IR laser ablative desulfurization of poly(1,4-phenylene sulfide)

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Abstract

Pulsed infrared laser-induced ablation (PLAD) of poly(1,4-phenylene sulfide) (PPS) results in the extrusion of sulfur and deposition of thin films that are a blend of initial PPS and sulfur–polyaromatic polymer composite. The process is demonstrated to differ from the conventional heating which leads to a solid material with S content and bonding similar to those in PPS. The PLAD of PPS thus represents a unique example of the desulfurization of S-containing polyaromatic materials.
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1. Introduction

Poly(1,4-phenylene sulfide) (PPS) is an important polymer with many potential applications due to its exceptional thermal and mechanical durability and chemical resistance [1]. Thermal behaviour of PPS studied by pyrolysis–mass spectroscopy/gas chromatography [2–7] and thermogravimetry [8,9] has revealed complex mechanism of PPS decomposition. It was proposed [5] that the heating of PPS to over 300 °C induces polymer branching, the heating to ca. 300–500 °C results in the formation of cyclic oligomers $[1,4\text{-}C_6H_4\text{-}S\text{-}]_n$ (n = 4–7) [3,4,6] and the heating to still higher temperatures (up to 900 °C) yields [5–7] benzene, aromatic compounds with C_6H_n–S units (n = 4, 5) and dibenzothiophenes along with H_2S and CS_2 and a number of other minor products. The predominant degradation process at up to 550 °C takes place as a random (S–C) chain scission followed by cyclization. The degradation at higher temperatures proceeds as a (S–C) chain random scission ensued by H-abstraction reactions by (i)

C_6H_n–S radicals (produced at lower temperatures) and (ii) S atoms (produced at higher temperatures). In these studies, heterogeneous stages of decomposition cannot be utterly excluded and the heating of the polymer takes place as a relatively slow process.

A completely different mode of thermal decomposition of polymers is pulsed infrared laser-induced ablation (PLAD) that can take place by exposing a polymer with pulsed IR laser radiation [10–18]. This specific thermal process occurs within a T-jump and is controlled by kinetic rather than thermodynamic polymer degradation. The process is currently of high interest due to feasible fabrication of various polymeric films which can be deposited on substrates near to the irradiated polymer target. Its importance largely stems from facile ejection of large macromolecules and/or fragments that can efficiently recombine into polymeric structures. Side reactions of the fragments (decompositions, rearrangements, radical reactions) lead to the deposition of structurally modified (cross-linked) polymeric films that are of use due to their intractability and high temperature stability.

The importance of these side reactions is affected by the structure of the initial polymer and by irradiation conditions. IR laser ablative deposition of almost structurally identical

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films was demonstrated with irradiation of poly(ethylene glycol) [16,17], polysilanes and polycarbosilanes composed of $-(CH_3)_2Si-$, $-(CH_3)_2Si(CH_3)_2SiCH_2-$, $-R(CH_3)Si-$ and $-R(CH_3)Si(CH_3)_2SiCH_2CH_2-$ units (R = methyl, adamanthyl, phenyl and H [14]) and poly(ethylene-alt-maleic anhydride) [18], whereas significant structural modifications (cross-linking) of the polymer was reported with irradiation of poly[oxy(tetramethyldisilane-1,2-diyl)] [15].

In this work we continue our previous effort on pulsed IR laser ablation for deposition of thin polymeric films [15,18] and report on PLAD of PPS. We show that this process represents a unique example of desulfurization of S-containing aromatic compounds and results in fabrication of films that are composites of initial PPS, elemental sulfur and polyaromatic material.

2. Experimental

The laser irradiation experiments were performed in a continuously evacuated metal chamber with a rotating substrate holder. The laser beam was focused (KBr lens, focal length 15 cm) on the target of PPS compressed in a tablet (10 mm in diameter and 5–7 mm thick). The TEA CO_2 laser (a Lumonics model TE-820 HP) operated at the P(20) line of the $(0\,0^\circ\,1) \rightarrow (1\,0^\circ\,0)$ transition ($944\ cm^{-1}$) at different repetition frequency and pulse energy (Table 1) and the films (of the area of $\sim$3 cm^2 and ca. 0.1–1 μm thickness) were deposited on KBr plates positioned 3 cm afar from the PPS target. The films thickness (not measured) increased from runs 1 to 3 as observed by the naked eye.

The X-ray photoelectron spectra (XPS) were measured using ESCA 310 (Scienta, Sweden) electron spectrometer equipped with a high power rotating anode, wide-angle quartz crystal monochromator and a hemispherical electron analyzer operated in a fixed transmission mode. The photoelectron take-off angle was 90° with respect to the sample surface. The pressure of residual gases in the analyzer chamber during spectra acquisition was typically 6×10^{-10} mbar. The surface static charge was suppressed using flood gun (Scienta). The spectra were curve-fitted after subtraction of non-linear background using Gaussian–Lorentzian line shape. The spectra of the S 2p electrons were fitted with a doublet structure with spin–orbit splitting 1.18 eV. Quantification of the elemental concentrations was accomplished by correcting photoelectron peak intensities for their cross-sections, analyzer transmission function and assuming a homogeneous sample.

Table 1
Irradiation experiments with PPS

Run	Pulse energy (mJ)	Repetition frequency (Hz)	Deposition time (min)
1	40	1	75
2	50	1	75
3	57	2	45

SEM analyses were obtained using a Philips XL30 CP scanning electron microscope equipped with energy-dispersive analyzer (EDAX DX-4) of X-ray radiation. A PV 9760/77 detector in low vacuum mode (0.5 mbar) was used for quantitative determination of C and S elements.

Thermal gravimetric analysis (TGA) of PPS was carried out by heating the sample (44 mg) in a stream of argon at the rate of 4 °C min^{-1} using Cahn D-200 microbalance.

Poly(1,4-phenylene sulfide) (pellets, viscosity (310 °C, 1200 s^{-1}) 1400 P) was purchased from Aldrich.

3. Results and discussion

IR laser irradiation of PPS affords materials different from that obtained by the conventional heating (TGA); the former process and the obtained materials are first discussed and later compared to the material obtained by TGA of PPS. Several complementary analytical methods – XP, FTIR and UV spectroscopy and electron microscopy – are used in order to obtain a true picture of the composition and bonding of the elements in both materials.

3.1. IR laser ablation of PPS

Pulsed IR laser irradiation of the PPS tablets results in the deposition of thin films whose colour depends on the irradiation conditions: transparent films were obtained in run 1, yellowish in run 2 and brown in run 3. These films show somewhat different morphology: the film obtained in run 1 shows a smooth pattern, that from run 2 consists of a smooth surface and sub-μm-sized agglomerates and those from run 3 are formed by a smooth surface along with μm-sized spheres (Fig. 1a–c).

EDX-SEM analysis of the films gives an insight into the depth of up to almost 0.3 μm and is compatible with bulk stoichiometries of the films as follows: $S_{1.00}C_{14.4}$ (run 1), $S_{1.00}C_{14.6}$ (run 2) and $S_{1.00}C_{26.8}$ (run 3). These values indicate that the content of sulfur is remarkably decreased in all the films as compared to the initial PPS (theoretical value $S_{1.00}C_6$, experimental value 5.70), and that the brown film contains far less sulfur than the transparent and the yellowish film.

The XPS analysis of the films, giving an information on the composition of the topmost (up to $\sim$5 nm) layers, reveals the following stoichiometry: $S_{1.00}C_{8.70}$ (run 1), $S_{1.00}C_{36.4}$ (run 2) and $S_{1.00}C_{82.5}$ (run 3) as compared to the results obtained for the initial, authentic sample of PPS for which the composition is $S_{1.00}C_{6.8}$ (the overstoichiometric carbon comes from the sample surface contamination by adventitious carbon). These results are in line with the EDX-SEM analysis and confirm that the ablatively deposited films contain less sulfur. The lower S content in the topmost layers (seen by XPS) as compared to that in the bulk film (observed by EDX-SEM) is likely due to a removal of the volatile S from surface layers under the vacuum of the XPS analysis.
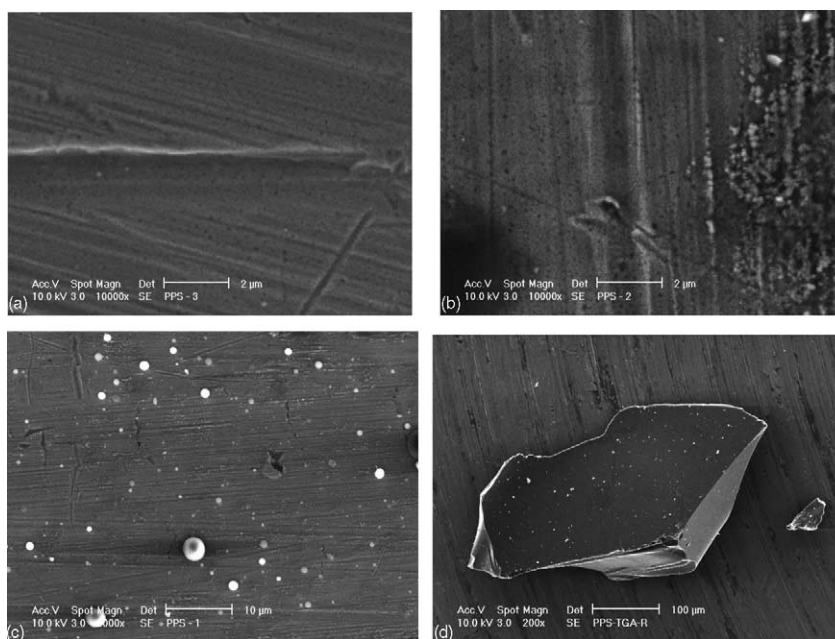
Fig. 1. SEM images of the deposited films in run 1 (a), run 2 (b) and run 3 (c) (bar is 2 μm) and of the PPS residue after TGA; (d) bar is 100 μm.

The XP spectra of S 2p electrons (Fig. 2) are dominated by the component with a binding energy of an S $2p_{3/2}$ peak of 163.7 eV, which is consistent with the value reported in literature for sulfur in a –C–S– bonding configuration [19]. The minor components located at 166.0 and 167.9 eV, respectively, belong to –S(O)– and C–S(O)$_2$– moieties [19]. The presence of oxygen lines in the spectra is in agreement with this interpretation. These sulfoxide and sulfone groups arise through oxidation of the remaining S-centers on exposure to air. The satellite belonging to π–π^* excitation and characteristic of aromatic systems is observed in the

spectra of C 1s electrons of the deposits even though this feature is less intense than that of the initial PPS sample. About 10% of the total amount of carbon in the surface layer of deposited films is bonded to oxygen.

The UV spectra of the deposited films differ (Fig. 3) from that of the initial PPS. The latter possesses two overlapping bands at 275 and 310 nm both of which get lost upon ablative deposition. This change is only minor at mild irradiation conditions (run 1), but gets more pronounced at harsher irradiation conditions (runs 2 and 3). The disappearance of the two bands assignable to π–π^* excitation of the –C$_6$H$_4$– S–C$_6$H$_4$– system is in line with elimination of –S– units from the PPS skeleton, while the residual absorbance above 200 nm is in keeping with polyaromatic (polyphenylene)
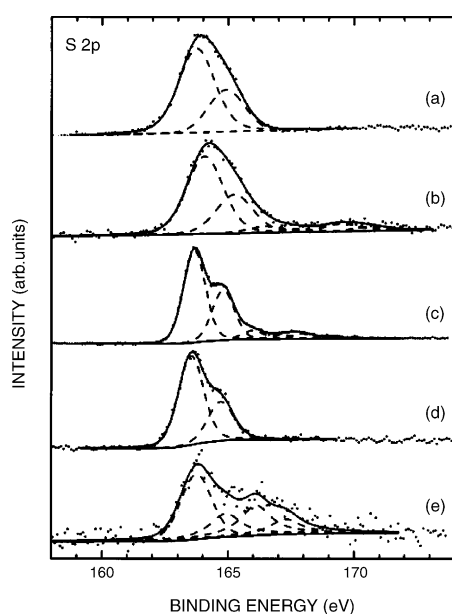

Fig. 2. Fitted spectra of S 2p electrons in the initial PPS (a), residue of PPS after TGA (b) and in deposited films from run 1 (c), run 2 (d) and run c (e).
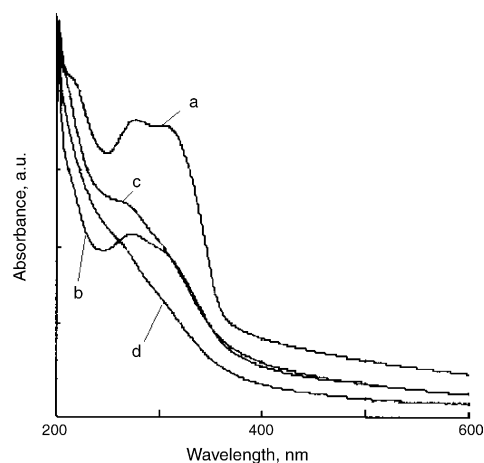

Fig. 3. UV spectrum of poly(1,4-phenylene sulfide) (a) and films deposited upon its ablation with run 1 (b), run 2 (c) and run 3 (d).

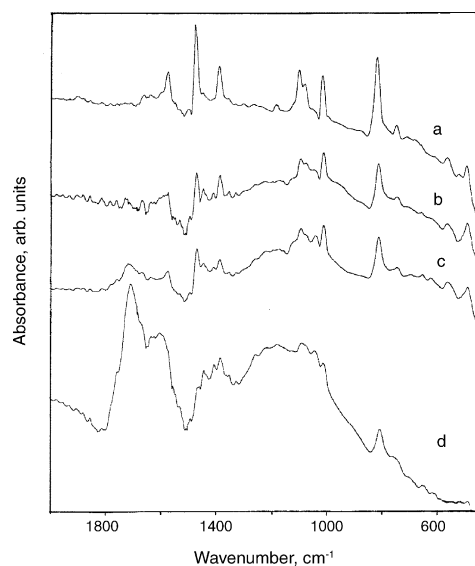Fig. 4. IR spectrum of poly(1,4-phenylene sulfide) (a) and films deposited upon its ablation with run 1 (b), run 2 (c) and run 3 (d).

Fig. 5. Thermal decomposition of PPS.

structures that display absorption at ∼190–220 nm (the E band) and ∼240–300 nm (the K band) [20–22].

The FTIR spectra of the transparent (run 1) and yellowish (run 2) films possess pattern similar to that of PPS, while the spectrum of the film deposited in run 3 is rather different (Fig. 4, Table 2). The characteristic bands in the PPS spectrum are those at 1572, 1471, 1390 cm^{-1} (ring stretch in S–C$_6$H$_4$–S), 1096 and 1075 cm^{-1} (ring-S stretch in S–C$_6$H$_4$–S), 1010 and 818 cm^{-1} (C–H bending modes) and 743, 556 and 483 cm^{-1} (ring bending) [23]. These bands at about (±3 cm^{-1}) these wavenumbers and of only little modified relative absorbance are also observed in all the deposited films (Fig. 4, Table 2). This feature cannot be, however, taken as a support for structural similarity of the deposited films with PPS, since similar spectral bands are
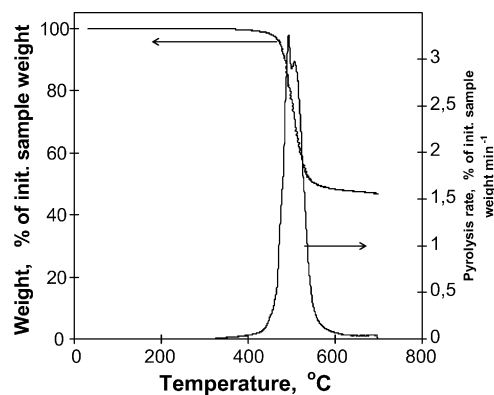
also prominent in polyphenylenes [22,24]. The new band at 1040 cm^{-1} observed in the deposited films correspond to the ν(S=O) mode in sulfoxides [25] and the band at 411 cm^{-1} (whose relative absorbance grows from runs 1 to 3) confirms the presence of stable S$_8$ allotrope [26]. We also conclude on the absence of –S–S– bridges in aromatic disulfides, which have characteristic absorption at 470–480 cm^{-1} [26] and on the presence of the ν(C=C) bands (and possibly of ν(C=O) bands at 1600–1700 cm^{-1} in the spectrum of the brown film obtained in run 3.

3.2. Thermogravimetry of PPS

The thermogram of PPS shows a sharp decrease of the weight to 47% around 500 °C, the pattern (Fig. 5) similar to that reported previously [8]. A sublimed portion (FTIR spectrum with prominent absorption at 3140, 3036 cm^{-1} (aromatic C–H stretch) and 1403 cm^{-1} (possibly C=C and/or thiophene ring stretch) that are of little diagnostic value) was produced together with a compact shiny black residue (for SEM image see Fig. 1d) whose FTIR and UV spectra

Table 2
FTIR spectra of PPS and deposited films

Wavenumber (cm^{-1})	Relative absorbance[a]				Assignment for PPS [23,27] and polyaromatics [22,24]
	PPS	Run 1	Run 2	Run 3[b]	
1570	0.39	0.26	0.50	–	Ring stretch in S–C$_6$H$_4$–S, C=C stretch in polyphenylenes
1472	1.00	1.00	1.00	1.00	Ring stretch in S–C$_6$H$_4$–S, C=C stretch in polyphenylenes
1385	0.45	0.70	0.44	1.20	Ring stretch in S–C$_6$H$_4$–S, C=C stretch in polyphenylenes
1178	0.10			–	C–H in plane bending in S–C$_6$H$_4$–S
1094	0.53	0.53	0.55	0.50	Ring-S stretch in S–C$_6$H$_4$–S, C–H deformation in polyphenylenes
1074	0.39	0.43	0.30	0.40	Ring-S stretch in S–C$_6$H$_4$–S
1040	0.00	0.17	0.33	0.40	S=O stretch
1012	0.73	0.93	1.1	1.00	C–H in plane bending S–C$_6$H$_4$–S, C–C in plane deformation in polyphenylenes
810	0.90	1.00	1.27	1.40	Not assigned
742	0.16	0.20	0.30	–	Ring out of plane bending S–C$_6$H$_4$–S, C–H out of plane deformation in polyphenylenes
617	–	–	0.13	–	
558	0.13	0.20	0.30	–	Ring-S deformation S–C$_6$H$_4$–S
486	0.26	0.50	0.55	–	Ring-S out of plane deformation S–C$_6$H$_4$, C–C deformation in polyphenylenes
416	0.90	1.60	2.50	4.00	Ring out of plane bending in DPS + S$_8$ [26]

[a] Wavenumbers ± 3 cm^{-1}; Relative absorbance normalized to the band at 1472 cm^{-1}.
[b] Also strong bands at 1702 and 1607 cm^{-1}.

could not be measured. The composition of this residue assessed from the EDX and XPS analysis is $S_{1.00}C_{9.5}$ and $S_{1.00}C_{12.8}$, respectively. These values reveal that substantial amount of S remains in the residue when heating occurs as a slow process.

3.3. Specificity of PLAD process

The comparison of the PLAD- and TGA-derived materials clearly reveals significant differences in their composition and is therefore indicative of remarkable differences in both processes. While the slow conventional heating of PPS is a surface-assisted reaction and can be described as elimination of cyclooligomers and S-containing aromatic compounds [3–7], the laser ablation achieved through multiple-photon absorption of energy-poor infrared photons, a high vibrational excitation density in the solid and particularly through high heating and cooling rates (respectively, $\sim 10^{6-11}$ Ks^{-1} and $\sim 10^{3-6}$ Ks^{-1}) [28–30] results in the formation of thin films poor in sulfur.

The only possible explanation of sulfur depletion is an extrusion of S atoms (a two-fold C–S bond fission) yielding the identified elemental sulfur (S_8 allotrope). The sulfur being deposited together with the aromatic films is relatively volatile species and can be removed from the S-polymer composite (especially from superficial layers) under high vacuum [31].

The S content in the films is significantly decreased at higher laser fluence and repetition frequency, which indicates that more sulfur extrusion is favored at these conditions.

4. Conclusion

TEA CO_2 laser-induced ablation of PPS results in the deposition of polymeric films consisting of unchanged polyphenylene moieties, polyaromatic (presumably polyphenylene) moieties and elemental sulfur.

The harsher irradiation conditions lead to more efficient extrusion of sulfur and favour deposition of polyaromatic films containing elemental sulfur.

The laser-induced ablation differs from conventional heating of PPS, which yields the residue having S chemically bonded to a polymeric network.

The reported process conducted at low fluence and repetition frequency allows fabrication of smooth films, which contradicts with the reported deposition of rough (seemingly unmodified) PPS films achieved via visible laser radiation [32].

The PLAD technique applied to PPS represents a way for deposition of polyaromatic films and sulfur—polyaromatic polymer composites. It is also promising as a procedure for desulfurization of aromatic materials.

More work related to the detailed elucidation of polymeric film structure, mechanism of S extrusion and of thermal stability of the fabricated films is under way.

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