Characterization of Surface-Modified Polyurethane Blends, Poly(vinyl alcohol), and Poly(4-hydroxybutyl acrylate) for Biomedical Application by Electron Spin Resonance Spectroscopy

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SYNOPSIS

Two polyurethane blends—poly(carbonate urethane)/poly(vinyl alcohol) [PCU/PVA] and the aliphatic poly(ether urethane) (Tecoflex®)/poly(pentanedioic acid mono-4-(acryloyloxy)butyl ester) [Tecoflex®/COOH]—were surface-modified. Poly(vinyl alcohol) [PVA] and poly(4-hydroxybutyl acrylate) [PHBA] were used as model surfaces. 4-Isocyanato butanoic acid methyl ester was coupled as a spacer molecule to PVA and the PVA-containing polyurethane blend. Saponification of the generated ester group was verified by means of Electron Spin Resonance (ESR) spectroscopy using the nitroxyl radical 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO) as a reporter group. In the case of Tecoflex® and PHBA, glutaric anhydride served as a spacer molecule. 4-Amino-TEMPO was coupled to this spacer as well. ESR spectroscopy as a bulk method was used together with the surface-sensitive method X-Ray Photoelectron Spectroscopy (XPS) verifying the modification steps by elemental composition, ESR line shapes, and determination of the rotational correlation time τ_c. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Interaction between the biological system and the artificial material is a central issue in the development of biomedical polymers. Surface modification is one approach to create surfaces with various properties. The advantage of this approach is the possibility to design suitable devices with surface characteristics adapted to the environment in the human body and constant physical bulk properties.[1,2] It has to be pointed out that the outermost surface layer is of central importance. Recently, Ratner suggested a new definition of biocompatibility in terms of surface characteristics.[1]

In order to develop a small diameter vascular graft, the surface, which is in contact with the blood, has to be modified to result in ideal antithrombogenic properties. The aim of our research is the endothelialization of the inner surface of a polyurethane tube to imitate the inner wall of a natural blood vessel. To create optimum conditions for endothelial cell seeding, the polymer surface has to be modified chemically. A possible strategy is the attachment of cell adhesion reagents to promote endothelialization, e.g., amino acids or fibronectine fragments.[3] To couple these species, functional groups have to be introduced into the polymer surface.

In the field of biomaterials research, chemical surface modification is often carried out as a solid phase synthesis. For characterization, surface-sensitive methods like Secondary Ion Mass Spectrometry (SIMS), X-Ray Photoelectron Spectroscopy (XPS), and Infrared Spectroscopy (IR), using different techniques like Attenuated Total Reflection (ATR) or Photoacoustic Spectroscopy (PAS) are

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applied. Although these methods are surface-sensitive with different information depth, they are often not unambiguous concerning the course of a modification step. This is because bulk and surface information are simultaneously obtained as, for example, with IR techniques. XPS characterization of modification steps leading to surfaces with similar elemental composition is a problem as well. To circumvent these difficulties, reporter groups can be coupled on the functionalized polymer surface. The detection of the reporter groups leads to indirect information about the number of functional groups. In the XPS technique, for example, fluorine-containing reporter groups[4] are coupled to generated functional groups. In this case, the F-atom serves as a tracer. The measured fluorine content correlates roughly with the number of functional groups. However, this method leads to incorrect results, if the reporter group is not covalently bound, but immobilized by adsorption. In the latter case, the introduced molecule is rather an impurity than a reporter group. Polymers that often lead to analytical difficulties are polyurethanes, as they possess a complex composition. Nevertheless, these polymers are often used because of their good blood compatibility properties.[5]

The polymer systems used in our work are blends, composed of poly(carbonate urethane) and poly(vinyl alcohol) (PCU/PVA) and, additionally, commercially available Tecoflex™ blended with poly(pentanedioic acid mono-4-(acryloyloxy)butyl ester. (Tecoflex™/COOH).[6] The analytical results obtained from ESR and XPS are compared with similarly treated poly(vinyl alcohol) (PVA) and poly(4-hydroxybutyl acrylate) (PHBA), serving as model surfaces.

The aim of this article is to point out the advantage of Electron Spin Resonance (ESR) spectroscopy as a useful tool in the field of surface characterization. On the one hand, the method is specific because only paramagnetic molecules are detected; on the other hand, it is possible to distinguish between a covalently coupled reporter group and a reporter group that is not covalently bound.

EXPERIMENTAL

Instrumental Settings

Electron Spin Resonance Spectroscopy

ESR measurements were made on a Bruker ER 200 D/ESP 3220 spectrometer operating at 9.3 GHz at room temperature. The computer unit corresponds to ESP 300 E configuration. Samples were cut in stripes of 1 mm × 10 mm and introduced into a Pyrex tube (2 mm i.d.) closed at one end. Samples were swollen by adding solvent without leaving any air bubbles. The tubes were dropped into standard 4 mm i.d. quartz ESR sample tubes. Spectra were recorded using the following instrumental parameters: sweep width, 100 G; time constant, 82 ms; sweep time, 168 s; three scans; modulation frequency, 100 kHz; microwave power, 5 mW. Modulation amplitude: Figures 1, 4, and 6, 2 G; Figure 5, 0.5 G. Samples from PCU/PVA and PVA system were swollen in DMF, samples from Tecoflex™/COOH and PHBA/COOH were swollen in THF.

X-Ray Photoelectron Spectroscopy

All XPS spectra were recorded on a X-Probe™ 206 spectrometer (Surface Science Instruments, Mountain View, CA). An aluminium anode producing Al K_α x-rays at 1486.6 eV was used as x-ray source. The binding energies were referenced to unfunctionalized carbon at 285.0 eV. The emission angle of electrons was set at 55° with respect to the sample normal, which results in an information depth of about 6 nm.

Bulk compositions of polymers were investigated by taking down the surface region (0.2 mm) with a scalpel. The new surfaces were investigated by XPS.

Microwave Plasma

Plasma treatment was carried out with a Hexagon Plasma unit of Technics Plasma GmbH (Kirchheim, Germany). We used oxygen plasma with plasma power of 300 W for 3 min. Gasflow was 20 mL min^{-1} at the pressure of 0.4 mbar.

Materials and Syntheses

Syntheses of Spacers

Synthesis of 4-Isocyanato Butanoic Acid Methyl Ester.[7] Into a solution of 8.24 (0.127 mol) sodium azide (Merck) in 30 mL H_2O, a solution of 15 g (0.09 mol) glutar chloride monomethyl ester (Fluka) in 30 mL acetone was added within 25 min under stirring and ice cooling. After 2.5 h, the ice bath was removed and the organic layer was separated. The water layer was extracted with 100 mL of toluene. The combined organic phases were washed with 100 mL of saturated K_2CO_3 solution and twice with 100 mL H_2O, dried with Na_2SO_4 and

P_4O_{10} subsequently under ice cooling, and dropwise put into a heated flask (60°C) within 15 min. After 1.5 h, N_2 development was finished. The solvent was removed at 50°C under vacuum. Destillation (9 mbar) yielded 9.4 g (73%) isocyanate (bp.: 78–79°C). Spectroscopic data cf. appendix.

Synthesis of Pentanedioic Acid Mono-4-(acryloyloxy)butyl Ester (*3*): HBA [44.4 g (0.308 mol)], 7.6 g (0.062 mol) 4-dimethylaminopyridine (DMAP),[8] 28.4 g Et_3N, and 300 mL CH_2Cl_2 were placed in a three-necked flask with magnetical stirrer and condenser. After addition of 32 g (0.28 mol) recrystallized glutaric anhydride, a slightly exothermic reaction started. The mixture was stirred for 60 h at room temperature. Then 200 mL H_2O were added and acidified with diluted HCl (pH: 5–6). After the adding of 100 mL ether, the organic phase was separated and the water phase was extracted three times with 100 mL ether. The combined organic phases were washed twice with saturated NaCl solution and dried over Na_2SO_4. After removal of solvent 53 g, crude product resulted. After purification, 32 g (40%) product was obtained. Purification and spectroscopic data cf. appendix.

Modification Steps of the Poly(carbonate urethane)/Poly(vinyl alcohol) Blend [PCU/PVA] and the Model Surface Poly(vinyl Alcohol) [PVA]

PCU/PVA. The poly(carbonate urethane) was composed as described in ref. 9. In comparison to the described preparation, polymer synthesis was carried out solvent free in an extruder. The PCU was compounded with poly (vinyl alcohol) (PVA) to yield a polymer blend (PCU/PVA) with 10, 20, and 30% PVA (Freudenberg, Germany). The polymer was extruded into tubes with an inner diameter of 2 mm and an outer diameter of 3 mm (Vygon, Germany) and extracted with the azeotropic mixture of hexane/ethanol (79 : 21; w/w).

Coupling of 4-isocyanato butanoic acid methyl ester (the reaction was carried out in a sealed flask): 7.43 g of PCU/PVA (30%) were heated at 55–60°C for 30 min in 50 mL dry cyclohexane. Isocyanate (3.62 g) was added and the mixture was heated for a further 16 h at that temperature. Then the samples were extracted with hexane/ethanol (79 : 21, w/w) for 8 h and dried.

Saponification of the methyl ester group: 6.6 g modified polymer were stored for 4–6 h in 200 mL H_2O with 1.74 g NaOH at 40°C. The specimens were washed for 24 h in 200 mL H_2O containing 4 mL conc. acetic acid followed by a Soxhlet extraction in H_2O under vacuum for 24 h.

Coupling of 4-amino-TEMPO: 0.51 g modified PCU/PVA (30%) were stored for 30 min in 15 mL of a 0.02*M* Na_2HPO_4 solution. After addition of 120 mg 4-amino-TEMPO (Sigma, Germany) and 167.8 mg 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC; Sigma), the mixture was kept at room temperature over night. The samples were treated six times with 50 mL portions of water and 50 mL of hexane/2-propanol (9 : 1, v/v; 30 min each) alternatingly.

PVA. *Saponification of the acetate groups:* hydrolytic treatment was carried out first, because the PVA-films (Hoechst, Germany) were not completely free of acetate groups.

Twenty PVA-films (3 cm × 5 cm, 1700 mg) were refluxed in a solution of 16 g NaOH in 400 mL methanol for 1 h. After washing in methanol/H_2O (80:20, w/w) for 1 h, films were extracted in methanol for 24 h and dried in vacuum at 35–40°C for another 24 h.

Coupling of 4-isocyanato butanoic acid methyl ester: four films (286 mg, 6.5 mmol) were placed in 50 mL DMF and heated to 70°C. After the addition of 0.93 g (6.5 mmol) isocyanate, films were kept at that temperature for 22 h. Then the samples were washed for 6 h in DMF. To remove DMF, films were washed four times in 50 mL portions of THF/hexane (1 : 1, v/v). After they were stored in THF/hexane (1 : 2, v/v), a 24 h drying in vacuum for 24 h at 35–40°C followed.

Saponification of the methyl ester group: four modified films were stirred in a mixture of 32 mg NaOH and 1.44 mL H_2O in 50 mL DMF for 6 h. After a 24 h Soxhlet extraction in the azeotropic mixture of THF/H_2O (94.6 : 5.4; w/w), films were dried as above.

Coupling of 4-amino-TEMPO: two films (176 mg) were swollen in 50 mL DMF for 20 min. Then 50 μL Et_3N, 92.1 mg (0.8 mmol) *N*-hydroxysuccinimide and 137 mg (0.8 mmol) 4-amino-TEMPO were added. After cooling for 10 min on an ice bath, 165.1 mg (0.8 mmol) dicyclohexyl carbodiimide (Merck, Germany) were added. The reaction mixture was stirred for 12 h without renewing the ice bath. Then the films were extracted in a Soxhlet extractor with DMF in vacuum for 24 h. To remove DMF, films were washed four times (10 min) in 50 mL portions of THF/hexane (1 : 1, v/v) and dried in vacuum for 24 h at 35–40°C.

Modification of the Aliphatic Poly(ether urethane) Tecoflex® and the Model Surface Poly(4-hydroxybutyl Acrylate) (PHBA)

Tecoflex®/poly(pentanedioic Acid Mono-4-(acryloyloxy)butyl Ester (Tecoflex®/COOH). Tecoflex EG 93 A® (Thermedix, USA) tubes of an inner diameter of 2 mm and an outer diameter of 3 mm were cut lengthwise, extracted in hexane/ethanol (79 : 21, w/w), and dried in vacuum for 24 h at 35–40°C. The specimens were placed in a microwave plasma apparatus and treated with O_2-plasma for 3 min.[10] After the plasma treatment, the apparatus was flooded with O_2 for another 3 min. The plasma-activated specimens were stored in a mixture of pentanedioic acid mono-4-(acryloyloxy)butyl ester/Darocur 1173® (Ciba Geigy, Switzerland)/1,4-butanedioldimethacrylate (Merck, Germany) (10 : 0.1 : 0.1, w/w/w) for 24 h. The samples were removed and shortly washed with 2-propanol. After irradiation for 1 h with a UV source (Ultravitalux; Osram, Germany) in 2-propanol under ice cooling, a 24 h Soxhlet extraction in ether was carried out and samples were dried for 24 h in a vacuum at 35–40°C.

The plasma pretreatment is necessary to fix the newly formed poly(pentanedioic acid mono-4-(acryloyloxy)butyl ester network covalently to the outermost atomic layers. It was shown that without a plasma pretreatment the bulk properties are quite different from the surface properties. In the bulk poly(pentanedioic acid mono-4-(acryloyloxy)butyl, ester was found, whereas on the surface, there was none.[6]

Coupling of 4-amino-TEMPO: to 312 mg modified Tecoflex® in 20 mL of a 0.04*M* NaH_2PO_4 solution, 12.3 mg 4-amino-TEMPO and 19.3 mg EDC were subsequently added. After stirring for 24 h, the samples were stored in H_2O for 24 h and dried in vacuum at 35–40°C for another 24 h.

Poly(4-hydroxybutyl acrylate) Films (PHBA). PHBA films were prepared by bulk polymerization. As a mold, glass plates (200 mm × 200 mm), coated with polypropylene films, were used. PHBA is a hydrophilic polymer and tends to adhere very strongly to glass. A thin silicon tube served as a spacer and a seal. The plates were clipped together and the space between them was filled with a mixture of distilled 4-hydroxy butyl acrylate (BASF, Germany) containing 0.14% Darocur 1173® as a photoinitiator. Afterwards, the plates were irradiated for 1 h with a UV source (Ultravitalux; Osram, Germany). In a Soxhlet extractor the prepared PHBA films were extracted for 24 h in the azeotropic mixture of hexane/ethanol (79 : 21, w/w) to remove impurities such as unreacted monomer and oligomers. After washing, the films were dried under vacuum for 24 h at 35–40°C. The obtained PHBA was crosslinked and insoluble in any solvent.

Reaction of the films with glutaric acid anhydride: a typical procedure was as follows (reaction was carried out under N_2). The films (18.9 g) were put into 150 mL THF/hexane (1 : 1, v/v) and 40 mL of a 15% BuLi/hexane mixture (Merck, Germany) was added under ice cooling. After removal of the ice and stirring at room temperature for 1 h, 150 mL of the solution were removed and 8 g recrystallized glutaric acid anhydride (Merck, Germany) in 150 mL THF/hexane (1 : 1, v/v) were added. Afterwards, stirring continued for another hour. For cleaning, the samples were washed (5 min each) once in 100 mL THF/hexane (1 : 1, v/v) and three times in 100 mL methanol. The films were stored over night in 100 mL THF/hexane (1 : 1, v/v) and then dried in vacuum for 24 h at 30–40°C.

Coupling of 4-amino-TEMPO: The polymer films were covered with 50 mL of 0.02*M* Na_2HPO_4. After the addition of 33.5 mg 4-amino-TEMPO and 38.2 mg EDC, it was stirred for 10 h. The films were washed four times in 50 mL H_20 (5 min each) and dried as above.

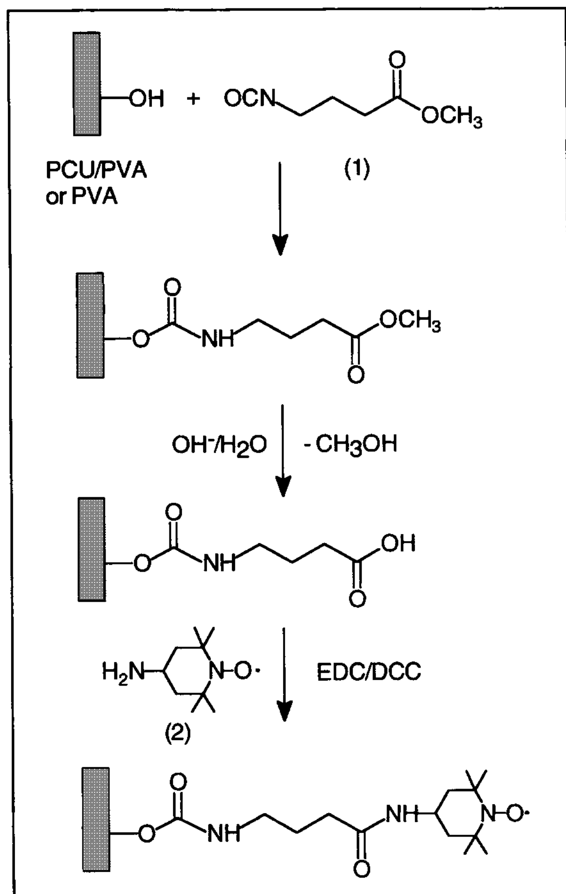
Preparation of Control Samples for ESR Spectroscopy (Uncoupled 4-amino-TEMPO)

Control samples were prepared under similar conditions as the samples described above. In contrast to these preparations, the carbodiimide coupling agent was missing. After the cleaning process, no spin label should be detected. However, it was normal that small amounts of spin label remained in the polymer bulk. The ESR spectra obtained from these samples served as control.

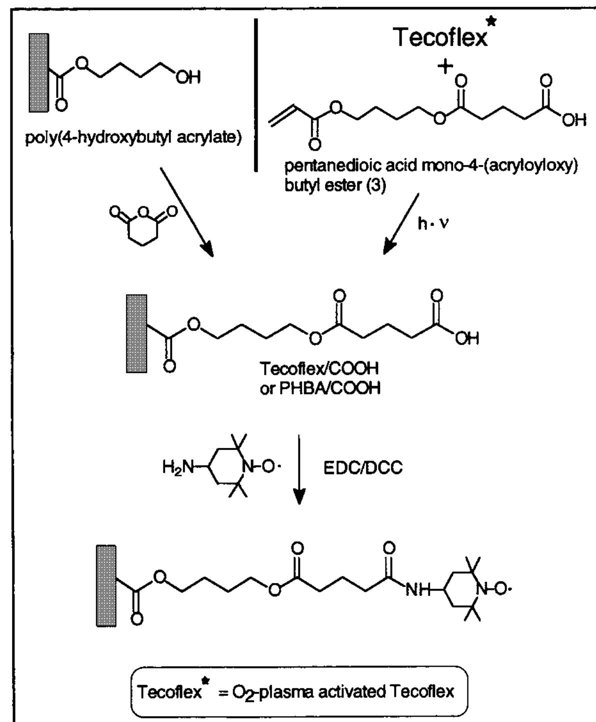
RESULTS

To couple amino acids or peptides the polyurethanes are modified with a spacer. In the case of PCU/PVA and PVA, the isocyanate (**1**) is used. Scheme 1 shows the modification steps for this polymer system.

A bifunctional spacer with an isocyanate and an ester group was synthesized to exclude the possibility of crosslinking, as it might occur with diisocyanates.[11,12] The isocyanate group serves as a highly re-



Scheme 1 Coupling of bifunctional isocyanate (**1**) and the saponification step at the polymer systems PCU/PVA and PVA. To follow the course of the modification, the spin label 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO) (**2**) is coupled.



Scheme 2 Modification of Tecoflex® and the model surface PHBA.

active binding site.[13] The generated urethane linkage is more stable concerning hydrolytic treatment than an ester function.[14,15] After the saponification step, the spacer is ready to couple an amino component via the carbodiimide method, e.g., amino acids, peptides, or 4-amino-TEMPO. The hydrolytic step is difficult to detect on this polymer system with the methods that are generally used.

In the case of Tecoflex™ and the model surface PHBA, modification steps are shown in Scheme 2. The spin label is used to verify these reactions.

The advantage of the spin label technique is that no other signals superimpose the ESR signal, because only paramagnetic species are detected. The three-line ESR spectrum shows features that are sensitive to the spin label mobility. If the mobility is reduced, as in the case of a covalent linkage, the ESR spectrum will show that by characteristic line

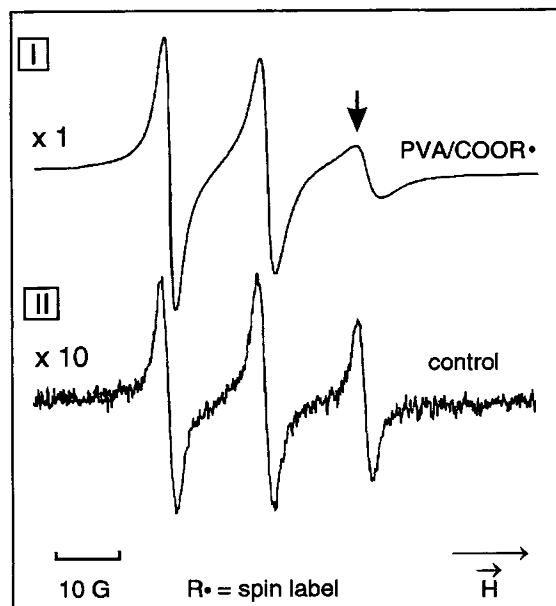


Figure 1 Superimposed ESR spectrum of surface-modified poly(vinyl alcohol) with covalently coupled 4-amino-TEMPO [**I**] and of an uncoupled spin probe as control sample [**II**].

Figure 2 ESR signal of free-tumbling 4-amino-TEMPO in THF at room temperature.

Figure 3 C_{1s} spectrum of unmodified PCU/PVA in comparison to the spectrum of the sample modified with the spacer (PCU/PVA/spacer). PVA content is 30%.

shapes. Figure 1 shows the ESR signals of a covalently coupled spin label on poly(vinyl alcohol) [**I**] and of an uncoupled species as control sample [**II**].

With decreasing mobility of the reporter group, as it occurs with covalent linkage, the line shape succumbs to characteristic changes.[16] A line broadening occurs and a decreasing height of the high-field line is observed (Fig. 1, **I**, ↓). In the case of the control sample, which represents uncoupled 4-amino-TEMPO in the PVA matrix, molecule mobility is higher. The line shape is similar to that of the spectrum of a free tumbling molecule in solution. Such an ESR signal consists of three narrow lines of equal heights (Fig. 2).

The modification steps are applied to the PCU/PVA blend that represents a more complex polymer system than the model surface PVA. The coupling of the spacer 4-isocyanato butanoic acid methyl ester (**1**) can be verified by XPS. This is because of the newly formed urethane group, containing N that is used as tracer. Figure 3 and Table I show the XPS results after spacer coupling.

Table I shows that the surface compositions detected by XPS of PCU/PVA blends (Ref.) with different PVA content are similar. The same situation is found for the bulk compositions of the blends (Bulk). A difference is found between the surface

Table I XPS Values of Three PCU/PVA Samples (10, 20, and 30% PVA) Surface-Modified with Spacer (Designated with Mod.) in Comparison to the Unmodified Species (Designated with Ref.); the Bulk Composition of PCU/PVA is Given as Well (Bulk)

PCU/PVA: –OH + OCN–(CH₂)₃–C(=O)–OCH₃ → PCU/PVA/Spacer: –O–C(=O)–NH–(CH₂)₃–C(=O)–OCH₃

PCU/PVA	N_{1s} Content (Atomic %)		
PVA-Content/%	Ref.	Mod.	Bulk
10	0.30	1.43	2.01
20	0.78	1.70	2.03
30	0.69	1.35	1.98

High Resolution XPS (C_{1s} Atomic %)	<u>C</u>—H			<u>C</u>—O			O—<u>C</u>=O N—<u>C</u>O—O			O—<u>C</u>O—O		
Energy/eV	285.0			286.7–286.8			289.4–289.7			290.6–290.7		
PVA/%	Ref.	Mod.	Bulk	Ref.	Mod.	Bulk	Ref.	Mod.	Bulk	Ref.	Mod.	Bulk
10	45.3	47.7	46.5	16.9	14.5	17.8	0.84	1.5	2.8	6.9	6.1	6.0
20	45.5	47.1	47.0	16.0	14.8	18.4	1.4	1.9	2.4	7.1	5.2	5.4
30	45.8	47.8	46.3	15.7	13.8	18.8	1.3	2.2	2.3	6.8	6.0	6.2

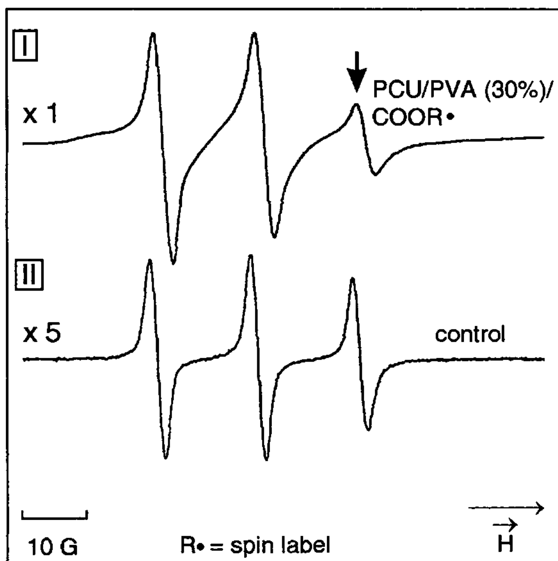


Figure 4 Superimposed ESR spectra of surface-modified PCU/PVA with covalently coupled 4-amino-TEMPO [I] and uncoupled spin probe as a control sample [II].

compositions of the blends and the bulk compositions, as indicated by the N_{1s} content from the element survey spectrum in Table I (double frame, compare ref. with bulk) and the C_{1s} content for the ester and the urethane group at 289.4–289.7 eV (bold frame).

After surface modification, the C_{1s} contents for the ester and the urethane group (289.4–289.7 eV) are slightly increased because of the newly formed urethane bond (bold frame in Table I, compare ref. with mod.). The increasing values of the N_{1s} content from the element survey spectrum (double frame in Table I) correspond herewith. This indicates that the coupling of the spacer was successful. However, it is obvious that the saponification step, where only slight changes in the carbon content are expected, cannot be evaluated by XPS. The use of the spin label technique is more favorable in this case. Coupling of the probe at the saponified spacer should lead to an ESR signal characterized by reduced molecular motion. Figure 4 shows such a specimen [I] in comparison to a control sample [II], which represents uncoupled 4-amino-TEMPO in the polymer matrix.

The broadening of the width and the decreasing height of the high-field line (↓ in Fig. 4) show that the coupling of the probe was successful. This confirms the spacer coupling as well as the saponification step.

The mobility of a paramagnetic molecule can be quantitated in terms of the rotational correlation time τ_c, which is evaluated with eq. (1).[17] This approximation derives from the Kivelson theory[18] for fast tumbling molecules. The lower the values, the faster the tumbling.

$$\tau_c = 0.65 \cdot \Delta H(0) \left[\sqrt{\frac{h(0)}{h(-1)}} + \sqrt{\frac{h(0)}{h(+1)}} - 2 \right] \quad (1)$$

τ_c: rotational correlation time in ns
$h(0)$: height of the center line
$h(+1)$: height of the low field line
$h(-1)$: height of the high field line
$\Delta H(0)$: width of center line in Gauss

The determined values for the polymer systems discussed here are not absolute rotational correlation times. The values are used here as a relative quantity in comparison to the values of the control samples. Table II shows the values derived from eq. (1) for the PCU/PVA/spacer and the PVA/spacer system.

The values of τ_c, which represent the uncoupled spin label (second column, Table II), are lower than those of the coupled spin label (first column, Table

Table II. Rotational Correlation Times τ_c for the PCU/PVA/Spacer System and PVA/Spacer with Saponified Ester Function and Coupled 4-Amino-TEMPO. The Values of the Corresponding Control Samples are Given as Well

PCU/PVA/Spacer τ_c/ns	Control τ_c/ns
0. 34	0. 11
0. 46	0. 11
0. 39	0. 14
0. 30	0. 15
0. 29	0. 12
PVA/Spacer τ_c/ns	**Control τ_c/ns**
2. 04	0. 34
1. 48	0. 14
1. 95	—*
1. 72	—*

* No value means that the cleaning process for this films lead to specimens where the measured ESR signal was too weak or not existing.

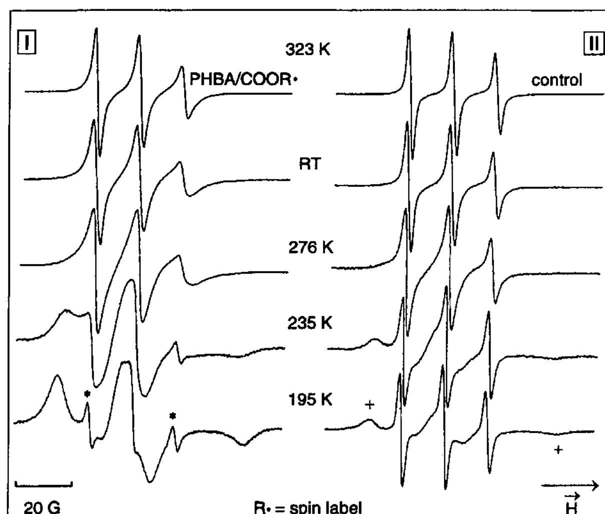


Figure 5 Temperature-dependent measure of spin label modified model surface PHBA (PHBA/COOR·) [I] in comparison to an uncoupled spin probe in the polymer matrix as a control sample; RT = room temperature.

II). The difference of the values of PCU/PVA/spacer and PVA/spacer can be explained by the different swelling behavior of the materials in the solvent. The asterisks (*) in the second column represent the ideal case, because detection of spin label means covalent linkage. But because of the high sensitivity of ESR spectroscopy, concentrations up to 10^{-8} mol/L^{-1} can be detected, it is normal that control samples show an ESR signal also.[19]

Further, temperature-dependent ESR spectra can be taken. An example is given in Figure 5. As model surface PHBA is used, modified with glutaric acid anhydride. Afterwards, spin label coupling is carried out.

On the left-hand side of Figure 5, ESR signals of the covalently coupled spin label [I] are shown in the temperature range from 323 to 195 K. The change of the line shape with decreasing temperature is readily recognized. At 323 K the spin label shows a high molecular mobility, however, lower than that of the control samples [II]. At 195 K, the covalently coupled spin label shows very low mobility. The ESR spectrum corresponds nearly to that of a powder (the rigid powder limit describes the case of randomly and rigidly oriented molecules), compared to the control.[16] The signals of the control sample show very high molecular mobility over the whole temperature range. The sharper lines designated with asterisks (*) in spectra series [I] represent a small amount of uncoupled spin label as an impurity (even a 24 h Soxhlet extraction in DMF under vacuum does not result in a spin label free control specimen). The peaks designated with a cross (+) in spectra series [II] indicate low molecular motion. That can be attributed to inhomogenities with regard to swelling behavior in the material at that temperature.[20] The same procedure as described above was applied to the complex Tecoflex® system. In Figure 6, ESR signals of modified and spin label coupled Tecoflex® are given.

Spectrum [I] shows the line shape of an immobile molecule, whereas the control specimen [II] indicates spin label of high mobility. It can clearly be distinguished between a covalently coupled spin label and an uncoupled species.

CONCLUSIONS

Surface modification of four polymer systems—poly(carbonate urethane)/poly(vinyl alcohol) [PCU/PVA], poly(vinyl alcohol) [PVA], Tecoflex®/poly(pentanedioic acid mono-4-(acryloyloxy) butyl ester) [Tecoflex®/COOH], poly(4-hydroxybutyl acrylate) [PHBA]—are investigated. PVA and PHBA serve as model surfaces to prove the modification steps. The polymers are modified with spacer molecules. As functional groups, COOH

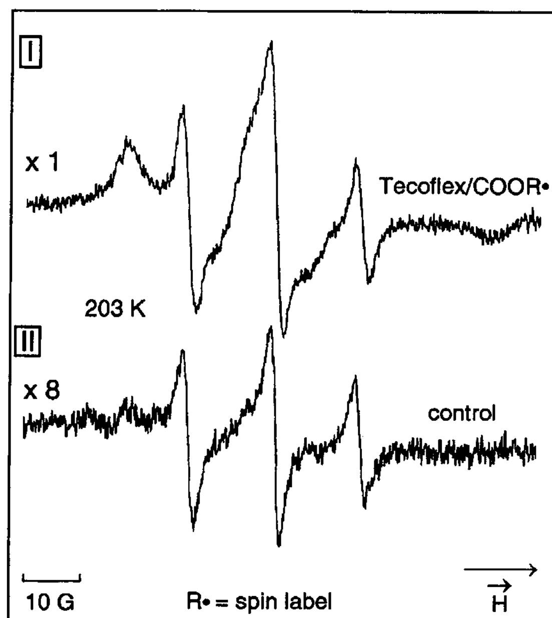


Figure 6 ESR signals of Tecoflex®, modified with pentanedioic acid mono-4-(acryloyloxy)butyl ester (**3**) and 4-amino-TEMPO in comparison to a control at reduced temperature.

groups are introduced. The nitroxyl radical 4-amino-TEMPO is used as reporter group.

The ESR spectroscopy is employed as a helpful analytical tool. In conjunction with surface-sensitive methods, unambiguous results about the course of surface modification are obtained. With surface-sensitive methods alone, this is sometimes very difficult. A special advantage of the ESR spectroscopy is the high selectivity, because it detects exclusively paramagnetic molecules. That means that exclusive information about the modification step the probe is involved in is obtained. No disturbing signals from the rest of the polymer occur. Furthermore, the ability of the method to distinguish between a covalently coupled and a free reporter group is to be emphasized. This is demonstrated by the control samples.

Covalently coupled 4-amino-TEMPO gives a clear evidence of the existence of COOH functions. Other reporter groups as they are used in the XPS technique, for example, sometimes lead to equivocal results.

Because of the great number of known stable paramagnetic molecules that can be coupled to different functional groups, the ESR spectroscopy is a useful tool to support the analysis of the surface of modified polymers.

APPENDIX

Spectroscopic Data

4-Isocyanato Butanoic Acid Methyl Ester

^{1}H-NMR (300 MHz, $CDCl_3$, TMS):

δ = 3.69 ppm (s, 3 H, —$\mathbf{OCH_3}$),
δ = 3.41 ppm (t, J = 6,6 Hz, 2 H, —$\mathbf{CH_2}$—NCO),
δ = 2.43 ppm
(t, J = 7,3 Hz, 2 H, —$\mathbf{CH_2}$—CO—O—),
δ = 1.93 ppm
(t, J = 6,9 Hz, 2 H, —CH_2—$\mathbf{CH_2}$—CH_2—)

^{13}C-NMR (75 MHz, $CDCl_3$, TMS):

δ = 173.0 ppm (—O—**CO**—),
δ = 122.1 ppm (—**NCO**, very weak),
δ = 51.8 ppm (—$\mathbf{OCH_3}$),
δ = 42.3 ppm (—$\mathbf{CH_2}$—NCO),
δ = 30.8 ppm (—$\mathbf{CH_2}$—CO—O—),
δ = 26.3 ppm (—CH_2—$\mathbf{CH_2}$—CH_2—)

IR (KBr):

$\tilde{\nu}$ = 3475 cm^{-1}, $\tilde{\nu}$ = 2956 cm^{-1}, $\tilde{\nu}$ = 1738 cm^{-1},
$\tilde{\nu}$ = 1438 cm^{-1}, $\tilde{\nu}$ = 1360 cm^{-1}, $\tilde{\nu}$ = 1260 cm^{-1},
$\tilde{\nu}$ = 1200 cm^{-1}, $\tilde{\nu}$ = 1172 cm^{-1}, $\tilde{\nu}$ = 1060 cm^{-1},
$\tilde{\nu}$ = 1000 cm^{-1}, $\tilde{\nu}$ = 895 cm^{-1}

Pentanedioic Acid Mono-4-(acryloyloxy)butyl Ester

Purification. Crude product (53 g) are immersed in 300 mL H_2O and $NaHCO_3$ powder is added until CO_2 development finishes. The solution is extracted three times with 100 mL ether to remove organic impurities. After acidifiing with diluted HCl and separation of the organic layer, the water layer is extracted four times with 100 mL ether. The combined organic phases are washed twice with 100 mL of saturated NaCl solution. Drying over Na_2SO_4 and evaporation of solvent yealds 32 g (40%) of colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, TMS) [$^{Hb}_{Hc}C = C^{Ha}_{R}$]:

δ = 6.41 ppm
(d/d, Jcb = 1.5 Hz/Jca = 17.3 Hz, 1 H, **Hc**),
δ = 6.13 ppm
(d/d, Jab = 10.4 Hz/Jac = 17.3 Hz, 1 H, **Ha**)
δ = 5.84 ppm
(d/d, Jbc = 1.5 Hz/Jba = 10.4 Hz, 1 H, **Hb**),
δ = 4.19 ppm and 4.12 ppm
(2 × mult, 2 × 2 H, —$\mathbf{CH_2}$—$(CH_2)_2$—$\mathbf{CH_2}$—)
δ = 2.44 ppm (t, J = 7.4 Hz, 2 H) and
δ = 2.41 ppm (t, J = 7.4 Hz, 2 H)
[—$\mathbf{CH_2}$—CH_2—$\mathbf{CH_2}$—],
δ = 1.96 ppm
(p, J = 7.1 Hz, 2 H, —CH_2—$\mathbf{CH_2}$—CH_2—),
δ = 1.75 ppm
(mult, 4 H, —CH_2—$(\mathbf{CH_2})_2$—CH_2—)

^{13}C-NMR (75 MHz, $CDCl_3$, TMS):

δ = 178.6 ppm (—**COOH**), δ = 172.9 ppm
(—CH_2—**CO**—O—CH_2—),
δ = 166.3 ppm (=CH—**CO**—O—),
δ = 130.8 ppm ($\mathbf{CH_2}$=CH—),
δ = 128.4 ppm (CH_2=**CH**—),
δ = 64.0 ppm (—$\mathbf{CH_2}$—$(CH_2)_2$—$\mathbf{CH_2}$—),
δ = 33.1 and 33.0 ppm (—$\mathbf{CH_2}$—CH_2—$\mathbf{CH_2}$—),
δ = 25.3 ppm (—CH_2—$(\mathbf{CH_2})_2$—CH_2—),
δ = 19.8 ppm (—CH_2—$\mathbf{CH_2}$—CH_2—)

IR (KBr):

$\tilde{\nu}$ = 3245 cm^{-1}, $\tilde{\nu}$ = 2960 cm^{-1}, $\tilde{\nu}$ = 1726 cm^{-1},
$\tilde{\nu}$ = 1410 cm^{-1}, $\tilde{\nu}$ = 1272 cm^{-1}, $\tilde{\nu}$ = 1192 cm^{-1},
$\tilde{\nu}$ = 1061 cm^{-1}, $\tilde{\nu}$ = 958 cm^{-1}, $\tilde{\nu}$ = 811 cm^{-1}

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