 3:2:1 ratio of the $\underline{C}$—C:$\underline{C}$—O:$\underline{C}$OO components (285, 286.5, 288.9 eV, respectively), while an increase of the lowest binding energy component is observed in plasma-coated samples (Fig. 1c).

Major differences were observed in the surface morphology: UV-grafted surfaces display the typical bumped surface texture,[13,14] while surfaces of polyolefins coated by deposition from plasma are smooth.

The surface amount of oxygen on O_2-plasma-treated samples ranged from 15% (PP) to 20% (HDPE) (Table I). Deconvolution of the C_{1s} peak shows that the treatment yields a complex mixture of oxygen-containing functional groups (Fig. 1d). SEM analysis shows that the smooth morphology of untreated samples is unaffected by plasma treatment.

TABLE I
Surface composition (at. %), as detected by XPS, of untreated and treated HDPE and PP

Sample	O	C
Untreated HDPE	0.8	99.2
PHEMA, theoretical	33.3	66.6
HDPE + HEMA photografting	30.4	69.6
HDPE + HEMA coating from plasma	28.2	71.8
O_2-plasma-treated HDPE	20.1	79.9
Untreated PP	1.1	98.9
PP + HEMA photografting	31.4	68.6
PP + HEMA coating from plasma	26.2	73.8
O_2-plasma-treated PP	15.4	84.6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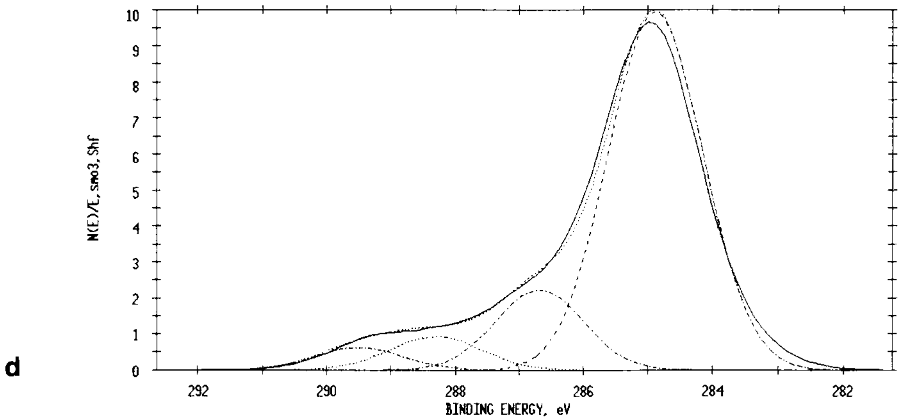

FIGURE 1 Curve fitting of C_{1s} peak of a) Untreated HDPE, b) HEMA-UV-grafted HDPE, c) HEMA-plasma-deposited HDPE, d) O_2-plasma-treated HDPE. Components are assigned to (in order of increasing binding energy): $\underline{C}$—H, $\underline{C}$—C; $\underline{C}$—O; O—$\underline{C}$—O, $\underline{C}$=O; O—$\underline{C}$=O.

Adhesion Tests and Composition of Fracture Surfaces

No adhesion was recorded on untreated samples and on photosensitized samples subjected to UV irradiation in N_2 purged water. Results of treatments and of post-treatment routines are shown in Figure 2. It is immediately clear that, despite the close chemical resemblance of the two polyolefins, both treatments and post-treatment routines yield rather different results. Fractures on HDPE are always cohesive within the substrate. The C_{1s} peak of fracture surfaces of HEMA-grafted HDPE are characterized by a sharp, symmetric peak (FWHM = 1.01 eV), which clearly indicates HDPE on both sides of fracture surfaces. Moreover, no effects of the post-treatment routine are readily detectable. On the other hand, PP shows more heterogeneous results: only in the case of surface-grafted PP are the adhesive strengths comparable to those measured on HDPE. Deposition of PHEMA and O_2 plasma treatment are clearly less effective: XPS analysis of the fractured substrate shows, in both cases, a higher amount of oxygen on the PP side of the site of fracture (Table II). This result indicates that the fracture is not cohesive in PP or, in other words, that some weak link exists in the composite structure made by the surface-treated samples and the adhesive.

Major effects are also observed when treated PP samples are extracted or heat-aged. Extraction with boiling ethanol destroys the adhesive properties in both cases. XPS analysis shows that the surface layer of PHEMA is removed by this treatment and only a small amount of oxygen is left on the extracted surface. On the other hand, no major modifications of the composition of the surface of O_2-plasma-treated PP are detected (as compared with the unextracted, plasma-treated PP), despite the dramatic decrease of the adhesive strength (Table III).

Also, a heat treatment lowers adhesion in PP/epoxy joints. In the case of deposition from plasma the general features arising from XPS analysis are similar to those observed in the as-treated case. O_2-plasma-treated, heat-aged PP, on the other hand, shows adhesive fracture at the epoxy-substrate interface.

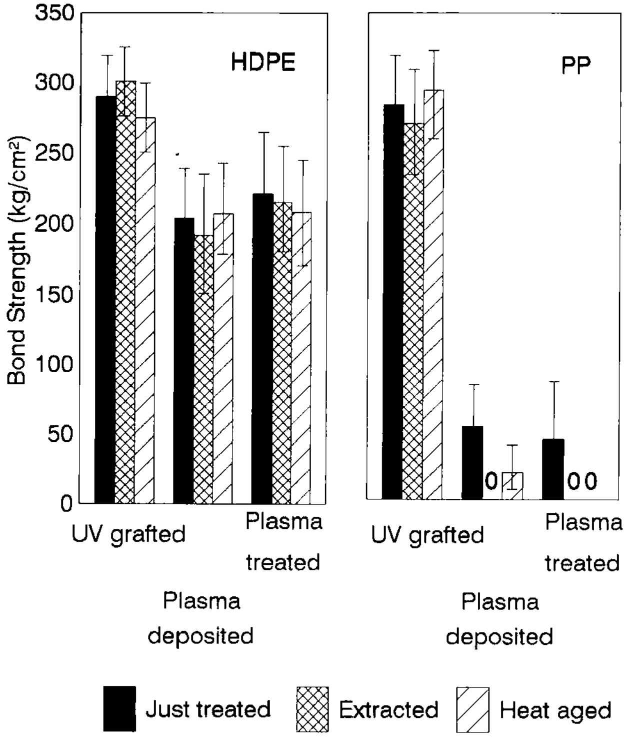

FIGURE 2 Bond strength as a function of treatment and post-treatment routine.

TABLE II
Surface composition (at. %), as detected by XPS, of the PP side of the fractured PP/epoxy joints after different treatments

Sample	O	C
PP + HEMA photografting	0.0	100.0
PP + HEMA coating from plasma	4.2	95.8
O_2-plasma-treated PP	4.6	95.4

TABLE III
Surface composition (at. %), as detected by XPS, of treated PP after extraction in boiling ethanol for 24 h

Sample	O	C
PP + HEMA photografting	30.3	69.7
PP + HEMA coating from plasma	4.5	95.5
O_2-plasma-treated PP	14.6	85.4

DISCUSSION

The previous results clearly underline the very different behavior of the two chemically-closely-related polyolefins. HDPE is one of the polymers most readily crosslinked by plasma:[1] as a consequence, the bonding of the plasma-deposited layer and of the plasma-modified layer with the substrate is very strong and stable. Cohesive fractures within the substrate occur and the adhesive strength is unaffected by extraction and heat aging. Under the same plasma conditions, PP undergoes chain scission: the strength of the adhesive bond in the case of O_2 plasma treatment is limited by the mechanical strength of the plasma-modified layer. In plasma deposition, the weak boundary layer lies at the coating-substrate interface (that is, in that part of PP which actually "sees" the plasma). Accordingly, the surface composition of fractured PP is very similar (Table II) in the two cases.

Post-treatments deeply affect the joint strength of treated PP: extraction with ethanol removes the plasma-deposited layer, weakly bonded to the substrate. Heat treatment promotes the reorientation of the polar groups away from the surface, in a layer thinner than the XPS sampling depth.[8] In the latter case, no polar groups are directly available for the adhesive-substrate interaction, and no adhesion is recorded (Fig. 2).

For both substrates, on the other hand, UV-grafted surfaces are very stable: in the case of HDPE, the *ca.* 90 kg/cm^2 increase in bond strength over the smooth plasma-deposited coating of similar composition is likely the contribution of the increase of the surface area and of mechanical interlocking promoted by the bumped surface texture to the adhesion strength. A further possible contribution arises from the greater atomic concentration of oxygen-containing groups (Table I, Fig. 1), and UV-induced cross-linking of the surface and sub-surface layers.

Fractures are cohesive within the substrate also in the case of PP, with an average strength close to that observed on HDPE, showing that the milder environment created in UV grafting, in comparison with plasma, does not produce a weak boundary layer. Plasma, on the other hand, due to its higher energy density, allows one to use far lower treatment times. The energy involved in the UV grafting process (about 300 kJ/mole) is much lower than the energy involved in plasma treatments[16] and, while sufficient for promoting polymerization, it is too low to produce fragmentation of the substrate chains,[17] at least in the present case.

The latter aspect is clearly demonstrated by the strength of HEMA UV-grafted PP/epoxy joints after extraction and heat aging, which indicates the excellent thermodynamic and kinetic stability of the interfaces. Thus, it is possible to conclude that UV grafting is a useful approach for the surface modification of those polymers which are easily degraded by more energy-intensive techniques, such as plasma.

References

1. S. Wu, *Polymer Interface and Adhesion* (Marcel Dekker, New York, 1982).
2. M. Morra, E. Occhiello, L. Gila and F. Garbassi, *J. Adhesion* **33,** 77 (1990).
3. L. Lavielle, *Polymer Surface Dynamics,* J. D. Andrade, Ed. (Plenum Press, New York, 1988), p. 45.
4. M. Morra, E. Occhiello and F. Garbassi, in *Metallized Plastics 2,* K. L. Mittal, Ed. (Plenum Press, New York, 1991), pp. 363–371.

5. H. Schonhorn, F. W. Ryan and R. H. Hansen, *J. Adhesion* **2,** 93 (1970).
6. J. R. Hall, *J. Appl. Polym. Sci.* **13,** 2085 (1969).
7. E. Occhiello, M. Morra, G. Morini, F. Garbassi and D. Johnson, *J. Appl. Polym. Sci.* **42,** 2045 (1991).
8. M. Morra, E. Occhiello and F. Garbassi, *J. Coll. Interf. Sci.* **132,** 504 (1989).
9. H. Kubota, N. Yoshino and Y. Ogiwara, *J. Appl. Polym. Sci.* **39,** 1231 (1990).
10. Y. Ogiwara, M. Kanda, M. Takumi and H. Kubota, *J. Polym. Sci. Polym. Lett. Ed.* **19,** 457 (1981).
11. K. Allmér, A. Hult and B. Rånby, *J. Polym. Sci. Polym. Chem. Ed.* **26,** 2099 (1988).
12. K. Allmér, A. Hult and B. Rånby, *J. Polym. Sci. Polym. Chem. Ed.* **27,** 1641 (1989).
13. B. D. Ratner, in *Surface and Interfacial Aspects of Biomedical Polymers,* J. D. Andrade, Ed. (Plenum Press, New York, 1985), p. 373.
14. M. Morra, E. Occhiello and F. Garbassi, *J. Colloid Interface Sci.* **149,** 290 (1992).
15. J. D. Andrade, in *Surface and Interfacial Aspects of Biomedical Polymers,* J. D. Andrade, Ed. (Plenum Press, New York, 1985), p. 181.
16. H. Yasuda, *Plasma Polymerization* (Academic Press, Orlando, 1985).
17. A. N. Wright, in *Polymer Surfaces,* D. T. Clark and W. J. Feast, Eds. (Wiley, New York, 1978), pp. 155–184.