Thin-Film Plasma-Polymerized Iso-t-pentinol and its Postpolymerization Properties

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ABSTRACT: Thin films of plasma polymer were prepared from unsaturated precursor with one triple bond, iso-t-pentinol. This precursor was injected either in a vapor state itself or using argon as a carrier gas, bubbled through a precursor. These polymers were prepared under different fixed conditions when only one parameter of plasma polymerization among all the others was changed in each measurement during the process of polymerization (i.e., power in a matched reactor, precursor partial pressure, total pressure in reactor, electrode gap, and polymerization time). The samples were deposited on thin solid substrate having oxygenless molecules. Infrared Spectroscopy, IRS, Electron Spectroscopy for Chemical Analysis, ESCA (XPS), and Electron Paramagnetic Resonance (EPR) were used for analyses of these samples. The results of analyses proved generation and growth of oxygen-containing groups by plasma polymerization (IRS); they also proved that C—O— group concentration increased and C=O group concentration decreased in polymer surface layers during 24 h after plasma polymerization (ESCA). A drop of free radical concentration (measured by EPR) was steep from the end of plasma polymerization to 60 min and mild later on (to approximately 215 h). Amount of free radicals depended on the power in reactor. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 677–686, 1999

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INTRODUCTION

It has been shown in many articles that plasmapolymerized thin films can be deposited on solid substrates. If precursors are unsaturated and oxygen containing, plasma polymerization on surfaces can be used in many cases to prepare hydrophilic films (having OH— groups).¹⁻⁷ These authors dealt with postplasma properties of plasma-polymerized layers and with an investigation by ESCA (XPS) and by IR spectroscopy (but results of some authors that dealt with ESCA and EPR are not cited too often).

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Our aim and idea was to prepare more stable and durable plasma polymers from a certain unsaturated aliphatic monomer. We want to make surfaces of these polymers with more stable hydrophilic properties (to make a better and stable contact angle between water drops and polymer surface). We know from previous investigations that saturated alcohols are not used frequently because OH- groups are eliminated in a substantial amount during a plasma polymerization process that occurs in gas and evaporated hydrocarbons. That is why plasma polymers are less hydrophilic than would be anticipated and expected.^{1,2,7} Therefore, we selected iso-t-pentinol, C₅H₇—OH (some other authors successfully developed plasma polymer foils also having hydro-

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philic polymers from unsaturated aliphatic alcohols^{1,2}). We measured the change in concentration of free radicals after plasma polymerization by EPR. The changes of some group concentrations on a plasma polymer film surface were measured by ESCA. We can compare the ESCA results, obtained by means of ref. 8 (assignment of chemical formulae of atom bonds), with the EPR ones. We investigated the structure of plasma polymers, according to ref. 9, by IR spectroscopy to obtain more results about chemical analysis of a formed polymer, about radical and group concentrations (their changes) in bulk of a polymer. The method of polymerization on thin foil substrate is usually used (we used it, too) because the foil can be cut in small areas for analyses.

Some authors investigated and dealt with concentration of free radicals.¹⁰ Others investigated only an influence of hydroxyl groups -OH on surfaces of plasma polymers.^{7,11} Some authors were investigating hydrophilic surfaces of plasma polymers for different applications of this plasma technique^{1,6,7} in time. The authors made these polymers with the intention of trying to control surface reactions (see refs. 6,11); others carried out some experiments with interesting results in ESCA (XPS) and IR spectroscopy, as seen in refs. 3-6. The authors who measured changes or decrease of free radical concentrations (measured by EPR) in plasma polymer after polymerization (or in postplasma time) are not referred to as often. The author¹⁰ presented remarkable conclusions concerning the exponential dependence of the increase of free radical concentration vs. time during plasma polymerization. This dependence is expressed through an exponentially increasing function: $C = \operatorname{Co} e^{A.t}$ when the free radicals are formed in bulk of a plasma polymer. Here, Co is the initial free radical concentration in a surface film; A is always positive constant, depending on a plasma process; *t* is the time of plasma polymerization or the time of a surface film exposition; C is the final state of free radical concentration in a deposit film after plasma polymerization (this polymerization process was carried out without interruption) in the formula mentioned above (in contrast, we wanted to measure something opposite to ref. 10, i.e., to investigate the time dependence of the free radical concentration decrease after the end of plasma polymerization). The author⁷ also mentioned very similar results and dependence.

We can compare their aims (ESCA, EPR measurements, etc.) with our measurements of

plasma polymers made by IR spectroscopy, EPR, and ESCA. In addition we used NMR (Nuclear Magnetic Resonance) only to compare the results.

We show that each spectroscopic result is compatible with results of other methods of spectroscopy: ESCA, IRS, and EPR; our supporting measurement (NMR) also confirmed results of methods of spectroscopy mentioned above.

EXPERIMENTAL

We polymerized the vapors of iso-t-pentinol on the thin foils that were cut and placed on the bottom electrode of a plasma reactor.

We chose the method of polymerization on thin-foil substrate of high-density polyethylene, HDPE, mainly for the principal reason (they do not contain any atoms of oxygen in macromolecules except for an impurity) of the possibility to easily identify oxygen atoms in plasma polymers. We did it because of the later use of IR Spectroscopy, ESCA, and EPR measurements, and thus, we were sure that the atoms of oxygen had to be eliminated from plasma and incorporated into plasma-polymerized iso-t-pentinol during the plasma polymerization.

Schematic drawing of a glass bell jar-type plasma reactor for plasma polymerization is shown in Figure 1.

The plasma reactor was fed by vapors of iso-tpentinol through the hollow top (upper) electrode (1). The carrier gas argon bubbled through liquid iso-t-pentinol (2) because the iso-t-pentinol is in a liquid phase at normal room temperature and at normal atmospheric pressure (argon was saturated with vapors of iso-t-pentinol). The polymers were prepared in a radio frequency (R.F.) glow discharge, operated in a mixture of argon and vapors of iso-t-pentinol at a total pressure from 30 to 200 Pa. We could mix both gases using glass and needle values (7). The reactor was pumped by a diffusion pump and a rotary oil pump (5) through a cold trap (6). Pressure in the plasma reactor was controlled and measured by a Pirrani gauge (8). The plasma was excited by R.F. discharge at 13.56 MHz and was powered by a special power R.F.generator (13.56 MHz frequency) (3) through a match box (4) when one terminal of the generator as well as the metal components of the generator, the lower electrode, and the other metal parts were grounded.

The partial pressures were fixed by needle valves, or throttle valves (7), by precise throttling

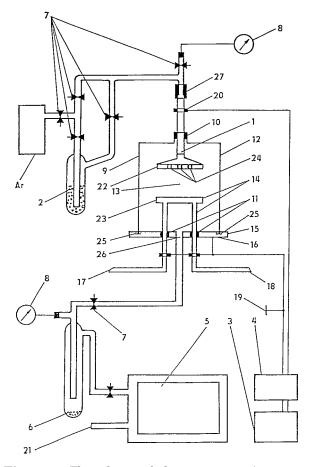


Figure 1 The scheme of plasma reactor: Ar-argon pressure flask; 1-hollow upper electrode; 2-flask with iso- τ -pentinol; 3—R. F. generator f = 13.56 MHz; 4-match box; 5-pump unit; 6-cold trap; 7-throttling valves; 8-pressure gauges; 9-reactor glass cover; 10—special pass for upper brass electrode into glass reactor cover; 11-holes for a cooling of lower electrode; 12-glass bell jar-type reactor; 13-reaction plasma space exited by R. F. discharge; 14-lower electrode with a cooling by a flowing liquid; 15-reactor aluminum bottom; 16-earth terminal connected with the reactor bottom; 17-cooling water input; 18-cooling water output; 19-grounded terminal; 20-R. F. terminal connected with the upper electrode; 21-gas output; 22-upper electrode made like a shower; 23lower electrode centred in a table form; 24-holes into the upper electrode on bottom side for a gas input; 25-rubber sealing ring between glass reactor wall and reactor bottom; 26-total reactor gas output; 27-flexible reduction hose between a glass input tube and the upper brass electrode.

of each gas input. We defined parameter $B = P_{\rm Ar}/P_{\rm isopt}$, as the ratio of partial pressure of argon carrier gas to partial pressure of precursor. In our

case, B was kept approximately at 1.0 in almost all our experiments and a little bit lower than 1.0 for our samples for measurements and spectroscopic analyses where the optimum B ranged from 0.6 to 1.0. The greatest deposition rate was measured at the optimum B.

As may be seen from Figure1, we used a parallel plate electrode system: both electrodes were made from brass, the grounded lower one (23) was water cooled (17) and (18), the upper excitation one (22) was hollow with holes (24) on the bottom side. This shower type electrode was used because it provided homogenous supply of the gas mixture (1), and could be adjusted and changed by moving up and down before a start of polymerization (because the electrode hangs). The movement is enabled through the feed pass (10), seen in Figure1. The upper electrode height was usually adjusted to 130 mm from the bottom of the reactor. Also, the distance between electrodes was adjusted to 50 mm.

When we tested the dependence of deposition rate on the distance between electrodes, the optimum and maximum deposition rates were at the distance of 50 mm (all experiments at a constant ratio B). We also chose this distance (for the same value B) and we named this one as a standard electrode distance condition for a preparation of samples to analyses because of the maximum polymerization rate (maximum chemical conversion) at this distance in the plasma reactor.

We carried out polymerization deposition on the thin foil at a power in the range between 12.5 and 360 W for a completely matched plasma reactor (without reverse irradiation) and at a total pressure in the reactor in the range between 30 Pa and almost 185 Pa. The base bottom (15) of the plasma reactor was made from aluminum.

The match box (4) that we used was made by Annecke (Germany). A match process was ready by turning changeable inductance at some time, and the plasma reactor was thus prepared to work.

Electron Paramagnetic Resonance (EPR) or Electron Spin Resonance (ESR) measurements were carried out by a Bruker EMS 104 EPR Analyzer.

ESCA measurements were carried out using the equipment Specs Sage 100 with a high resolution, and IRS analysis by Fourier Transformation Infrared Spectrometer, FTIRS (FTIR Perkin-Elmer Spectrometer, model 1706X); the R.F. generator, type OEM 6 (750 W), was made in by ENI, USA. Samples of plasma polymers, prepared on thin foils, for ESCA, IR (FTIR), and EPR were stored and tested under argon atmosphere. The samples for EPR were cut (into small pieces) from the same foils with special defined dimensions and were carefully put into special quartz glass test tubes.

For IR measurement evaluation, two samples from the IRS analyses were selected and are described here. Conditions of plasma polymerization for the polymerized samples changed only in the level of partial pressure of precursor. The polymerization processes were repeated under the conditions mentioned here and were separately analyzed three times to confirm whether the changes were the same (analyses were the same except for intensity of signals according to the level of partial pressure of precursor). Physical conditions for the two samples are as follows.

In the first case the sample (S 1) was polymerized under the physical conditions: a power of 100 W, a total pressure of 60 Pa, a partial pressure of the precursor of 35 Pa, so the ratio *B* was 25:35, the standard electrode gap, cooling at 156 C, a polymerization time of 5.0 min. This sample was cut from the same support foil as the sample for the ESCA analysis. IRS apparatus enabled us to plot one difference of an IR spectrum of transmittance of energy (IR analysis signals of plasma polymer on foil were corrected with respect to the used background, polyethylene foil, and thus the pure difference of signals was obtained).

In the second case, the sample (S 2) was polymerized at the conditions: a power of 100 W, a total pressure of 50 Pa, a partial pressure of the precursor of 25 Pa, so the ratio of *B* was 25:25. The other conditions were the same (see sample S 1). IRS apparatus plotted one spectrum of absorption energy. This IR spectrum for absorption had to be compared with the IR spectrum of pure polyethylene foil (background) to see which changes occurred.

For EPR measurement evaluation, three samples were selected: (a) conditions of plasma polymerization in the first case: a power of a matched reactor of 360 W, a total pressure of 183 Pa, a partial pressure of the precursor of 95 Pa, a substrate standard cooling (at 15°C, a standard condition for electrode gap (50 mm), a polymerization time fo 3.0 min (sample **S** 3). We note that the ratio of partial pressures *B* was about 1.0.

In the second case, conditions of plasma polymerization were as follows: a power of a matched reactor of 120 W, a total pressure of 95 Pa, a partial pressure of the precursor of 55 Pa, a substrate cooling at 15°C, a standard electrode gap, a polymerization time of 3.0 min (sample **S** 4). We remark that the ratio of partial pressures *B* was also in the optimum range.

Conditions of plasma polymerization in the third case: the power of a matched reactor of 100 W, a total pressure of 110 Pa, a partial pressure of the precursor of 60 Pa, a substrate cooling at 15°C, a standard electrode gap, a polymerization time of 3.0 min (sample **S 5**). We note that the ratio of partial pressures *B* was again about 1.0.

For ESCA, EPR, and IR these experiments were repeated three times for powers of 50, 100, 120, 170, and 360 W.

RESULTS AND DISCUSSION

Results from ESCA (XPS) and Their Discussion

The plasma polymerization was carried out at the powers described above, in the matched plasma reactor. Other parameters were fixed, namely, the standard contitions (electrode gap, cooling of lower electrode at 15° C), the time of plasma polymerization between 3.0 min and 5.0 min, and the total pressure in the reactor in the range mentioned above for the control experiment of a power influence.

The results obtained from ESCA measurements showed that samples contained from 17 to 28 atomic percent of oxygen in the structure after plasma polymerization. This relatively high percentage of oxygen in the structure was also found after 21 days; over 15 atomic percent of oxygen was obtained in the plasma polymer later. Besides of some standard resolution for the measurement of a total atomic concentration, analysis of high resolution was also used for ESCA measurement.

We used foils that were hydrophobic. Hydrophilicity of our polyethylene foil was very low before plasma surface treatment. Much greater and better hydrophilicity was observed immediately after plasma polymerization. Quantitatively, from a water drop shape, the hydrophilicity of handled foils was also quite great after 21 days.

The analysis of one selected sample **S 1** is presented here. Conditions of plasma polymerization is described above.

The results of the measurement made immediately after the end of plasma polymerization are

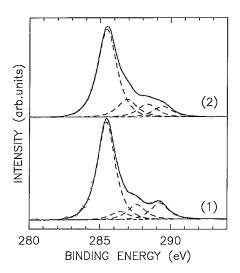


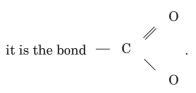
Figure 2 Results from ESCA made by a high resolution: Graph (1)—measurement made immediately after the end of plasma polymerization; graph (2)—measurement made 24 h later after the end of plasma polymerization.

shown in Figure 2 [below in the graph (1)]. The results of the measurement made 24 h later after the end of plasma polymerization can be seen in Figure 2 [above in the graph (2)]. We see the difference immediately by comparing the two curves (the area of each envelope curve of all signals was practically the same for each measurement, without any change for 24 h). An assignment concerning these groups and radicals concentrations that increased (also concerning those other concentrations that decreased) during the relaxation time after the end of plasma polymerization was carried out with the help of ref. 8. The diagram of difference between the measurements mentioned above is obvious in Figure 2 (signal vs. binding energy of C 1s electrons in eV).

We describe binding energy signals and assign chemical formulae to the mentioned groups and radicals that occurred in the plasma polymer sample. The results of high-resolution analysis that are seen in Figure 2 are the following: (a) increasing peak (in 24 h) at the binding energy 286.7 ± 0.1 eV (the first of smaller peaks from left to right in both of these graphs) is in agreement with ref. 8, where this peak corresponds to the energy 286.6 eV: it is the bond —C—O—.

This peak was assigned to alcoholic groups —C—O—H , —OH radicals, ether groups —C—O—C—, or hydroperoxide groups on carbon atoms —C—O—O—H, peroxide groups on carbon atoms —C—O—O—, respectively. (b) The decreasing peak (in 24 h) at the binding energy $287.9 \pm 0.2 \text{ eV}$ (the next peaks in the middle in both graphs) is in agreement with ref. 8, where the peak corresponds to the energy 287.8 eV: it is the bond =C=O.

This peak was assigned to =CO ketone groups by which ketones are characterized. (c) the decreasing peak (in 24 h) at the binding energy 289.3 \pm 0.3 eV (the last small peaks at the right in both graphs in Fig.2) is in agreement with ref. 8, where the peak corresponds to the energy 289.1 eV:



This peak was assigned to ester groups (see ref. 8).

The experiment was repeated and similar results (ESCA) were obtained at powers of 50 and 170 W.

By comparing of the results of ESCA and IRS (they are described later), we can assume that some oxygen-containing radicals and groups reacted from other oxygen-containing ones during 24 h, mainly to R1—C—O—O—, R2—O—R3, R4—OH groups and to —OH hydroxyl radicals where R1, R2, R3, and R4 are hydrocarbon radicals.

We can say that the possibility was that -C-O- radicals and groups were formed in surface layers or that they diffused from deeper layers to surface layers, that deeper positioned molecules or their fragments with some oxygencontaining radicals and groups of the -C-Okind penetrated to upper positioned layers [the total concentration of oxygen (O) was measured and it decreased from 19.0 to 15.7 atomic percent]. These results from ESCA (we mention the changes during 24 h) were also compatible with the results from EPR.

The measured values of binding energy of C 1s electrons (in the cases of A, B, C mentioned above) were in good agreement with those of O 1s electrons of the groups and the radicals in plasma polymer (the assignment seems to be correct).

Results from IR Spectroscopy and Their Discussion

Oxygen was found to be incorporated somehow in the plasma polymer, presumably originating from the —OH groups of the precursor molecules.

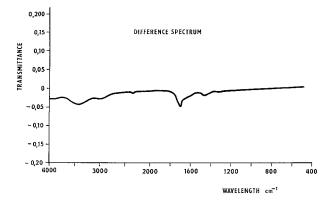


Figure 3 Difference IR spectrum of IR photon transmittance. The spectrum made after the end of plasma polymerization was corrected to used background. This spectrum did not change with time during the 24 h after the polymerization end. The results of the spectrum are described in Table I.

Very similar results were obtained at a power between 5O and 170 W, and at total pressures between 30 and 185 Pa during the polymerization.

It seems that difference between IR spectra occurs only when different partial pressures of the precursor are used, although partial pressure of neutral gas (Ar) is the same (different ratio *B* of partial pressures is used at the same neutral gas partial pressure).

Results of IRS analyses of two samples selected (**S 1** and **S 2**) are described here (conditions of plasma polymerization mentioned above).

In Figure 3 we see one different spectrum for the sample S 1, the differenence of the IR spectrum of transmittance of energy (IR analysis signals corrected to the used background, polyethylene foil, the pure difference of obtained).

In Figure 4 we see one spectrum of absorption energy for the sample **S 2**. This IR spectrum for absorption had to be compared with IR spectrum of a pure polyethylene foil (background). We can see changes that occurred. In Figure 4, three significant peaks (and some small ones) are characterized for standard polyethylene foil by lines approximately at 750, 1500, and 3000 cm⁻¹ (very high energy absorption obtained). These three significant and some small peaks belonging to polyethylene are neglected if corrected IR spectrum of plasma polymer is obtained, and this spectrum is consequently evaluated.

When different partial pressures of the precursor were used under the other fixed polymerization conditions, the efficiency of forming of oxygen-containing groups was different in both cases. When partial pressure was higher (35 Pa, **S 1**, see Fig. 3), a greater signal at characteristic spectral lines was detected than in the case of the lower pressure (25 Pa, **S 2**, see Fig. 4).

It was observed that the magnitudes of signals increased. The increase of signal magnitudes occurred at the same IR spectral lines in both cases; therefore, results of IRS can be described together in Table I. The chemical assignment (chemical bonds and formulae of groups or radicals) is seen there, too. This assignment of groups was carried out with the help of many tables in ref. 9. These groups can also stay as a retention of alcoholic monomer. Above all, spectral lines confirmed μ OH radicals or groups, indicated R—CO—CH₃ where R are radicals-unsaturated but also saturated hydrocarbons, confirmed --CO-- or -COH, i.e., saturated ketones and aldehydes of aliphatic hydrocarbons, indicated aliphatic esters with unsaturated substituent after -CO-Oand groups and hydroperoxide groups -O-OH (or peroxide groups -O-O-) (see Table I). Further, the IR spectra did not change with time up to 10 days.

The higher power in the reactor and the longer plasma polymerization process, the greater the efficiency of plasma polymerization (concentration of oxygen-containing groups and radicals increased). When the ratio B ranged from approximately 0.6 to 1.0 and the higher was the partial

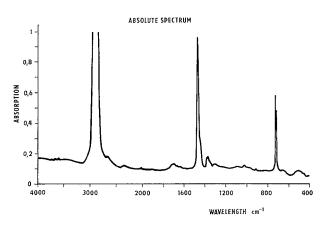


Figure 4 IR spectrum of IR photon absorption. The spectrum made after the end of plasma polymerization was not corrected to a background-polyethylene foil; therefore, three great packs of polyethylene have to be neglected at lines approximately at 750, 1500, and 3000 cm⁻¹. This spectrum did not change with time during the 24 h after the polymerization end. The results of the spectrum are given in Table I also.

Spectral Line in (cm ⁻¹)	Bond Assignment to Chemical Groups
First area with oxygen atom from 3	3200 to 3700s
In details	Stretch
3455	—OH groups or radicals
3355	-OH groups or radicals
End of first area with oxygen atom	s from 2800 to 3030
	Stretch
	—C—H groups in aliphatics $\mathrm{C_nH_{2n+1}}$ —R or in aromatics
In details	Stretch
3027	CH in aromatics, in benzene-like hydrocarbons
2928	Out-of-phase stretch
	$-C-H$ in CH_2 groups
2870	Symmetric stretch
	—C—H in CH_3 groups
Second area with oxygen atoms fro	m 1770 to 1800
	Stretch
	esters: e.g., $-(CH_2)_n$ $-CO$ $-O$ $-X$ with unsaturated substituent X
	hydroperoxides, —O—OH,
	peroxides —O—O—
1750	Stretch
	CO
1720	stretch C==O: e.g., R=-(C==O)CH ₃ or X(C==O)CH ₃ ,
	R-saturated, X-unsaturated substituent, respectively stretch
	C=O: R-CO-, X-CO-, R-saturated, X-unsaturated
1680	substituent, respectively
End of second area with oxygen ato	oms
1460	scissoring $(CH_2 -)$ in CH_2 groups
	deformation (CH ₃ —) in CH ₃ groups
1380	deformation (CH_3) in CH_3 groups

Table I Results of IR Spectroscopy

pressure of the precursor at the same partial pressure of argon (under constant operating conditions), the efficiency of the plasma polymerization was greater also (the higher signals of the peaks were found, which indicated the change after the polymerization process). Influence of the ratio B can be also observed. One can obviously see that the efficiency of forming of oxygen-containing groups and radicals in sample **S 2** is lower (Fig. 4) than the efficiency in sample **S 1** (see Fig. 3). Naturally, the oxygen-containing groups and radicals were discussed at first: we are interested in how to produce them in as great an amount as possible (by plasma polymerization under low pressure).

Results from EPR Measurements and Their Discussion

Three significant samples were selected for EPR measurements (S 3, S 4, and S 5). Plasma poly-

merization conditions for these samples are described above. We investigated how many free radicals were formed or trapped in the plasma polymer. A great amount of them was formed after plasma polymerization. But the amount of radicals decreased quickly with time and free radical concentration drop was measured after each plasma polymerization process. The reduction of radicals is the topic of our interest.

The energy absorption for free radicals in plasma polymer (at a magnetic induction of 3480 Gauss) was measured in percentage of the maximum intensity of a calibrated energy standard (relative units are the most convenient for these free radical concentration measurements, absolute concentration reached by a multiplication).

Remarkable results from the EPR measurement are given in Table II and Figure 5 for sample **S** 3, in Table III and Figure 6 for sample **S** 4,

Relative Concentration of Free Radicals	Time after the End of Plasma
(Percent of Maximum Energy)	Polymerization (h
7.90	0.417
3.93	0.500
3.82	0.917
2.56	5.083
1.10	100.080
1.09	100.250
1.09	192.050
	before plasma
0.15	polymerization

Table IIResults of EPR, Sample S 3 (Power360 W, etc.)

and in Table IV and Figure 7 for sample **S** 5, respectively. We remark that the diagrams given in Figure 6 are two curves (the curve corresponding to values in Table II can be compared to the curve corresponding to values in Table III, the curves are plotted in the same scale (Fig. 5) in one figure).

Maximum concentrations of free radicals were found at the beginning of the EPR signal measurement for each sample.

The dependence (graphs) of free radical concentration is shown on plots of log(t) vs. the EPR signal.

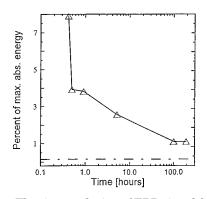


Figure 5 The time evolution of EPR signal for sample 1 that was polymerized under the first case conditions in EPR measurements. Conditions of plasma polymerization: power of matched reactor 360 V. total pressure 183 Pa, precursor partial pressure 95 Pa, substrate cooling at 15°C, electrode distance 50 mm; polymerization time 3.0 min. The values for this diagram are given in Table II. The EPR signal of support foil without plasma treatment is shown by the dashed and dotted line.

Relative Concentration of Free Radicals (Percent of Maximum Energy)	Time after the End of Plasma Polymerization (h)
1.41	0.420
1.06	0.750
1.00	21.750
0.69	213.100
	before plasma
0.15	polymerization

Table IIIResults of EPR, Sample S 4 (Power120 W, etc.)

We are able to describe each diagram by two significant approximately linear functions (which we assign to the line-like curves) of this concentration decrease. It can be defined very well in terms of a mathematical formulae in the form: C_i $= -K_i \log(t_i) + P_i$. Thus, for two significant parts for each sample (for each plot) after polymerization process, i = 1, 2, respectively (Figs. 5 and 6). In Figure 7 we can see the first part i = 1.

The parameters in the mathematical formula given above are as follows: C_i is the instant concentration of free radicals in the time t_i , and con-

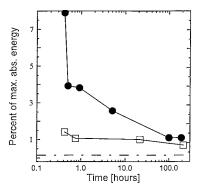


Figure 6 The time evolution of EPR signal for sample 2 that was polymerized under the second case conditions in EPR measurement (the diagram of comparison to the graph in Fig. 5 is made in the same scale). Conditions of plasma polymerization: power of marched reactor 120 V, total pressure 95 Pa, precursor partial pressure 55 Pa, substrate cooling at 15°C, electrode distance 50 mm, polymerization time 3.0 min. The influence of a grater power in reactor at plasma polymerization is seen. The values for this diagram are given in Table III. The EPR signal of support foil without plasma treatment is shown by the dashed and dotted line.

Relative Concentration of Free Radicals	Time after the End of Plasma
(Percent of Maximum Energy)	Polymerization (h)
0.95	0.167
0.92	0.200
0.71	0.383
0.68	0.433
0.59	0.583
	before plasma
0.15	polymerization

Table IVResults of EPR, Sample S 5 (Power100 W, etc.)

stants K_i and P_i are positive numbers in every case.

It seems that generally $C_1 = -K_1 \log(t_1) + P_1$ for the time until 1.0 h (a steep drop), and $C_2 = -K_2 \log(t_2) + P_2$ for the time from 1.0 h to approximately 215 h in our case (a mild drop).

In Figure 6 we point out that the difference in initial free radical concentrations is obvious because of the greater reactor power at polymerization (360 W in case 1, a greater amount of free radicals was formed, compared with 120 W in case 2).

Also, the third part of a decrease curve (a fit line) is assumed. If it exists for each sample and measurement, it will obey function formula $C_3 = -K_3 \log(t_3) + P_3$. For a very long time after the end of plasma polymerization $C_3 = P_3$.

We remark that according to our measurements, constant K_1 was much greater than K_2 , constant K_2 was greater than K_3 , for each sample, and along with this result, constants P_1 and P_2 were much greater than P_2 and P_3 , respectively.

For changes in a polymer in bulk, the EPR signal of these polymer samples decreased very substantially (a steep drop by an hour interval, then a mild drop) for 24 h, while the signals of the IR measurement for significant groups in the plasma polymer did not change for 24 h.

The measurement comparison showed that some oxygen-containing radical or group concentrations increased, which was true only for surface layers. However, many group concentrations decreased for 24 h; in this case, results of EPR and ESCA were compatible.

In surface layers, many C—O— groups (also C—OH groups) with simple bonds between carbon and neighbor oxygen atoms (and only one oxygen atom per carbon atom) were formed later on 1 day after the end of plasma polymerization.

In addition, it has to be mentioned that the value of the EPR signal after a long time after the end of plasma polymerization was greater than the value of the EPR signal of a polyethylene foil (substrate) that was not handled by plasma treatment and was not in the plasma reactor at all.

CONCLUSIONS

The optimum polymerization rate for plasma polymerization of iso-t-pentinol was accomplished under partial pressure ratio $B = P_{AT}/P_{isopt}$ in the interval from 0.6 to 1.0. Our samples were deposited under *B* approximately equal to 1.0 for analyses.

The oxygen-containing radicals or groups with bonds C=O, -O-C=O, and C-O- were detected by ESCA and IRS in deposited polymers. (a) The groups C-OH (OH radicals), C-O-C(ether groups), C-O-O-, and C-O-OH having simple bonds between all neighbor atoms belong to C-O- groups. Concentration of these groups increased in surface layers (measured by ESCA) during 24 h after the end of plasma polymerization. (b) The groups C=O (ketones) and -O-C=O (ester groups) were found, and their concentration changes were proved. Concentration of those groups decreased in surface layers (ESCA) during 24 h after the end of plasma polymerization. (c) Concentration of all oxygen-con-

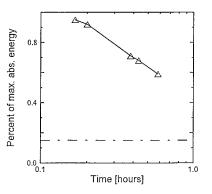


Figure 7 The time evolution of EPR signal for sample 3 that was polymerized under the third case conditions in EPR measurement. Conditions of plasma polymerization: power of matched reactor 100 V, total pressure 110 Pa, precursor partial pressure 60 Pa, substrate cooling at 15°C, electrode distance 50 mm, polymerization time 3.0 min. The values for this diagram are given in Table IV. The EPR signal of support foil without plasma treatment is shown by the dashed and dotted line.

taining groups was the same in bulk of the prepared polymer with time (IRS).

Our results showed that when the higher partial pressure of iso-t-pentinol was used at the same partial pressure of argon (under constant operating conditions, B ranged approximately from 0.6 to 1.0, maximum total pressure of 65 Pa), a greater concentration of all oxygen-containing groups was reached (measured by IRS), and, hence, a greater efficiency of plasma polymerization. Supporting NMR measurements also showed that the plasma polymer film contained an average of 80% of aliphatic hydrocarbons, 12% of olefins, and 8% of aromatic compounds.

The EPR measurements proved that free radical concentration decreased in two significant parts after the end of plasma polymerization. The first part exhibited a steep drop of free radical concentration within the time interval of 1 h after the end of plasma polymerization. The second part indicated a mild decrease of this concentration from 1 to approximately 215 h (measured by EPR) after the end of plasma polymerization. If we supposed the existence of the third part of the free radical concentration decrease, it would be approximately an EPR signal constant function with time, but a value of this constant signal would be greater than the value of the constant background signal (polyethylene foil without plasma exposition or treatment).

We observed the influence of greater power on increase of free radical concentration as follows: the higher was the power in the plasma reactor the greater free radical concentration was achieved (measured by EPR) after the end of plasma polymerization, but the dependence is not linear (it seems to be a function of a higher order).

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