



Studies of photochemical transformations in polystyrene and styrene–maleic anhydride copolymer

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ABSTRACT

Thin films of polystyrene (PS) and styrene–maleic anhydride copolymer (St-MAN) were exposed to monochromatic UV radiation (254 nm) for varied time intervals. The course of photochemical transformations was monitored by absorption spectroscopy (FT-IR, UV–vis) and thermogravimetry, which were also applied for the estimation of the thermal stability of samples studied. The changes of surface properties were monitored by contact angle measurements.

Changes in chemical structure were found in irradiated films (inside and at the surface). The efficiency of photooxidative degradation in St-MAN copolymer was slightly lower than that in PS homopolymer but photo-crosslinking and chromophore formation were enhanced. An increase of hydrophilicity and oxidation degree in UV-irradiated samples was accompanied by destruction processes. The thermal stability of St-MAN was lower in comparison to polystyrene alone.

The mechanism of photochemical reactions in the copolymer is proposed.

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1. Introduction

Polystyrene has been used all over the world due to its excellent physical properties and low production costs. Copolymers of styrene with maleic anhydride are preferred by plastics designers, engineers and processors for automotive applications, such as soft instrument panels, structural consoles, roof-mounted LCD video supports, interior trim and audio components [1]. The waste of PS plastics does not decompose spontaneously, so a large amount of plastic commodities cause serious environmental problems [2,3].

Earlier studies have shown [4–10] that polystyrene degrades under exposure to sunlight in air through two distinct processes: photolysis and oxidation. The initial decomposition of photolabile structures is responsible for the secondary, subsequent reaction in polymer chains.

It is well known that introduction of chromophores (such as carbonyl groups) to the conventional polymer chain through copolymerization may facilitate polymer degradation [11,12]. Absorbed light of wavelength up to about 380 nm causes breaking of chemical bonds and free radicals formed this way initiate the polymer decomposition or other chemical and physical transformations. The primary reaction in photodegraded polymer is

mainly abstraction of hydrogen atom from a macromolecule and formation of alkyl radicals.

The bulk properties of numerous polymers, including polystyrene, make them ideal for a wide range of structural and functional applications. However, the low surface energy in many cases limits their use. Thus, the pre-treatment or modification using UV irradiation is frequently used for improvement of polymer properties such as adhesion and printability. Special modification of polymeric surfaces is necessary to get required barrier properties, wettability and compatibility with other media.

This paper considers the influence of UV irradiation on chemical transformations of polystyrene (PS) and styrene–maleic anhydride copolymer in the solid state. The second aim of our work is to study the changes of surface properties of PS and St-MAN thin films upon UV irradiation.

2. Experimental

2.1. Polymers

Commercial polystyrene, $\overline{M}_w = 230,000$, was purchased from Aldrich Chemical Co. Random styrene–maleic anhydride copolymer was obtained in the laboratory by free radical copolymerization of maleic anhydride (Fluka) and styrene (Aldrich) at 70 °C in the presence of benzoyl peroxide as initiator. The details of the synthesis are described in the literature [13]. The molar percentage of maleic anhydride in the copolymer, calculated from the elemental analysis, was 34%.

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2.2. Preparation of polymer films

The polymers were dissolved in benzene (POCH, cz.d.a.) to obtain 2% solution. The homogeneous solutions were poured into a Petri dish. After solvent evaporation, the samples were dried at room temperature to a constant weight. The film thickness was about 10 μm . Samples for FT-IR and UV–vis spectroscopies were prepared by direct casting onto a ZnSe crystal or a quartz window.

2.3. UV irradiation

A low pressure mercury vapour lamp (TUV 30W, Philips, Holland), which emits radiation at $\lambda = 253.7 \text{ nm}$, was used. The intensity of the incident light was 24 W/m^2 . Films of the same thickness and surface area were placed at 6 cm distance from the light source. Irradiation times were 1, 2, 4, 6 and 8 h. All irradiations were performed at room temperature in air atmosphere. Irradiated samples were immediately put into spectrometer or goniometer for measurements.

2.4. Methods of study

Photochemical changes in polymer films were recorded by infrared and UV–vis absorption spectroscopies using FT-IR Genesis II Spectrophotometer (Mattson, USA) and UV PC 1600 spectrometer (Shimadzu, Japan), respectively.

Contact angles of two liquids (diiodomethane, Aldrich, and deionised water) on polymeric films were measured at 20°C using a goniometer equipped with the system of drop shape analysis (DSA 10, Kruss, Germany). The liquid drop (volume of $\sim 2\text{--}3 \mu\text{l}$) was placed onto the polymer surface by a micro-syringe. The drop image was recorded by a video camera and digitised. Each contact angle is an average of a minimum 10 measurements; the precision was 0.2° . The surface free energy γ_S and their dispersive γ_S^d and polar γ_S^p components were calculated using Fowkes, Owens–Wendt and Wu methods [14,15].

Insoluble gel fraction was separated from the solution, dried and weighted.

Thermogravimetric measurements of polymer films were carried out using TA Instrument SDT2960 Simultaneous analyser. The samples were heated up to 600°C at a heating rate of $6^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

3. Results and discussion

3.1. FT-IR spectroscopy

The IR spectrum of PS in the $3700\text{--}400 \text{ cm}^{-1}$ region is shown in Fig. 1a. The main bands are five peaks at $2800\text{--}3100 \text{ cm}^{-1}$ range attributed to C–H stretching vibrations in the main chain and in aromatic rings; the peaks at $1601, 1492, 1451, 1029, 757, 698 \text{ cm}^{-1}$ are due to deformation and skeletal vibrations of C–H in PS [6,9].

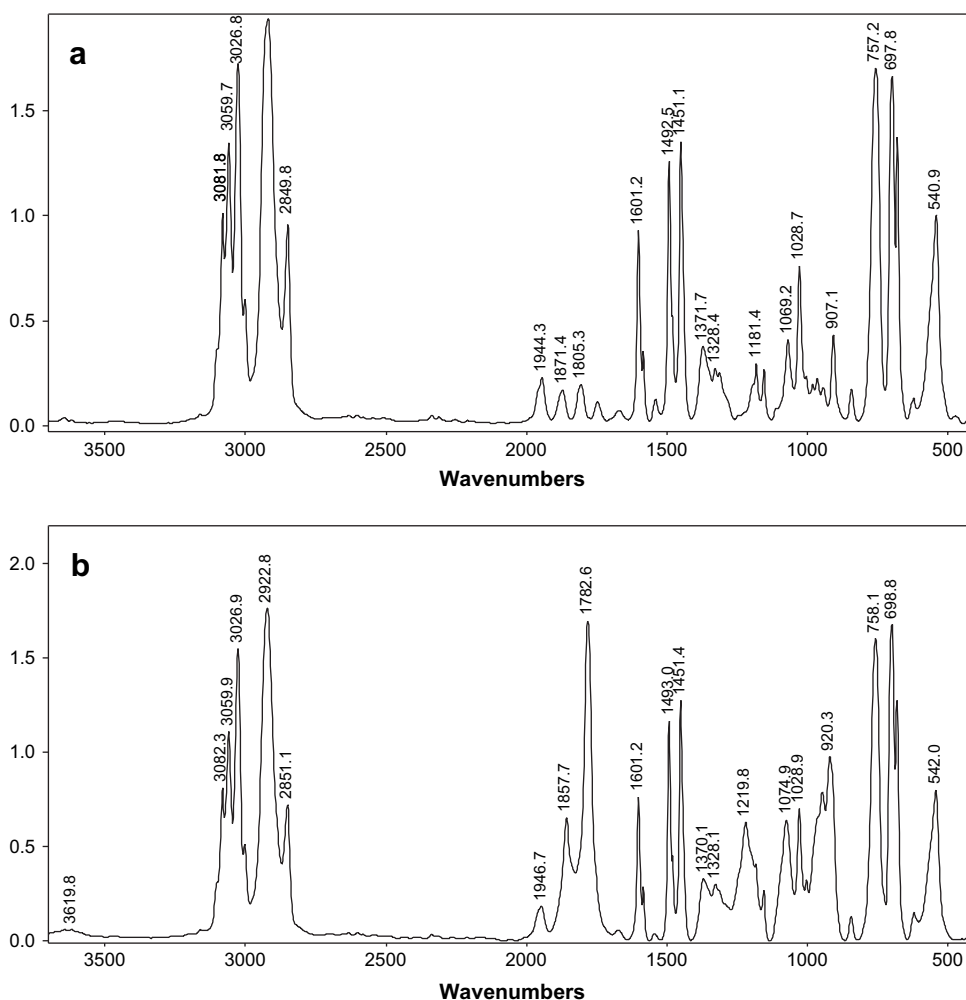


Fig. 1. FT-IR spectra of unexposed PS (a) and St-MAN copolymer (b).

The IR spectrum of St-MAN copolymer (Fig. 1b) shows the following characteristic regions: 2800–3100 cm^{-1} due to C–H stretching (similar to bands observed in pure PS), 1700–1900 cm^{-1} due to C=O vibrations, 1400–1700 cm^{-1} , where bands characteristic for aromatic rings appeared, and 700–1400 cm^{-1} , which is the typical dactyloscopic range. New bands (comparing to PS spectrum) were found at 1220, 1075, 946 and 920 cm^{-1} due to C–H deformation vibrations in cyclic carbonyl compounds. Moreover, the low intensity band at 3500–3700 cm^{-1} can be seen resulting from the presence of –OH functional groups. Symmetrical and asymmetrical stretching bands of C=O bond in maleic anhydride appeared at about 1858 and 1783 cm^{-1} . Bands found at 1601, 1493 and 1451 cm^{-1} , attributed to stretching vibrations of the substituted benzene rings, are almost in the same position as in the PS spectrum.

The lack of distinct shift of bands assigned to PS ring in the copolymer spectrum excludes the formation of charge transfer complex between maleic anhydride and styrene units in the solid state. Such complexes exist in dioxane solution, which was described in an earlier publication [16].

IR spectroscopy was also used to analyse the effect of UV irradiation on polystyrene and its copolymer. Because the competitive photo-processes take place simultaneously in the samples studied, spectral subtraction was used for better visualisation of UV effect (Figs. 2 and 3).

In UV-irradiated PS, the changes observed in the carbonyl and hydroxyl regions are evidence of photooxidation. The increase of

absorbance in the analysed ranges is attributed to the formation of aromatic and aliphatic ketones of the acetophenone type and OH/OOH groups in the main chain. According to literature data [5,6,9], carboxylic acids, esters, anhydrides and cyclic structures (lactone type) are other PS photoproducts. Moreover, low-molecular weight compounds such as benzoic acid, acetophenone, benzaldehyde, methyl benzoate, formic acid, acetic acid, styrene and benzene were identified in UV-irradiated PS in various conditions.

C=O functional groups, formed in the first step of irradiation, sensitise further PS oxidation. Indeed, prolongation of exposure leads to decrease of the absorbance at 1804 cm^{-1} (Fig. 2), indicating the decomposition of formed perester or peracids. For quantitative evaluation of photooxidation, we plotted the relative changes of the total amount of carbonyl and hydroxyl groups (calculated as an integral intensity of absorption band i.e. as surface area of peaks) versus irradiation time (Figs. 4 and 5).

In St-MAN copolymer, the intensity of the complex bands at 1640–1825 cm^{-1} and 3100–3600 cm^{-1} also increases during UV irradiation but changes of the total amount of carbonyl and hydroxyl groups, expressed as integral intensity changes, are more irregular. The shoulders in 1640–1750 cm^{-1} range can be assigned mainly to ketone groups in the polymer backbone, whereas the absorption at higher wavenumbers, i.e. above 1750 cm^{-1} , is attributed to acids, peroxyacids, esters and anhydride components.

The shape of the subtraction spectra of PS and copolymer is different (Figs. 2 and 3), which indicates that photoreaction

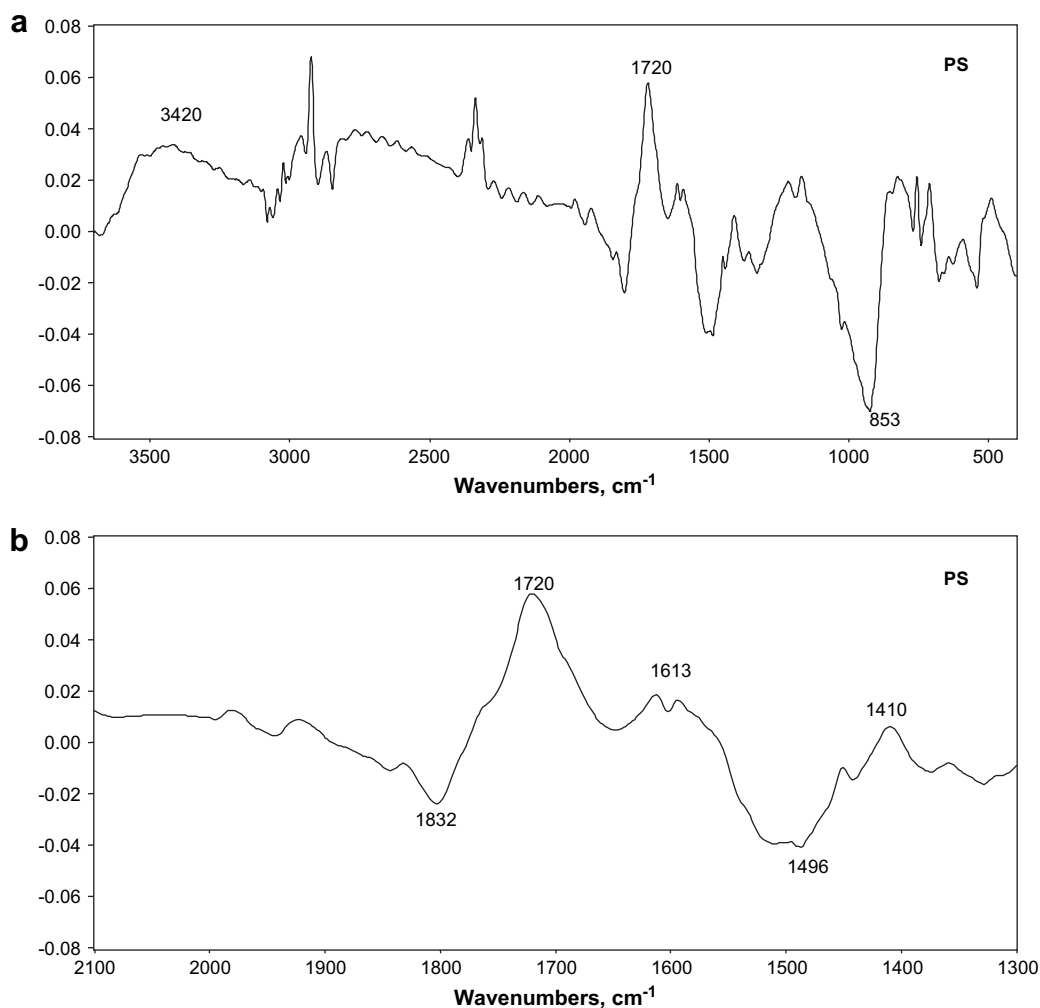


Fig. 2. Subtracted FT-IR spectra of PS (spectrum of 8 h-irradiated PS minus spectrum of non-irradiated PS) in whole IR range (a) and in 1300–2100 cm^{-1} range (b).

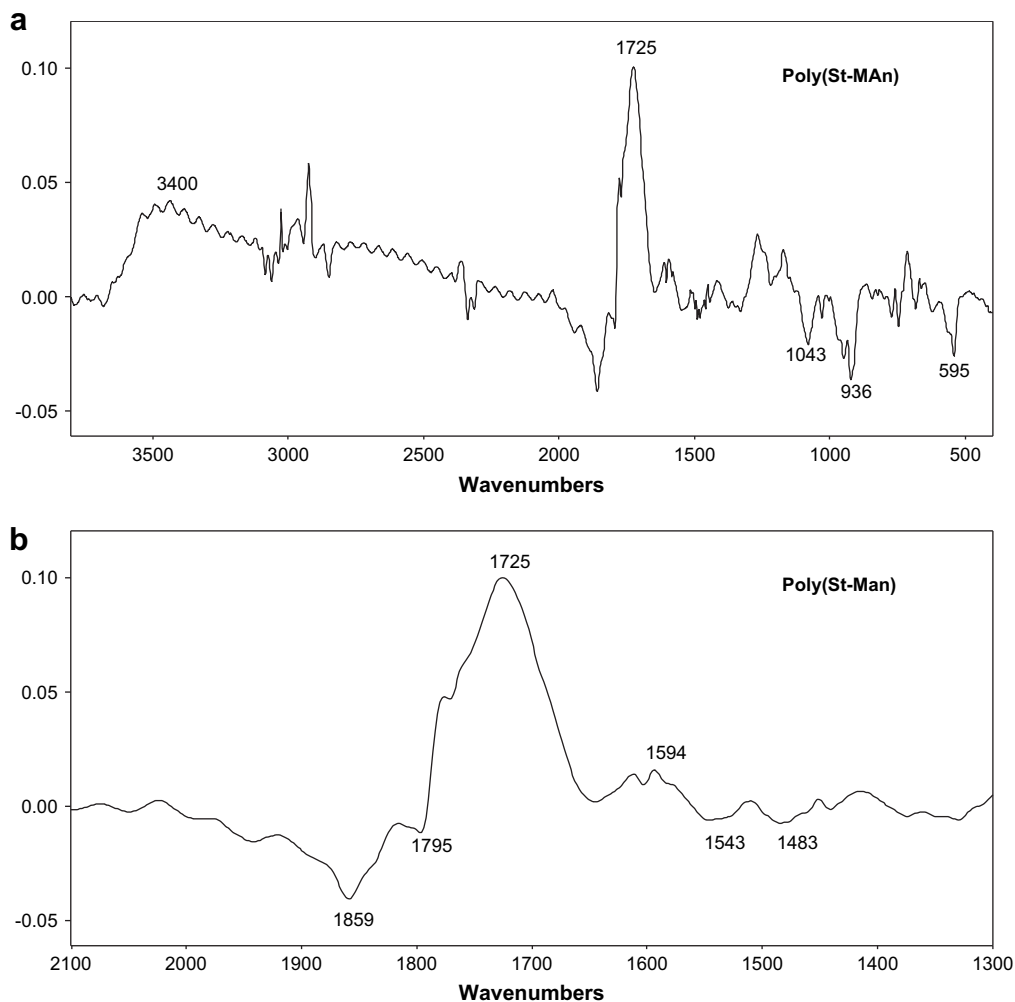


Fig. 3. Subtracted FT-IR spectra of poly(St-MAN), (spectrum of 8 h-irradiated copolymer minus spectrum of unirradiated copolymer) in whole IR range (a) and in 1300–2100 cm⁻¹ range (b).

mechanism also alters. It was expected that besides photooxidation, also the destruction or/and abstraction of pendant groups in maleic anhydride segments occurs. It is confirmed by increase of absorbance at 1725 cm⁻¹ and parallel drop of absorbance at 1859 cm⁻¹. The random, irregular changes were also observed in hydroxyl region in spectra of UV-irradiated copolymer. Thus, the kinetic curves in Figs. 4 and 5 (dashed lines due to copolymer) are not interpolated

because the irregularities observed are much higher than experimental error. The decrease of carbonyl band at 1859 cm⁻¹ is connected with evaporation of volatile, low-molecular degradation products e.g. CO or CO₂ evolved from maleic anhydride rings.

Although the initial C=O content in the copolymer is much higher than that in unirradiated PS, the kinetics of photooxidation leading to hydroxyl/hydroperoxide species does not differ

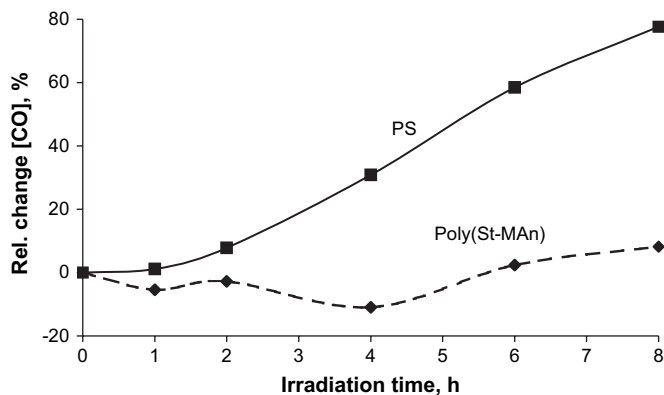


Fig. 4. The relative changes of carbonyl groups in PS and St-MAN copolymer during UV irradiation (measured as an integral intensity of carbonyl band at 1641–1826 cm⁻¹ range).

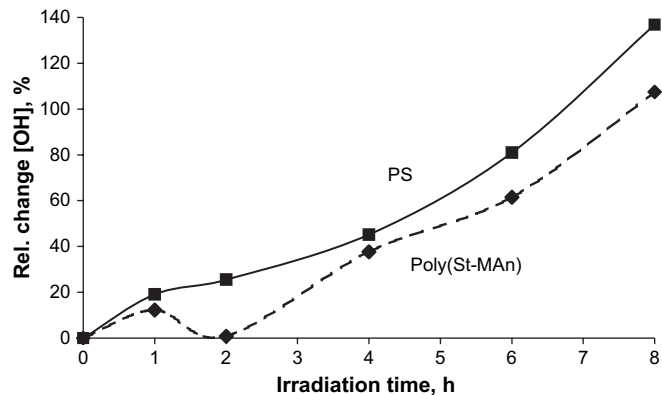


Fig. 5. The relative changes of OH/OOH groups in PS and St-MAN copolymer during UV irradiation (measured as an integral intensity of hydroxyl band at 3126–3546 cm⁻¹ range).

significantly in either case after longer exposure i.e. >4 h (Fig. 5). The formation of new C=O (accompanied by photodestruction) is markedly retarded in St-MAN copolymer compared to PS.

Only negligible changes were detected in bands assigned to vibrations of aromatic rings, which confirms the photo-stability of phenyl substituents.

3.2. UV-vis spectroscopy studies

UV-vis spectroscopy supplied information about the presence of chromophores. Polystyrene, containing a phenyl ring in each repeat unit, absorbs strongly at 240–280 nm range ($\lambda_{\max} = 262$ nm) [17–19]. This band, due to $\pi \rightarrow \pi^*$ transitions, is clearly seen in both spectra of unirradiated PS and poly(St-MAN) samples. Moreover, in the copolymer spectrum the band characteristic for carbonyl groups from anhydride rings overlaps the phenyl band. Carbonyl compounds exhibit an absorption at 200–300 nm due to $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions in C=O groups. An example of electronic spectra of St-MAN copolymer (before and after UV irradiation) is shown in Fig. 6.

An increase of absorbance is observed in the 200–600 nm range in spectra of both samples exposed to UV, which indicates that absorbing photoproducts (e.g. conjugated double bonds) appear in both PS and poly(St-MAN). For quantitative calculations, we selected a few wavelengths: 262 (maximum), 300 and 400 nm. The absorbance at 262 nm is very intense and increases rapidly during irradiation, thus very thin film has to be prepared for monitoring the changes of this band. The broad stretched band above 280 nm is much less intense. The trend observed for all mentioned wavelengths is similar (Fig. 7). The changes of absorbance are significantly higher for photodegraded copolymer than those for PS alone exposed at the same time and the same conditions (for films of the same thickness). It indicates that photooxidation leading to chromophoric group formation, absorbing in this range, is more efficient in poly(styrene-maleic anhydride) than that in PS (Figs. 4 and 5).

It is known from the literature [18,19] that PS absorption below 300 nm arises from the presence of various degradation products of the type of acetophenone, benzaldehyde or benzoic acid. The species absorbing above 300 nm are macromolecules containing conjugated double bonds and unsaturated bonds neighbouring carbonyl groups. These chromophores cause sample colour (mainly yellowing).

Polyenes with different numbers of double bonds are formed as a consequence of alkyl radical transformation to macroallyl radicals [1]. Polyene radicals cause an increase of absorbance in the UV-vis region and shift the absorption band to a longer wavelength (i.e. bathochromic shift).

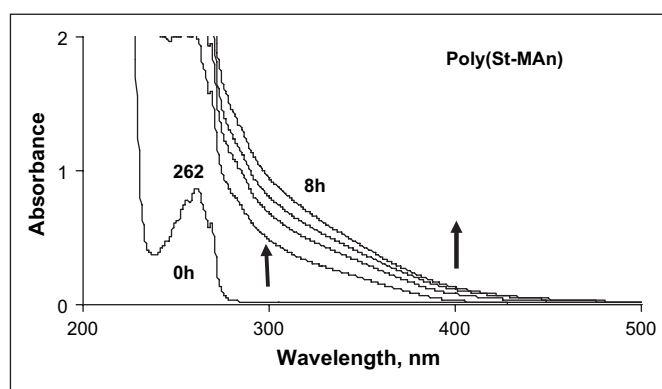


Fig. 6. UV-vis spectra of St-MAN copolymer before and after exposure to UV (irradiation times: 0, 2, 4, 6 and 8 h).

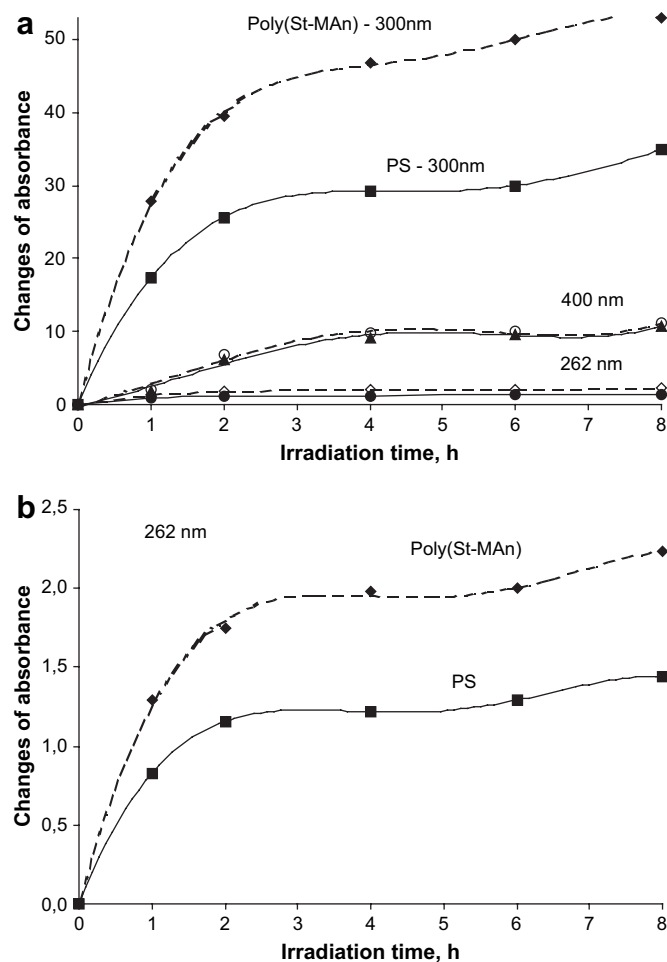


Fig. 7. Kinetics of chromophore formation in UV-irradiated PS (continuous lines) and St-MAN copolymer (dashed lines) on the basis of absorbance at 262, 300 and 400 nm.

As can be deduced from Fig. 7, the concentration of polyenes (resulting from high amount of macroradicals) is larger in copolymer than that in PS. The secondary processes such as radical recombination or dismutation lead to their disappearance.

3.3. Insoluble gel

Free radicals formed during primary photochemical reactions participate in propagation process and finally can recombine in the

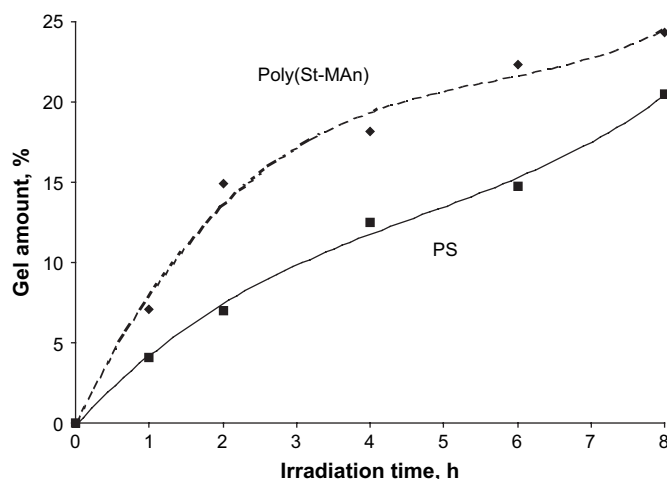


Fig. 8. Gel amount formed in PS and St-MAN copolymer during UV irradiation.

Table 1

The contact angles of two different liquids (H₂O and CH₂I₂) on PS and St-MAN copolymer before and after 8 h UV irradiation

Sample	Contact angle of liquid on polymer surface (°)			
	Before irradiation		After 8 h UV irradiation	
	Water	Diiodomethane	Water	Diiodomethane
PS	100	63	87	48
Poly(St-MAN)	92	59	75	45

termination stage. The insoluble gel is formed, when at least one crosslink is created per macromolecule. Fig. 8 shows the differences in gel amount in UV-irradiated PS and its copolymer. Photo-crosslinking in poly(St-MAN) is faster and more efficient than that in pure PS.

3.4. Contact angle measurements

The measurement of the contact angle allows calculation of the surface free energy of polymers and observation of changes of sample wettability during UV irradiation. The static contact angles of two liquids (deionised water and diiodomethane) deposited on the polymer surfaces were measured before exposure and immediately after UV irradiation (Table 1). According to prediction, contact angle of water on non-irradiated PS is higher (~100°) than on poly(St-MAN) (~92°). The contact angle of non-polar liquid (diiodomethane) is also greater on PS than that on the copolymer surface.

After 8 h UV irradiation, a significant decrease of contact angles is observed in both types of samples for two liquids used. It indicates that photo-modification of the polymer surfaces is very efficient.

The total surface free energy values (γ_s), for PS and St-MAN copolymer before and after 8 h UV irradiation, calculated on the basis of contact angle measurements, are listed in Table 2. Polymer surface free energy is a measure of its hydrophilicity and gives some qualitative information on oxidation in the surface layer. The increase of γ_s indicates that surface oxidation occurs during UV irradiation and functional groups are formed. It is well known that surface composition differs from bulk because polymers, as all material systems, approach the energy minimum. In the case of flexible chains, the minimisation occurs via rotation of polymer segments and achieve the preferred chain conformation. Comparing the γ_s values for both unirradiated polymers, one can conclude that significant amounts of maleic anhydride units (i.e. polar groups) are present at copolymer surface.

Photooxidation, which was previously proved by FT-IR spectroscopy, leads mainly to generation of carbonyl, hydroxyl and hydroperoxide groups in macro-chains. Owing to strongly electronegative oxygen atoms present in such groups and polarisation of C–O bonds, the total surface free energy rises. The other reason for γ_s increase is diffusion of low-molecular degradation product from the sample interior and their accumulation at the surface (especially in the case of low-volatility compounds).

Table 2

Total surface free energy (γ_s , mJ/m²) for PS and St-MAN copolymer before and after 8 h UV irradiation (calculated by three different methods)

Sample and irradiation time	Total surface free energy (mJ/m ²)				
	Calculation method			Average	Percentage change ^a (%)
	Fowkes	Owens–Wendt	Wu		
PS – 0 h	27	27	30	28	–
PS – 8 h	36	36	40	37	32
Poly(St-MAN) – 0 h	29	29	34	31	–
Poly(St-MAN) – 8 h	39	39	45	41	32

^a Percentage changes of average γ_s value after 8 h UV irradiation.

Table 3

The value of polar (γ_s^p) and dispersive (γ_s^d) components of surface free energy for PS and St-MAN copolymer films before and after 8 h UV irradiation (average from three different methods)

Sample and irradiation time	Components of surface free energy (mJ/m ²)			
	γ_s^p	Change of γ_s^p (%)	γ_s^d	Change of γ_s^d (%)
PS – 0 h	2	–	26	–
PS – 8 h	4	100	32	27
Poly(St-MAN) – 0 h	4	–	27	–
Poly(St-MAN) – 8 h	9	125	32	18

Unexpectedly, the changes of total γ_s in PS and St-MAN copolymer are the same after 8 h UV irradiation: 32% (Table 2) suggesting that the efficiency of photo-processes in both polymers is similar.

For better understanding the character of changes observed on the polymeric surface during photo-modification, polar (γ_s^p) and dispersive (γ_s^d) components of surface free energies were evaluated (Table 3). The results clearly indicate that photooxidation with formation of polar moieties at the polymer surfaces dominates over the destruction of carbonyl groups from MAn units. PS is also very susceptible to surface photooxidation. As can be seen from data in Table 3, the polar component of surface free energy (γ_s^p) in exposed copolymer changes more than that in PS: 125 and 100%, respectively. In contrast, the change of dispersive component of surface free energy (γ_s^d) is somewhat higher in PS than that in St-MAN copolymer after 8 h UV irradiation.

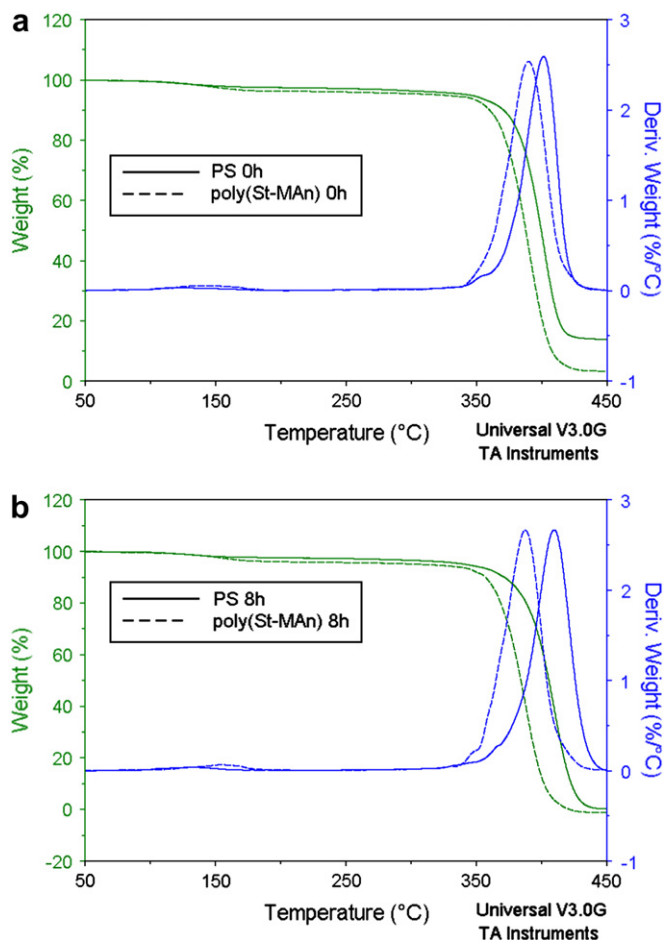


Fig. 9. TG and DTG curves of PS (continuous lines) and St-MAN copolymer (dashed lines) before irradiation (a) and after 8 h UV irradiation (b).

Table 4

The temperature of the starting point of thermal decomposition (T_I and T_{II}) and weight loss (Δm_I and Δm_{II})^a for PS and St-MAN copolymer before (0 h) and after 8 h UV irradiation

Sample	Stage I			Stage II		
	T_I^0 (°C)	T_I^{\max} (°C)	Δm_I (%)	T_{II}^0 (°C)	T_{II}^{\max} (°C)	Δm_{II} (%)
PS – 0 h	82	131	3.9	326	402	81.8
PS – 8 h	106	134	3.4	320	411	95.8
Poly(St-MAN) – 0 h	95	147	4.9	330	390	91.4
Poly(St-MAN) – 8 h	103	156	4.6	317	388	100.0

^a Δm_I and Δm_{II} were calculated at 200 and 450 °C, respectively.

3.5. Thermogravimetric measurements

Both samples were subjected to thermogravimetric analysis in nitrogen in order to estimate their thermal stability. Fig. 9 shows the TG and DTG profiles of polystyrene and copolymer samples before and after UV irradiation. The thermal decomposition occurs in two stages: the first (minor) at about 80–160 °C and the second (dominant) at 320–430 °C. The parameters that characterises the thermal behaviour of these materials, including decomposition temperatures (onset – T^0 and at maximum process rate – T^{\max}) as well as weight loss are given in Table 4.

The first stage of thermal decomposition (below 160 °C) is connected with a small drop of weight (≈ 3 –5%) is usually caused by elimination of low-volatility impurities (e.g. trapped solvent residues). The main important stage of thermal decomposition in PS starts at 326 °C and corresponds to the breaking of chemical bonds and evolution of radical or molecular products. Non-irradiated copolymer is characterised by somewhat higher values of T_I^0 , T_I^{\max} , T_{II}^0 (exception is T_{II}^{\max}) than those for PS.

UV irradiation decreases T_{II}^0 in both polymers and T_{II}^{\max} in copolymer, whereas T_{II}^{\max} of PS increases about 9 °C. It can be

explained by different types of photoproducts formed in PS and St-MAN copolymer. Generally, it is accepted that the increase of thermal stability can be achieved by crosslinking (which takes place in both polymers, Fig. 8) but results indicate that the nature of crosslinks in PS varies from those in poly(St-MAN). Probably, in copolymer more unstable oxygen containing bridges (C–O–C or C–O–O–C) are formed, in contrast to PS, where C–C bonds dominate.

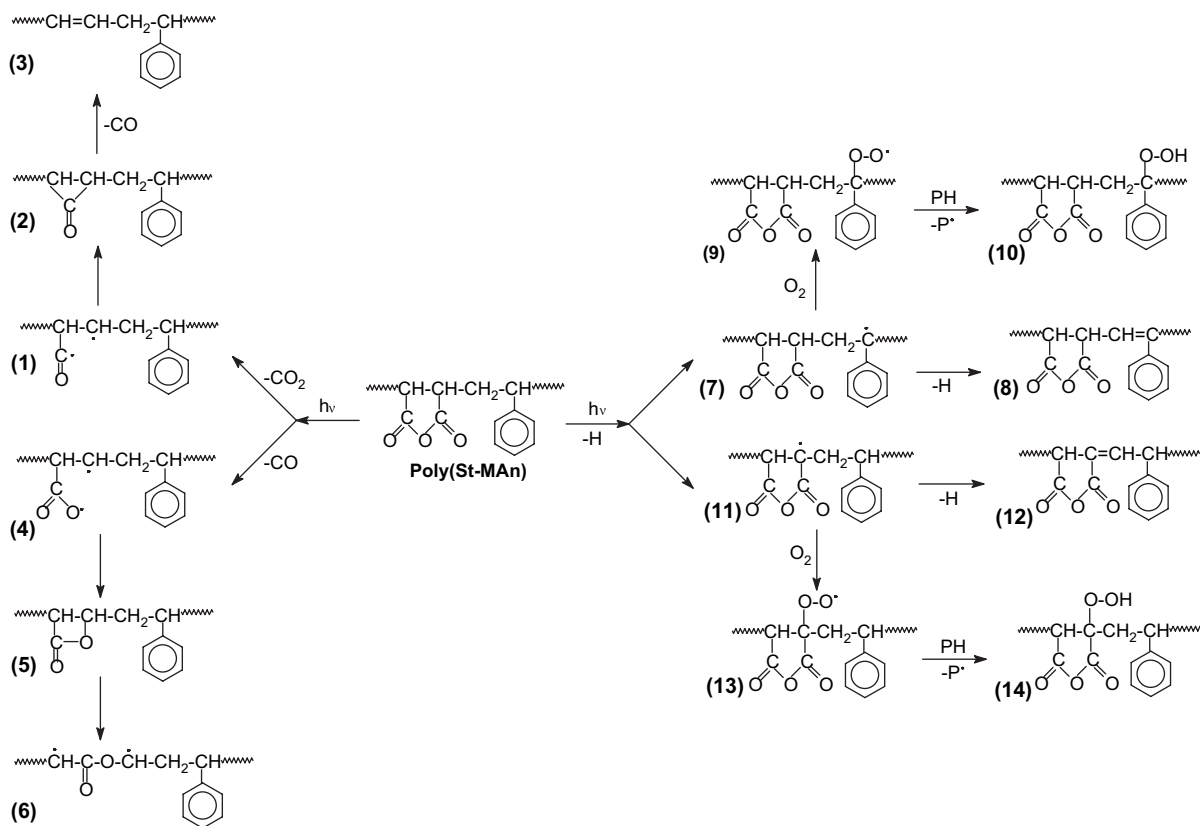
The weight loss is greater in copolymer than that in PS (in non-irradiated and UV-irradiated samples at both stages). It clearly indicates that copolymer is characterised by lower thermal stability. Eight-hour UV-irradiated copolymer decomposes completely at 430 °C, in contrast to PS, where the carbonised residue is about 4%.

Moreover, the difference between stability of UV-irradiated PS and poly(St-MAN) becomes bigger comparing to non-exposed samples. It means that during photodegradation less thermally stable structures are formed and this process is especially efficient in copolymer. It is confirmed by higher weight decrease in photo-degraded polymers.

The mechanism of thermal degradation of PS, its blends and copolymers was described earlier [13,20–25]. Resulting of random chain scission at elevated temperature, the various degradation products are released: monomer (styrene), benzene, methyl substituted aromatic compounds and oligomeric fragments. The main identified decomposition products during thermal decomposition of St-MAN copolymer were toluene, ethylbenzene, styrene, 1,3-diphenylpropane, 3-phenylbutyric acid, carbon dioxide and water [13].

3.6. Discussion of mechanism

PS photodegradation is a result of excitation of phenyl rings after quantum absorption. The main primary reaction is elimination of hydrogen atom from the backbone, mainly from carbon at α -position to benzene ring, but random chain scission also occurs.



Scheme 1. The main initial reactions in UV-irradiated styrene-maleic anhydride copolymer.

Macroradicals react with oxygen from the atmosphere and formed peroxy radicals are able to further react with macromolecules. The other initiation sites in PS are unsaturated chain ends, internal impurities and structural defects (hydroperoxides, ketones). The intermediate products (e.g. alkoxy and hydroxyl radicals) participate in subsequent decomposition. The complex mixture of photoproducts contains macromolecules with hydroxyl, acetophenone ($\text{CH}_3\text{-CO-Ph-}$), benzophenone (Ph-CO-Ph-), diketone, α,β -unsaturated ketone, peracid, peroxyester and ketolactone moieties [1,4,6,8,9].

Photooxidative degradation of polymers containing carbonyl groups occurs by Norrish I (α -cleavage) and Norrish type II (scission through a six-membered cyclic intermediate) mechanisms yielding a number of photooxidation products [18,19].

Thus volatile, low-molecular weight products and insoluble crosslinked macromolecules are simultaneously formed in irradiated polymeric samples.

The main initial steps of photooxidative degradation of styrene–maleic anhydride copolymer are proposed in Scheme 1. Both types of units in copolymer undergo excitation because phenyl ring as well as carbonyl groups absorb UV radiation. The effect of maleic anhydride excitation is decarbonylation via a biradical intermediate (**1**, **4**) leading to cyclopropanone (**2**) and β -propiolactone (**5**) inserted in the backbone. Those structures are capable of further reactions, for example, decarbonylation with generation of internal double bonds (**3**) [26] and ring opening polymerisation leading to ester group formation [27]. Polymerisation of lactones allows biodegradable polymer to be obtained [28]. Although polymerisation requires a significant amount of adjacent reactive species, such groups (**6**), sensitive to microorganism attack, can be also formed in our copolymer after photodegradation.

The other important reaction occurring in exposed copolymer is hydrogen abstraction (**7** and **11**). Formed macroradicals are transformed to macromolecules containing double bonds in main chain (**8** and **12**) or react with atmospheric oxygen. Peroxy-macroradicals (**9** and **13**) attack the next macromolecules (PH) and unstable hydroperoxides are formed. As a consequence, further secondary reactions take place and various degradation products, containing different functional groups (OH, C=O, C=C), are generated simultaneously.

The main reactions during thermal degradation of copolymer are similar to photooxidative processes. The difference is in the initiation step because degradation upon heat does not require the presence of chromophores in macromolecules; in this case decomposition starts at “weak points”, which means that chemical bonds characterised by lowest bond energy break firstly. Moreover, thermal degradation occurs in the whole sample volume, in contrast to photodegradation, which is limited to a thin surface layer.

The differences in thermal degradation of exposed PS and St-MAN copolymer are due to various chemical nature of photodegraded films. In spite of efficient photo-crosslinking, thermal stability decreases in both cases, which indicates that formed bonds are unstable. Probably, these structures contain oxygen bridges (ether, ester or peroxide type), which are destroyed at elevated temperature.

The complete (100%) copolymer decomposition at 450 °C indicates that there are no stable photo- or thermo-degradation products, in contrast to PS alone.

4. Conclusions

FT-IR and UV–vis spectroscopies proved that styrene–maleic anhydride copolymer, similarly to PS, undergoes complex photochemical transformation upon 254 nm radiation. The competitive

reactions such as chain scission, oxidation, abstraction of side groups, opening of anhydride rings and chromophore formation occur simultaneously in the copolymer studied.

The efficiency of photo-crosslinking and process leading to chromophore formation is higher in styrene–maleic anhydride copolymer than that in PS alone, in contrast to oxidation, which is a result of destruction competition.

As a result of ring opening reaction in maleic anhydride units, the copolymer becomes more sensitive to biodegradation owing to the presence of oxygen atoms in main chains.

UV irradiation causes surface modification in both polymers – increase of macromolecules' polarity, and in consequence, the increase of sample wettability. Although the structure of the original PS and poly(St-MAN) differs significantly (and initial values of surface free energy are also distinct), relatively low chemical changes between surface properties in both polymers after UV irradiation (254 nm) were detected. It is probably caused by similar accumulation of degradation products at the surface.

On the basis of thermogravimetric analysis, we can conclude that the thermal stability of St-MAN is somewhat lower than PS. UV irradiation decreases resistance to heat of both polymers. The efficiency of thermal degradation estimated by weigh loss is higher in the copolymer, which can be an advantage during incineration of plastic waste.

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