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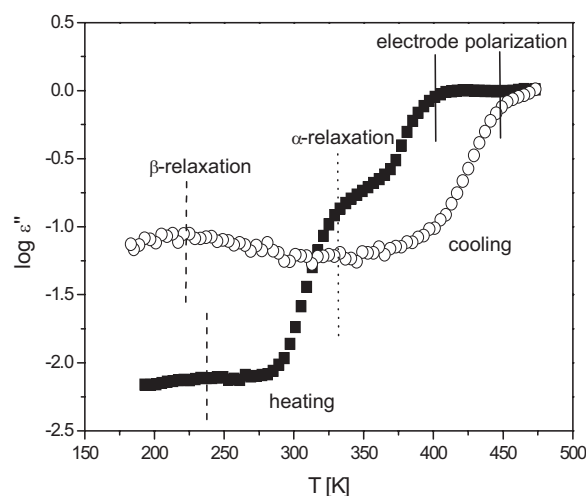
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Structure of Plasma-Deposited Copolymer Films Prepared from Acrylic Acid and Styrene: Part I Dependence on the Duty Cycle

Alaa Fahmy,* Renate Mix, Andreas Schönhals, Jörg Friedrich

Copolymers of acrylic acid and styrene (AA/S) were prepared by pulsed plasma deposition and their structures were studied in dependence on the duty cycle (DC) for a fixed composition of 1:1. As a result, low values of DC doses preserve the structure of monomers in the plasma deposited polymers while high DC leads to a higher degree of fragmentation and a loss in regular structure. Regarding plasma copolymerisation as a feasible method to finish surfaces with a definite number of functional groups it is necessary to characterize both, the chemical nature and the physical properties of the deposited layer. Therefore, a combination of different methods was employed for the characterization of thin plasma copolymer films (FTIR, dielectric spectroscopy, differential scanning calorimetry, X-ray photoelectron spectroscopy (XPS)). Special attention was paid on the unambiguous identification of COOH groups at the surface after derivatization with trifluoroethanol by XPS and in the volume by FTIR. The glass transition temperature of the copolymer system is lower than that for the both plasma deposited homopolymers and increases with the DC in difference to plasma deposited poly(acrylic acid). The dielectric measurements showed that the plasma deposited films were not thermally stable and underwent an undesired post-plasma chemical reaction. The results obtained by dielectric spectroscopy are discussed in detail in comparison with the data from FTIR and XPS measurements.



1. Introduction

Copolymerization is a method to create polymers with properties not-withstanding the properties of it depends on

the comonomer units used. Many chemical copolymerizations are based on free radical processes. One difference to plasma-assisted polymerization, however, is retention of the regular structure. If monomers A and B are copolymerized, the resulting copolymers can show random (–AA–B–AB–AAA–B–...), alternating (–A–B–A–B–...), or block (–AAA–BB–AAAA–BBB–...) structure. Different models were developed for mathematical characterization of radical copolymerization process.^[1]

Wang^[2] was prepared poly(styrene-co-acrylic acid) (St/AA) copolymer microspheres by batch emulsifier-free emulsion copolymerization of St with AA. They concluded

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that by chemical metal deposition, nickel particles were formed and deposited on the surface of St/AA microspheres, forming polymer/metal composite particles.

Plasma copolymerized organic films are of growing interest and have been studied by a number of groups in the last decade. The interest in plasma copolymers is driven by relevant technological applications in different fields where a tailoring of surface properties is appropriate.

Jiang et al.^[3] were synthesized acrylic acid–styrene composite plasma polymerized membranes by plasma polymerization of a mixture of acrylic acid and styrene monomers in a low-frequency after-glow capacitively coupled plasma (CCP) discharge process. The results showed that the partial pressure ratio between acrylic acid (AA) and styrene (S), applied discharge power and the energy of the extracted particles have considerable effects on the structure and the content of functional groups of the deposited membranes.

It is generally accepted that active species, such as excited molecules, free radicals and ions, are formed by collisions of energetic electrons with monomer molecules during plasma discharge.

The plasma processes allow, by the choice of the right precursors, to deposit materials with a very large range of properties and chemical functionalities, such as $-\text{COOH}$,^[4] $-\text{NH}_2$ ^[5,6] and their combination^[7] or antifouling polymers based for instance on polyethylene oxide (PEO).^[8,9] Due to their variable degree of crosslinking linked to the discharge conditions, these coatings are resistant to classical polar solvents, making them compatible with almost all standard patterning techniques including lift-off processes,^[10,11] but can also be selectively dissolved upon request. In the work summarized below, two different types of plasma polymers were used, namely plasma polymer of acrylic acid (PAA) containing COOH moieties and plasma polymerized styrene (PS).

The choice of the acrylic acid is motivated by the fact that the carboxylic functional groups are able to promote a large amount of chemical reactions with different biomolecules (enzymes, antibodies, DNA). It is likely that, if the distance between chains of the polymer increases, the hydrogen bond (more free COOH groups) and the crosslinking will decrease. Therefore, the styrene monomer was selected. It has not only vinyl group which can be activating by the plasma energy but also phenyl group as the bulky. Phenyl groups play an important role for the stability of styrene monomers due to the resonance of benzene ring. So, the feature of styrene monomer may be affects on the regularity of acrylic acid–styrene copolymer. Acrylic acid and styrene are very easily to polymerize as homopolymers. Moreover, copolymerization is possible to random copolymers because of the similar copolymerization parameters ($r_{\text{AA}} = 0.15$ and $r_{\text{S}} = 0.25$).^[12] Corresponding to the Lewis–Mayo equation these factors are rate constants. The

resonance-stabilized styrene assigns the acrylic monomer with its electron-accepting property a smaller copolymerization parameter.^[1] In each case the strange comonomer becomes added, thus, alternating copolymers should be formed. Here, such alternating copolymers were used as model.

Only a limited number of reports on the mechanism of plasma copolymerization have been published due to the complexity of plasma reactions.^[13] The literature survey indicates that till now the mechanism of plasma polymerization including copolymerization is only poorly understood. Fragmentation and poly-recombination reactions take place within the plasma at the same time, where the contribution of these reactions to polymer formation is not clear.

The effect of the plasma energy on the structure of the deposited thin films was studied in the literature by applying XPS, NEXAFS and FTIR or sometimes by mass spectrometry but a combination of volume sensitive methods with surface analytic by XPS or FTIR is not established till now. Generally, Organic films with defined chemistry and properties are required for many different industrial application and technology such as optics, medicine, electronics and biology.

In present work, adopted pulse and contentious plasma (co)polymerization technique to synthesize thin plasma acrylic acid–styrene copolymer films and investigate the structure. As reported by our previous work^[14,15] by a combination of dielectric spectroscopy, XPS and FTIR. Concerning the latter point, in addition to FTIR, dielectric spectroscopy is employed in a broad frequency and temperature range using molecular mobility as a probe for structure. If styrene monomer affects on the regularity and the crosslinking of copolymer films, the next part will discuss the effect of the comonomer ratio to obtain a more regular structure.

2. Experimental Section

2.1. Materials

Polyethylene (PE) and aluminium were used as substrates. PE (thickness 40 μm) was supplied by Alkor Folien GmbH, Germany. Aluminium (Al) was evaporated onto glass substrates. Al wires were obtained from Goodfellow with a purity of 99.95%. Acrylic acid and styrene were ($>99\%$ grade) obtained from Fluka. The monomers were distilled before use to remove stabilizers.

For derivatization of the COOH groups, trifluoroethanol (TFE, $>99\%$ purity, Merck, Germany), pyridine, (MERCK, Germany) and N,N' -di-tert-butylcarbodiimide to remove the water (Fluka) were used as received.

Additionally, the plasma polymerized layers were deposited on a glass cylinder (thickness 500 nm) and scratched off to investigate its thermal properties by differential scanning calorimetry.

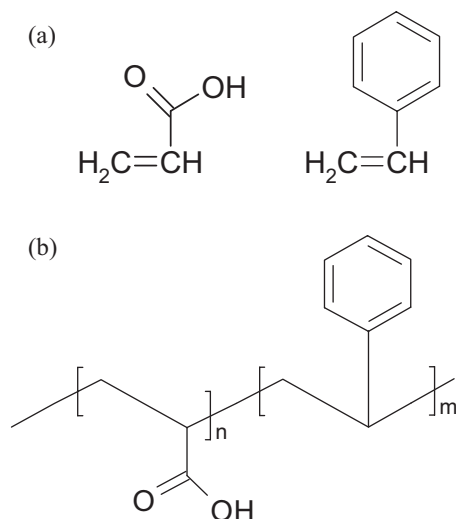


Figure 1. Chemical structure for: (a) acrylic acid (AA), styrene (S) monomers and (b) a classical acrylic acid-styrene copolymer (AA/S).

Figure 1 presents the chemical structure of acrylic acid (AA), styrene (S) and of a tentative AA/S copolymer.

2.2. Plasma Deposition

The deposition experiments were accomplished in a stainless steel reactor Ilmvac, Germany with volume of 50 dm³. The reactor was equipped with a pulsable radio-frequency (rf. 13.56 MHz) generator with an automatic matching unit and a flat rf. electrode (5 cm × 35 cm). The monomers were dosed by a mass flow controller for liquids (Liqui-Flow[®], Bronkhorst) adjusted to 1:1 molar ratio of both monomers. For details see ref.^[14]

Standard conditions for depositing copolymer films with 150 nm thicknesses composed of acrylic acid and styrene units were: power $W = 100$ W, pressure 10 Pa, flow rate 6.25 and 9.05 for acrylic acid and styrene comonomers, respectively, the total flow rate (F) equal to 15.3 g · h⁻¹ for 1:1 molar ratio (it is constant for all samples) and variable duty cycles (DC) (0.1, 0.2, 0.3, 0.5, 0.7 and 1.0 at a pulse frequency of 1 kHz). The data for PAA homopolymers is taken from ref.^[14] and PS homopolymers deposited at the same conditions. The DC is defined as:

$$\text{DC} = \frac{t_{\text{pulse-on}}}{t_{\text{pulse-on}} + t_{\text{pulse-off}}} \quad (1)$$

Where the effective power W_{eff} was defined as:

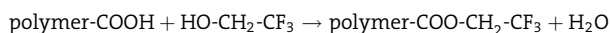
$$W_{\text{eff}} = W \times \frac{t_{\text{pulse-on}}}{t_{\text{pulse-on}} + t_{\text{pulse-off}}} \quad (2)$$

The reaction parameter power input per liquid flow (W_{eff}/F) equal to (0.65, 1.31, 1.96, 3.27, 4.58 and 6.54).

A quartz microbalance was used for controlling the deposition rate.

2.3. Characterization of the Plasma Polymers

The surface composition and functionality were investigated employing XPS by analysing the C1s, O1s and F1s peaks. The spectrometer used was a SAGE 150 (Specs, Berlin, Germany) equipped with a hemispherical analyser Phoibos 100 MCD-5 and used a non-monochromatic MgK α radiation with 11 kV and 220 W settings at a pressure of ca. 1×10^{-7} Pa in the analysis chamber.^[14] For quantifying the concentration of COOH groups at the surface of the deposited AA/S copolymer layers, derivatization with trifluoroethanol (TFE) was applied.^[16]



The concentration of the carboxylic groups per 100 carbon atoms was calculated using Equation (3) which corresponding to the above presented reaction.^[14]

$$c(\text{COOH}) = 100 \frac{y}{x} = 100 \frac{[F]}{3[C] - 2[F]} \quad (3)$$

where, $[C]$ and $[F]$ are the concentrations of carbon and fluorine of the derivatized sample measured by XPS.

FTIR spectra were recorded from 4 000 to 550 cm⁻¹ accumulating 64 scans at a resolution of 4 cm⁻¹ using a Nicolet Nexus 8700 FTIR spectrometer (Nicolet, USA) in the ATR mode (Diamond Golden Gate, Nicolet, USA).^[15]

Moreover, the thermal analysis was carried out by differential scanning calorimetry (DSC, Seiko[®] Instruments). N₂ is used as protection gas. The samples were measured in the temperature range from 173 to 470 K with a heating rate of 10 K · min⁻¹. The glass transition temperature T_g was taken as the inflection point of the heat flow of the first heating run.

Broadband dielectric relaxation spectroscopy (B-DRS) is sensitive to structural changes across the whole thickness of the sample. It detects the molecular mobility in the plasma polymerized layers, such as molecular fluctuations of dipoles (including radicals). For polymers these fluctuations are related to the molecular mobility of groups, segments or the whole polymer chain as well. For details see ref.^[17] A high resolution alpha analyser (Novocontrol[®]) is used to measure the complex dielectric function $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$ (f , frequency; ε' and ε'' , real and imaginary part of the complex dielectric function, $i = \sqrt{-1}$) in the frequency range from 10⁻¹ to 10⁷ Hz and in the temperature (T) range from 173 to 453 K. The temperature was controlled by a Quatro Novocontrol[®] cryo-system with temperature stability better than 0.1 K. For more details see ref.^[18]

For the dielectric investigations the samples must be electrically contacted. Therefore the polymer was prepared between two thin aluminium electrodes as described in ref.^[14,15,19]

3. Results and Discussion

3.1. Kinetics of AA/S Copolymer Deposition

Monomers are difficult to plasma polymerize under complete retention of the monomer structure as compared to conventional polymerization.^[14] Plasma polymers are characterized by an irregular structure and often a large

concentration of C-radical sites responsible for extensive post-plasma oxidation is formed. Using pulsed plasma techniques this situation could be considerably improved.^[20]

Styrene and acrylic acid are a vinyl and acrylic monomer and they are easily to polymerize by a radical mechanism. Corresponding copolymerization parameters are given in ref.^[12] Also under exposure to low-pressure plasma both acrylic acid and styrene have a high tendency of polymerization as shown by high deposition rates in Figure 2a. The thickness of the deposited layer versus the deposition time for the different values of DC was recorded. For each value of DC, the data can be described by a straight line. From its slope the deposition rate R is obtained. In detail the deposition rate of AA/S copolymer is close to that of poly(acrylic acid) PAA homopolymers (see Figure 2a).

The calculated values of deposition rate for both PAA and PS as $\sum \text{PAA} + \text{PS}$ are more or less equal to that obtained from AA/S copolymer except at higher values of DC. The difference between calculated and measured rate at high values of DC depends on the deposition rate of PS.

For styrene the deposition rate increases strongly for higher values of the DC. This can be interpreted as dominance of fragmentation followed by a poly-recombination mechanism. As discussed in detail in ref.^[14] the deposition rate of acrylic acid shows a non-linear behaviour. This behaviour depends on the mechanism of the film formation corresponding to high energy density of the plasma.

During the plasma deposition there are two main processes. Firstly, the double bond can be broken by only a 1 eV energy input and a normal chain-growth polymerization (chain propagation) process can be started during plasma off. This process takes place with a rate R_{chain} and

will lead to regular structures similar to that obtained by a conventional polymerization process. Secondly, due to high energy density of the plasma a fragmentation of the monomer takes place followed by a poly-recombination with irregular, unsaturated, branched or crosslinked structures throughout plasma on. The rate of the latter process is denoted as R_{frag} .

In addition to these processes a depolymerization and a partly removal of the deposited layer may take place.^[21]

To compare the deposition rates for the different DC directly the deposition rate has to be normalized by the time where the plasma was on (t_{on}). Equivalently the deposition rate can be divided by the DC (Figure 2b).

Figure 2b shows that the normalized deposition rate of plasma (co)polymer is maximal for the lowest DC. This means that the rate for the chain propagation process is essentially higher for low DC.^[22] This might also imply that for low DC a more regular structure is formed. The marked increase in deposition rate for AA/S copolymers compared to the both monomers. The plasma chamber consists of acrylic acid and styrene as monomers vapour before plasma inlet. Additionally, an interaction between acrylic acid, an electron accepting monomer and styrene, an electron donating monomer can takes place.^[23] So the deposition rate of AA/S copolymer contains deposition rate for three compounds.

3.2. Retention of Functional Groups During Copolymerization

The concentration of carboxylic groups at acrylic acid and acrylic acid–styrene copolymers was analysed according to Equation (3).

Fahmy et al.^[14] discussed the C1s peak of plasma deposited PAA at DC = 0.5 and derivatized with TFE. Five peaks were analysed due to C–C, C–H groups (285.0 eV),

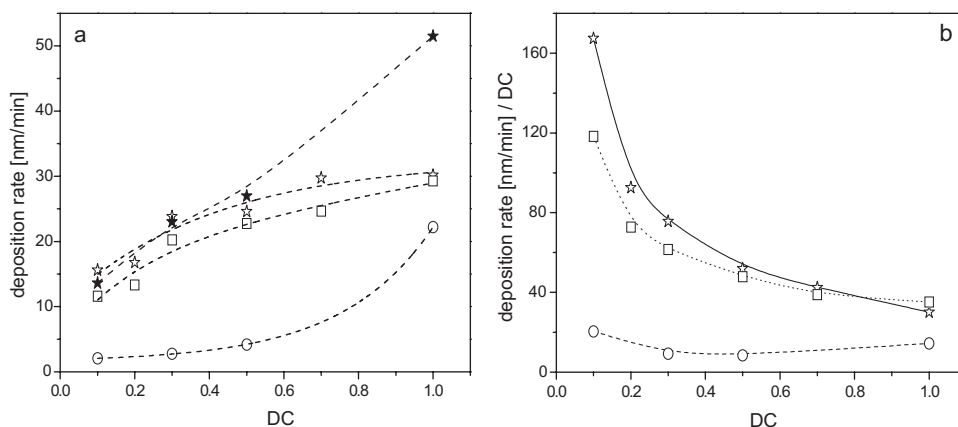


Figure 2. (a) Deposition rates versus DC for different systems: square, PAA; circle, PS homopolymers; solid star, PAA + PS calculated; and star, AA/S copolymer. Lines are guides for the eyes. (b) Normalized deposition rate versus DC for different systems: square, PAA; circle, PS homopolymers; and star, AA/S copolymer.

C–OH groups (286.3 eV), ($>\text{C}=\text{O} + -\text{CH}=\text{O}$) (287.4 eV), $\Sigma\text{COOH} + \text{COOR}$ (289.1 eV), and CF_3 (293.2).

Figure 3a and b shows the $\text{C}_{1\text{s}}$ spectra of a deposited AA/S copolymer films before and after derivatization with TFE of a sample prepared at a DC value of 0.5. The deconvolution of the $\text{C}_{1\text{s}}$ peak of AA/S copolymer before derivatization (Figure 3a) was done assuming five components assigned to the following bonds: C–C/C–H: 285.0 eV, C–O: 286.3 eV, C=O: 287.5 eV COO: 289.1 eV and shake up caused by $\pi \rightarrow \pi^*$ ^[24] interaction at (291.5 eV) was observed hinting to aromatic structures. The corresponding fractions of the components were estimated by fitting Gaussians to the data (see Figure 3a as example). The corresponding concentrations are given in Table 1.

The $\text{C}_{1\text{s}}$ spectrum of the derivatized AA/S (Figure 3b) copolymers layer was analysed by six Gaussians, including an additional component at 293.0 eV for the CF_3 bond as shown in Figure 3b.

The comparison of Figure 3a and b reveals that the contribution of the CF_3 which related to COOH group is equal to 1.6%. Therefore, the concentration of COOR groups defines as: $(\text{C}_{\text{COOR}} = \text{C}_{\text{COO}} - \text{C}_{\text{COOH}} = (3.79 - 1.6) \% = 2.19\%$. This means that some COO bonds have to be rather assigned to ester-type linkages than carboxylic groups, which do not participate in the derivatization reaction and remain therefore, unchanged.

Increasing DC produces a decrease in COOH functions. It is apparent that at longer plasma off-times the concentration of carboxylic groups in the deposits increases and a fragmentation of monomers and decarboxylation of acrylic acid decrease (see Figure 4a).^[22,25,26]

A strong difference in COOH-group retention between acrylic acid homopolymers and acrylic acid–styrene copolymers is obvious (Figure 4a).

Acrylic acid–styrene copolymer (molecular ratio of both monomers = 1:1) contains 9 COOH groups per 100 C-atoms theoretically. The low number of COOH groups is a

Table 1. Analysis of the $\text{C}_{1\text{s}}$ peak for plasma deposited AA/S copolymers as synthesized.

DC	C	O	O/C
0.1	88.7	11.3	0.127
0.2	89.8	10.2	0.114
0.3	91.1	08.9	0.098
0.5	90.7	09.3	0.103
0.7	92.0	08.0	0.087
1.0	92.8	07.2	0.078

consequence of a high carbon content introduced by the styrene monomer.

However, for the plasma-deposited copolymer the number of detected COOH groups was found to be in the order of 1–2 COOH groups (see Figure 4a). It can be interpreted as dominance of fragmentation of the monomers followed by a poly-recombination, and the same behaviour was observed for the thermal degradation of poly(acrylic acid) in argon atmosphere.^[27]

Figure 4a shows that with increasing DC the concentration of carboxylic group decreases. This is similar to the plasma deposition of pure acrylic acid but the dependence on DC is different for both systems. To investigate this in more detail, the concentration of COOH groups in the copolymer is plotted versus that of the homopolymer in Figure 4b. A constant slope should be observed in this figure if similar deposition mechanisms occur. Figure 4b shows that for higher values of DC a smaller amount of COOH groups is found than that expected from the structure of the plasma deposited homopolymers. This can be discussed in two directions:

Figure 2a shows that the deposition rate of styrene increases strongly for the highest values of the DC. This

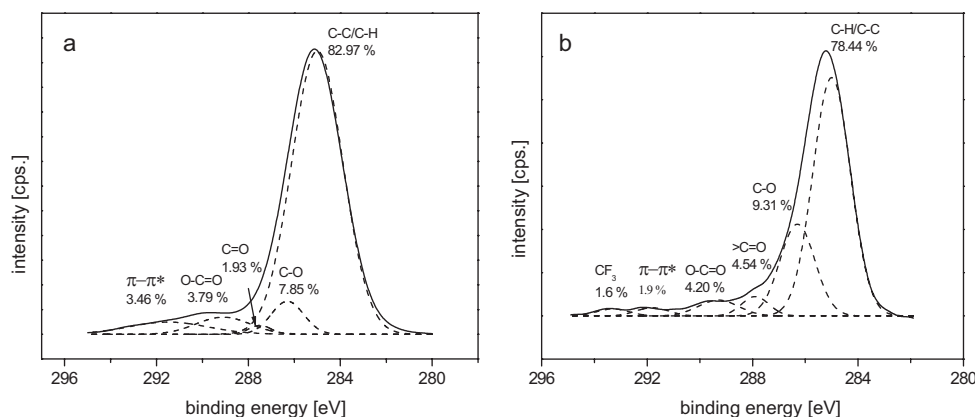


Figure 3. $\text{C}_{1\text{s}}$ peak of plasma-polymerized acrylic acid–styrene copolymer: (a) before derivatization and (b) after TFE-derivatization (DC = 0.5). The solid line represents the experimental data. The dashed lines represent the individual contributions.

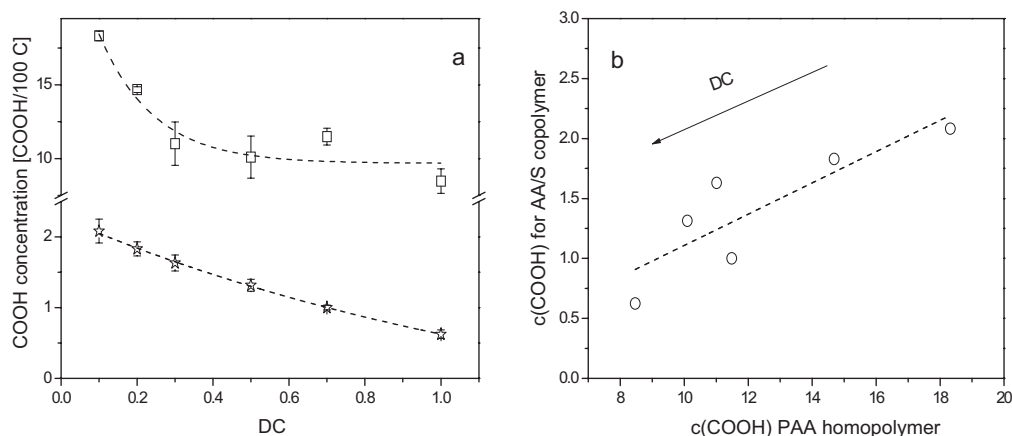


Figure 4. (a) Dependence of COOH per 100 C atoms for different systems: square, PAA (data taken from ref.^[17]); star, AA/S copolymer on applied DC. The dashed lines are a guide for the eyes. The error bars results from three different measurements of the same sample. (b) Concentration of COOH for AA/S copolymer versus the concentration of COOH for PAA homopolymer. The line is a linear regression to the data. For details see text.

might indicate that for high values of DC the introduction of styrene is favored and lower concentrations of acrylic acid units are obtained than expected from the corresponding homopolymer.

The second direction of the discussion is related to the monomer fragmentation due to the energy input as discussed before. Unfortunately one cannot discriminate between both explanations in the moment.

3.3. ATR-FTIR Analysis of the AA/S Copolymers

FTIR spectra of plasma deposited PAA, PS homopolymers and the AA/S copolymer are shown in Figure 5. All spectra exhibit stretching vibrations of the polymer backbone consist of: the ν CH (as/sym) in the wavenumber range from 2916 to 2844 cm^{-1} and associated with the C=O stretching near 1700 cm^{-1} . With regard to the PS segments at 700/760 cm^{-1} the aromatic C–C stretching, at 1494/1601 cm^{-1} the aromatic C=C stretching is observed and the aromatic δ C–H takes place at 3080/3060/3020 cm^{-1} .^[28–30]

The most important band for the following discussion is the C=O stretching vibration which is described by three components (Gaussians).

Wang^[31] discussed three components with a maxima at 1749, 1715 and 1685 cm^{-1} measured for conventional poly(acrylic acid) and copolymers of acrylic acid with styrene.

For plasma deposited PAA05 sample (see Figure 6a) the band at 1680 cm^{-1} is assigned to the C=O stretching of dimers as well as intermolecular hydrogen bonding or C=C double bonds.^[28] The main component at 1712 cm^{-1} is attributed to stretching vibration (C=O) of carboxylic groups. To describe the contribution of ester^[32] formed by COOR groups a third Gaussian is located at 1737 cm^{-1} .

The ester groups may be formed by self condensation of $\text{CH}_2=\text{CH}-\text{COOH} \rightarrow \sim\text{CH}_2-\text{CH}_2-\text{CO}-\text{O}\sim$.^[1]

Figure 6b gives the FTIR spectra for plasma polymerized AA/S copolymer deposited with a DC of 0.5. Compared to plasma deposited PAA homopolymers the main peak of the C=O stretch is shifted from 1712 to 1706 cm^{-1} (see Figure 6b). The peak located at 1737 is also shifted to 1732 cm^{-1} which describes the contribution of ester units. This indicates a difference in the structure compared to those expected from plasma deposited PAA (COOH). A third Gaussian is located at 1680 cm^{-1} similar to that observed for plasma deposited PAA homopolymers. From the XPS measurements it is known that C=O, COOH and COOR groups are formed.

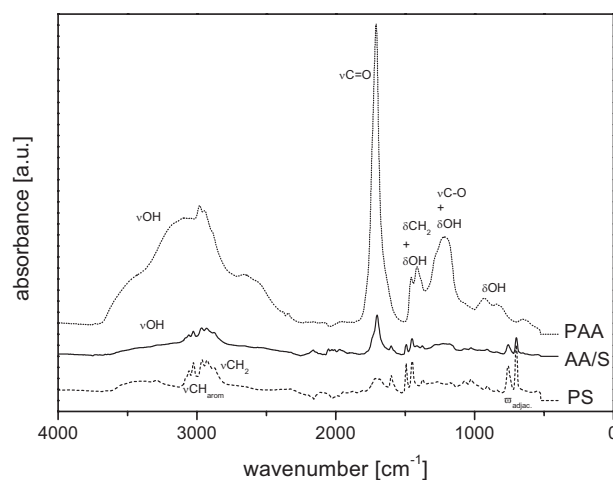


Figure 5. FT-IR spectra of plasma deposited PAA, PS homopolymers and the AA/S copolymer (DC = 0.5).

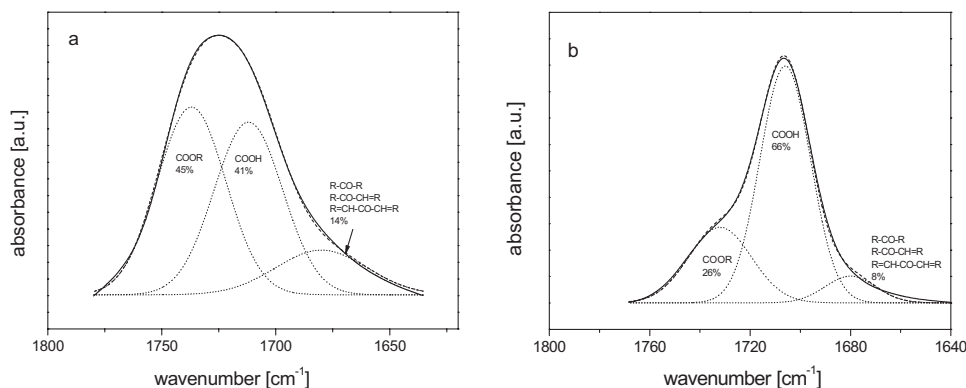


Figure 6. Analysis of the C=O band of a plasma deposited (DC = 0.5): (a) PAA homopolymers film and (b) AA/S copolymers. The solid line represents the experimental data. The dashed line is a fit of a sum of three Gaussians to the data. The dotted lines represent the individual contributions.

From the fits the areas of the peaks at 1706 cm^{-1} (A_{1706}) and 1732 cm^{-1} (A_{1732}) are taken and its ratio is calculated as a measure for the ratio of COOH groups estimated by FTIR.

A_{1706}/A_{1732} is plotted versus DC (Figure 7) to discuss the concentration of carboxylic groups of AA/S copolymers in comparison to PAA plasma deposited homopolymers. This graph shows firstly, that the concentration of COOH groups decrease with increasing DC for both PAA and the copolymer and secondly, that there is a strong difference between the homo- and the copolymer. Acrylic acid tends to self-condensation as discussed above. Additionally, decarbonylation and dehydrogenation may produce α,β -unsaturated ketones as found by the FTIR analysis. A more refined discussion requires additional investigations which are beyond the scope of this paper.

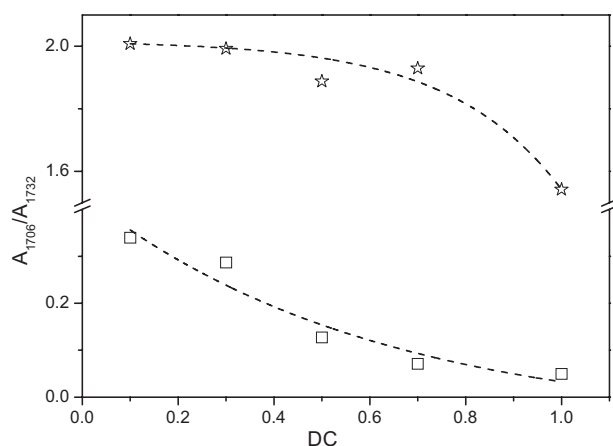


Figure 7. A_{1706}/A_{1732} versus DC for different systems: square, PAA (data taken from ref.^[17]); star, AA/S copolymer. The lines are a guide for the eyes.

Moreover, for copolymers the dependence of the ratio of carboxylic groups to ester groups obtained by FTIR on DC is much higher than that for the plasma deposited homopolymers. It is concluded that AA/S copolymer is more regular than PAA homopolymers.

XPS und FTIR should provide the same information about the concentration of COOH groups. Therefore, Figure 8 displays (A_{1706}/A_{1732}) versus the concentration of COOH groups per 100 C atoms estimated from the XPS measurements. This Figure shows that the concentration of COOH groups per 100 C atoms decreases with increasing DC. From the theoretical point of view a constant value should be obtained. To discuss this result the different analytical depth of both methods has to be considered. XPS is sensitive to a layer with a thickness of 5–7 nm whereas FTIR provides information across the whole sample thickness. This indicates that the already deposited

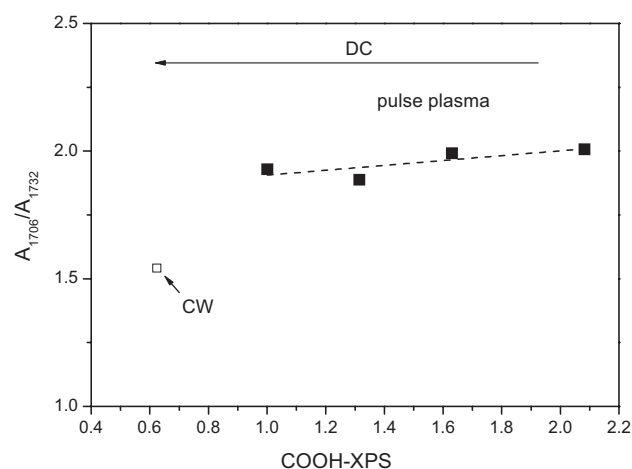


Figure 8. Correlation between the concentration of COOH groups measured by XPS (TFE-derivatization) and A_{1706}/A_{1732} calculated from FTIR for the AA/S copolymer system. The dashed line is a linear regression to the data.

material is damaged or even depolymerised at a larger distance from the surface due the high energy impact of the plasma which includes also UV radiation. For a more extended discussion see ref.^[14,15] However, this behaviour is obvious for low DC and continuous wave plasma.

3.4. Thermal Analysis of AA/S Copolymers

From the DSC curves for AA/S copolymers deposited for different value of DC, the glass transition temperature T_g is estimated from the inflection point of the heat flow of the second heating run and plotted versus DC in Figure 9. These data are compared with the values obtained for plasma deposited PAA homopolymers.

Firstly, for all plasma deposited homopolymers (PAA, PS) and the AA/S copolymer samples the values of T_g are lower than those measured for conventional poly(acrylic acid) (379 K)^[33] and polystyrene (373 K).^[34] It can be concluded that plasma polymerization technique results in products with a lower molecular weight and probably with a highly branched structure compared to the conventional polymerized materials.^[35,36] In the latter case the dangling ends of the branched structures act as internal plasticizer like for conventional poly(*n*-alkyl methacrylates).

Secondly, the glass transition temperatures for the plasma deposited AA/S copolymers are also lower than those of plasma deposited PAA homopolymers. Probably, the introduction of the bulky styrene units increases the free volume and also avoids the formation of hydrogen bonds. Both effects will lead to a reduction of the glass transition temperature.

For the copolymers T_g decreases for low values of DC up to DC = 0.5. A similar dependence was observed for the plasma deposited PAA homopolymers (see Figure 9). Then the T_g increases with increasing DC in difference to plasma PAA homopolymers. This behaviour confirms the results obtained by monitoring the deposition rate, XPS and FTIR measurements. As argued for the deposition rate, the rate

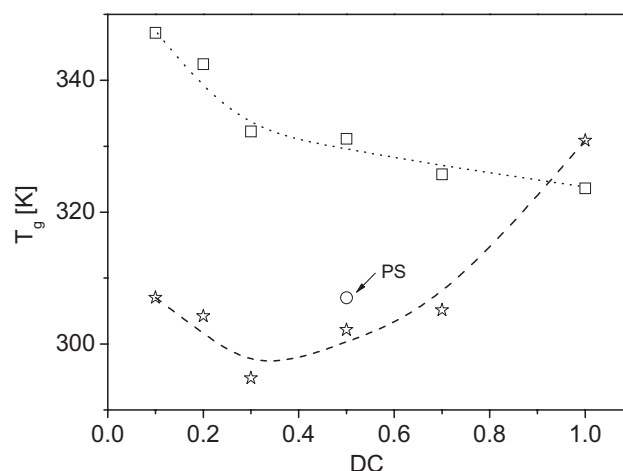


Figure 9. T_g versus DC for different systems: star, AA/S copolymer; square, PAA; and circle, PS. Lines are guides for the eyes for AA/S (dashed line) and PAA (dotted line).

for the chain propagation process is essentially higher for low DC. Especially, the crosslinking increases with increasing values of DC which lead to an increased T_g .

3.5. Dielectric Relaxation Spectroscopy (DRS)

Dielectric relaxation spectroscopy was used to investigate the molecular dynamics of the thin plasma deposited polymer films.^[37,38]

Before the dielectric properties of the plasma deposited AA/S copolymers are discussed, the dielectric loss versus frequency (f) and temperature (T) for plasma-polymerized PAA and PS homopolymers should be considered (Figure 10).

The dielectric relaxation behaviour of plasma deposited poly(acrylic acid) is discussed in detail elsewhere.^[14] A relaxation process indicated by a peak in the dielectric loss

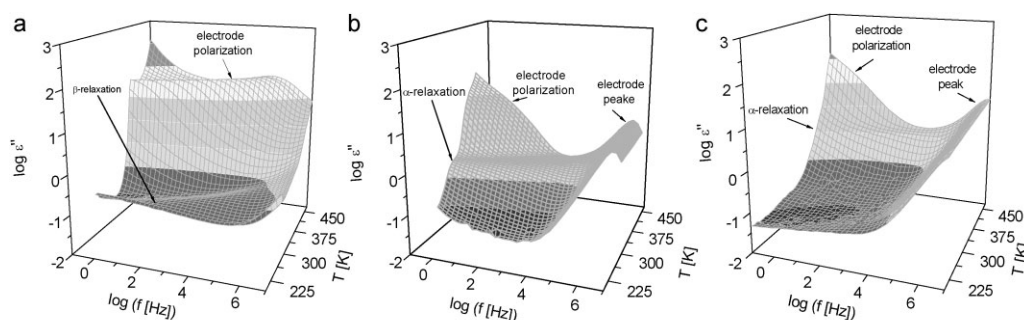


Figure 10. Dependence of dielectric loss ϵ'' versus frequency and temperature for different systems for DC = 0.1 for the cooling cycle: (a) PAA, (b) PS homopolymers and (c) AA/S copolymer.

is observed at low temperature for this material (Figure 10a), which is assigned to the β -relaxation. The β -relaxation corresponds to localized fluctuations of the carboxylic group. For higher T the dielectric loss increases strongly. This increase is related to conduction phenomena which are related to the drift motion of charge carriers, originating from the carboxylic group in the presence of water.

At even higher temperatures a clear indication of a further process is visible called electrode polarization which is due to accumulation of charges at surface of the electrodes and the formation of electrical double layers.

Additionally, at the high frequency side of the spectra with a time constant of $\tau_{\text{Res}} = R * \hat{C}$ (\hat{C} , sample capacity) the electrode peak was observed due to the resistance of aluminium electrodes.^[14]

In case of plasma deposited PS the electrode peak and the electrode polarization were also observed like for plasma deposited PAA (see Figure 10b). In the range of glass transition measured by DSC, a relaxation process takes place, which corresponds to the dynamic glass transition due to segmental dynamics (α -relaxation). The α -relaxation is related to glass transition temperature of the system and therefore, called dynamic glass transition.

For the AA/S copolymer similar to PAA and PS plasma deposited homopolymers an electrode peak (higher frequencies) and the electrode polarization (higher temperatures) are observed. In difference to plasma deposited PAA homopolymers no unambiguous β -relaxation is observed for the copolymer deposited with DC = 0.1 (see Figure 10c) because the dielectric loss covers a wide range. In ref.^[14] the β -relaxation is assigned to the localized fluctuations of the carboxylic groups. Therefore, the decrease of the intensity of the β -process has to be attributed to a decrease in the number density of carboxylic groups. This line of argumentation is in complete agreement with the XPS investigation.

In the temperature range where for plasma deposited polystyrene the α -relaxation is observed. This process is detected also for the copolymer, indicating that the free volume increases and crosslinking decreases due to the presence of styrene units.

The electrode peak is taken into consideration by a Debye function as described in ref.^[19] Therefore the whole fit function reads as

$$\varepsilon''(f) = \text{Im} \left\{ \frac{\Delta\varepsilon}{(1 + (if/f_0)^\beta)^\gamma} \right\} + A * f \quad (4)$$

where f_0 is a characteristic frequency related to f_p . β and γ are fractional parameters ($0 < \beta \leq 1$ and $0 < \gamma \leq 1$) characterizing the shape of the relaxation time spectra. ε_∞ gives ε for $f \rightarrow \infty$ where $\Delta\varepsilon$ denotes the dielectric

strength of each process; A is a fitting parameter which is mainly due to τ_{Res} .

Figure 11 compares the temperature dependence of the relaxation rate of the α -relaxation $f_{p,\alpha} f$ versus T^{-1} for the plasma deposited polystyrene and the corresponding copolymer for DC = 0.5. Because of the fact that the rate for the electrode polarisation f_{EP} is related to $f_{p,\alpha}$ (see^[14]) f_{EP} for PAA is added as well. At the first glance the temperature dependence of the relaxation rate of the plasma-deposited copolymer is similar to that of polystyrene. This might be due to the fact that for poly(acrylic acid) the segmental dynamics is strongly influenced by the formation of hydrogen bonds. The possibility of the formation of hydrogen bonds is strongly reduced for the copolymer. For chemically stable polymers, the temperature dependencies of relaxation rates might be described by the Vogel–Fulcher–Tamman–Hesse (VFT)^[39–41] Equation (5)

$$f_{p,\alpha} = f_\infty \exp \frac{A}{T - T_0} \quad (5)$$

In Equation (5) $\log f_\infty$ and A are parameters. T_0 is the so called Vogel or ideal glass transition temperature found to approximately 40–60 K lower than the T_g measured by DSC. General it is believed that a dependence according to Equation (5) is a signature of glassy dynamics. A dielectric glass transition temperature can be estimated by $T_g^{\text{Diell}} = T(f_p = 1 \text{ Hz})$ (see Figure 11).

Figure 12a compares the temperature dependence of the relaxation rate of the α -relaxation for different values of DC for heating. Firstly, with increasing DC the rate of α -relaxation more or less shifts to higher temperatures. Secondly, the temperature dependence on $f_{p,\alpha}$ cannot be

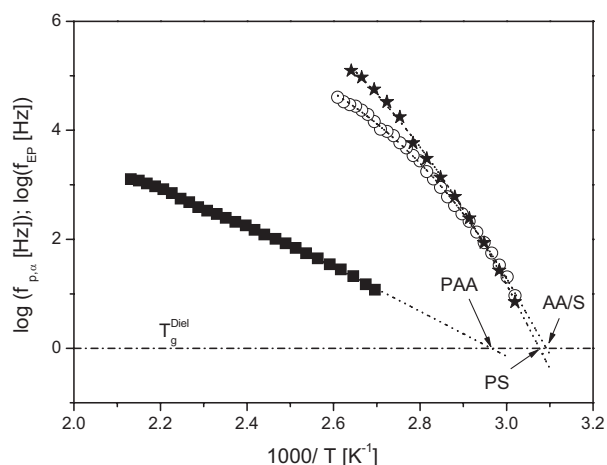


Figure 11. Relaxation rate versus inverse T solid square, PAA; circle, PS; and solid star, AA/S copolymer (DC = 0.5). Lines are guides for the eyes.

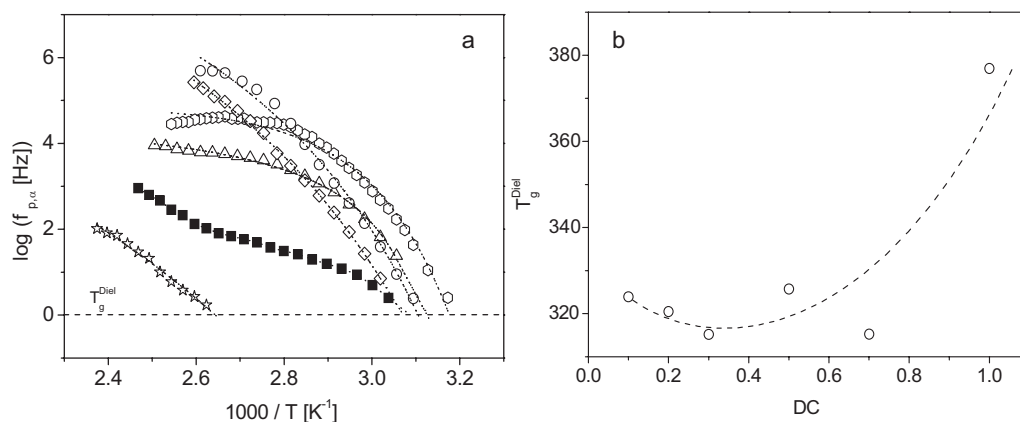


Figure 12. (a) Relaxation rate of the α -process versus inverse temperature for plasma deposited AA/S copolymers for different DC: square, 0.1; circle, 0.2; triangle, 0.3; lozenge, 0.5; hexagon, 0.7; star, 1. (b) Dynamic glass transition temperature T_g^{Diel} versus DC. The line is a guide for the eyes.

described in the whole temperature range by the VFT-equation. This dependence is non-monotonous and carries some structure (see for instance data for $\text{DC}=0.1$ or $\text{DC}=0.7$). To discuss this behaviour one has to bear in mind that during the plasma polymerization a large number of radicals are formed which do not react completely during the deposition process. After deposition these radicals are quenched and the deposited layer is in a metastable but non-equilibrium state. By heating up the segments become mobile at the glass transition these radical undergo a post plasma reaction. Therefore this structure in the temperature dependence is related to the kinetics of the chemical reaction that takes place during the heating process.

Nevertheless, a T_g^{Diel} can be estimated and plotted versus DC in Figure 12b. T_g^{Diel} decreases firstly with the DC up to a DC value of 0.5. Then the T_g increases with increasing DC. This behaviour is similar to that obtained by DSC. Firstly, that proves that dielectric spectroscopy measures the glass transition for these systems. Secondly, this behaviour can be discussed in the same way like for the DSC measurements and the results that obtained by monitoring the deposition rate, XPS, FTIR and DSC measurements are consistent.

To discuss the dielectric behaviour for the heating and cooling run in more detail Figure 13 gives the dielectric loss versus temperature at a fixed frequency for the different thermal histories for the sample AA/S deposited with $\text{DC}=0.1$ as an example. The first run is a heating measurement of the as prepared sample from low to high temperatures as described above. The second run is the subsequent cooling from high to low temperatures. For both cases at low temperatures the β -relaxation is observed as a well defined peak in the spectra. For the first heating run a shoulder is observed at higher

temperatures than that of the β -relaxation which corresponds to the α -relaxation.

It was observed the dielectric loss is dramatically reduced in the range of α -relaxation. Moreover, the electrode polarization is shifted to higher temperatures. This hysteresis between the first heating and the cooling run for plasma deposited AA/S copolymer with $\text{DC}=0.1$ as example can be explained by the following consideration. As discussed above during the plasma deposition of polymer a highly branched product with many free radicals is formed.^[14,15] These free radicals were able to react with each other to form a more crosslinked network during heating. So, the α -relaxation process seems to disappear and maximum peak of the electrode polarization shifted to high temperature indicating also a change in structure.

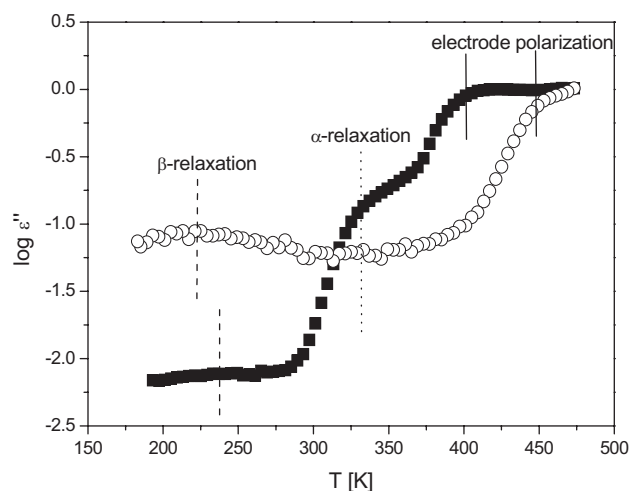


Figure 13. Dielectric loss ϵ'' versus T at a frequency of 1 kHz: solid square, heating; and circle, cooling ($\text{DC}=0.1$).

Otherwise, the dielectric loss is increased in the range of β -relaxation and this process is shifted to lower temperatures. As discussed above the β -relaxation is assigned to the localized fluctuations of the carboxylic groups. Therefore, the increase of the intensity of the β -process after heating run has to be attributed to increase the number density of free carboxylic groups.

4. Conclusion

Thin AA/S copolymer films were deposited by pulsed-plasma polymerization for a 1:1 composition. The structure-property relationships of AA/S copolymers were studied in dependence on the DC by different techniques and probes.

XPS measurements were accomplished to analyse the chemical surface composition of the deposited films. A derivatization technique in combination with XPS measurements were used to obtain information about the concentration of carboxylic groups at the surface of the plasma deposited AA/S copolymer. FTIR-ATR measurements were carried out to compare the ratio of COOH groups to ester groups across the whole sample thickness for AA/S copolymers in comparison to PAA homopolymers. It was found that AA/S copolymer is more regular than PAA homopolymers.

DRS gives information about the dynamic mobility and thermal stability of the film in dependence on the DC. The dielectric measurements reveal that the structure of plasma-deposited copolymer is dependent on the DC. Otherwise, the crosslinking decreases at AA/S copolymer in comparison to PAA homopolymers due to the presence of styrene repeat units.

However, the dielectric measurements show that the plasma deposited AA/S copolymer films are not thermally stable but undergo a post-plasma chemical reaction during heating. Radical-radical recombination ($R_1\bullet + \bullet R_2 \rightarrow R_1-R_2 + \Delta$) may occur or auto-oxidation ($R\bullet + \bullet O-O\bullet \rightarrow R-O-O\bullet \rightarrow$ hydroperoxides \rightarrow oxidized products). The occurrence of chemical reactions is evidenced by a hysteresis in the dielectric spectra between the heating and the subsequent cooling run. So after heating run a thermal stable and homogenised sample is obtained.

Acknowledgements: A. Fahmy gratefully acknowledges the Egyptian Government's Ministry of Higher Education, Cultural Affairs & Missions Sector (CAMS) for their support and funding. Thanks are given to G. Hidde and F. Milczewski for technical assistances.

Received: June 8, 2011; Revised: September 30, 2011; Accepted: October 11, 2011; DOI: 10.1002/ppap.201100117

Keywords: acrylic acid–styrene copolymer; dynamic mobility; plasma copolymerisation; surface functionalization; thin film properties

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