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The influence of polychromatic UV-irradiation on new thiophene copolymers

Halina Kaczmarek*, Wojciech Czerwiński

Faculty of Chemistry, Nicolaus Copernicus University, Gagarin 7, 87-100 Toruń, Poland

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Abstract

Three new thiophene-based copolymers, characterising the electrical conductivity and photosensitivity, were obtained in a four-step reaction. The acrylic or methacrylic substituents as well as nonyl or pentyl side groups were incorporated into thiophene rings. All thiophene copolymers were then exposed to UV-irradiation in air atmosphere and in room temperature using polychromatic high-pressure mercury lamp. The process of photooxidative degradation was monitored by FT-IR and UV–VIS spectroscopy. It was found that these polymers undergo chain scission, oxidation and decomposition in side groups with different efficiency. The decrease of conjugated double bonds amount, influencing the conducting properties, was also observed. It was concluded that copolymer containing methacrylic substituent was less photostable than that with acrylic one. The type of alkyl group (pentyl or nonyl) in copolymers has no significant influence on their photodegradation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thiophene copolymers; UV-irradiation; Photodegradation; Photooxidation; Photodecomposition

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1. Introduction

Intensive investigations of semiconducting, conducting and photoconducting polymers [1–11] arise from the fast development of electronic industry in recent years. Polymers with delocalised π-electrons along the main chain such as polyacetylene, polyphenylene, polyaniline, polythiophene and polypyrrole combine advantages of metals and plastics: changeable electrical conductivity, elasticity, chemical stability and low density. Although their electrical conductivity (dependent on the concentration of charge carriers, their mobility and charge transfer between individual macromolecules) is not high compared to metallic conductors, but it can be efficiently improved by doping with donor or acceptor compounds. Moreover, the conductivity also increases during orientation and crosslinking of conducting polymers [12,13].

It was previously suggested that doping of polymers in many cases does not produce physical defects, contrary to the doping of inorganic semiconductors. Dopants such as AsF_5, I_2 or BF_3 rather oxidise macromolecules; reducing dopants (such as lithium naphthalide) are also known [12]. Recent hypothesis assumes that in π-conjugated polymers neutral or charged defect structures play a major role in the electron transfer mechanism. Such quasi-particles are called solitons (radicals), polarons and bipolarons (radical ions or diradical ions). Transport of quasi-particles can be considered as a set of redox processes following one by one.

Polymeric conducting systems may be used in various branches of industry as batteries, light emitting diodes (LEDs), integrated circuits, field-effect transistors, optical memory storage devices, electronic displays, photoconductors for xerography, different sensors and their further, new applications are predicted in the near future.

Main disadvantage of conducting polymers is their low stability, especially in doped state. Therefore, the search of new and better materials, characterising the good electronic conductivity, processability, stability, good mechanical properties, solubility and easy to synthesise is the aim of many scientists and technologists. The considerable interest is the chemical modification by copolymerisation as well as by introduction of specific functional groups into side substituents to control the physicochemical properties of materials.

One of the most important conducting polymers is polythiophene (PT) and its derivatives [1,6,13,14]. PT macrochains are built up mainly from α–α connected thiophene rings but the presence of α–β linkages were also experimentally confirmed (Scheme 1) [13].

Recently, light emitting polymers have been extensively investigated since Friend and coworkers [15–17] first reported about LED using conducting polymer (polyphenylene-

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* Corresponding author. Tel.: +48-56-6114312; fax: +48-56-6542477.
E-mail address: halina@chem.uni.torun.pl (H. Kaczmarek).

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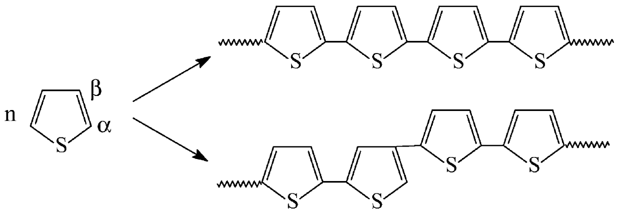


Scheme 1. Competitive reactions in PT synthesis [13].

vinylene (PPV)). Later Heeger and coworkers [18–20], and Inganas and coworkers [21,22] reported about new light emitting polymer (PPV and PT) derivatives with bulky side substituents. The choice of these side groups allows polymer solubility and enlarges the photoluminescence (PL), electroluminescence (EL), and their quantum efficiency [23–27] as well as electrochromic properties [28]. Unfortunately, the presence of these bulky side groups can play an important role in the degradation of the polymer [29,30]. Photooxidation of such polymers can be a result of the reaction with highly reactive singlet oxygen formed via energy transfer from excited polymer groups.

This is a lack of information about the photostability of conducting polymers. As was reported by Ettedgui et al. [31], conjugated polymers (polyphenylenes) were degraded during operation and the changes of morphology influencing conducting and optical properties were observed.

Recently, IR spectroscopy studies of photooxidised films of polyalkylthiophene with long side groups (eight carbon atoms) on different supports indicated that the polymer purity as well as the regiopurity plays a significant role in the degradation process of this material [32–34].

The polymer with the regioregular defects (head-to-head (HH) or tail-to-tail (TT)) is more stable on degradation because these structural impurities are responsible for the quenching either in the excited states of oxygen (singlet state) or excited state of polymer.

To integrate polymer organic compounds into electronic and optoelectronic devices, spectral control of deposition of this type material is important. Several reports of forming π-conjugated micron-size polymer channels in controlled and reproducible fashion have emerged [35–37]. Recently [35,38], it has been shown that lithographic pattering of poly(3-alkylthiophene) in the form of thin film undergo photoinduced crosslinking upon exposure to UV. The irradiated regions are crosslinked and insoluble, but part of film, which was covered by photomask (unexposed regions) is soluble and may be dissolved in typical organic solvents (CH_2Cl_2, THF, CH_3Cl). So, it gives the possibility to achieve the electrochemically conducting pattern (after doping the profile) by photolithography technique. Condition for such process is to produce π-conjugated polymers, which are soluble and have a UV-sensitive group attached to the backbone of the chain. But crosslinking under UV, which takes place between the side groups, may also change the composition of main chains leading to the decrease of π-electrons conjugation.

The aim of this work was to study the influence of polychromatic UV-irradiation on the novel conducting thiophene-based copolymers containing photosensitive groups. The estimation of photostability of such a polymer is very important from a practical point of view because they can be exposed to light during usage.

2. Experimental

2.1. Synthesis

Firstly, the monomer (3-nonylthiophene or 3-pentylthiophene) was synthesised by crosscoupling of 1-nonylmagnesium bromide or 1-pentylmagnesium bromide with 3-bromothiophene in the presence of Ni(dppp)Cl_2 as catalyst.

The three copolymers,

1. poly[(3-(2-acryloyloxy)-ethyl)thiophene-co-3-pentylthiophene], P[AET-co-3PT] (**1**),
2. poly[(3-(2-methacryloyloxy)-ethyl)thiophene-co-3-pentylthiophene], P[MET-co-3PT] (**2**),
3. poly[(3-(2-methacryloyloxy)-ethyl)thiophene-co-3-nonylthiophene], P[MET-co-3NT] (**3**),

were obtained in a four-step reaction as follows [35–40]:

1. substitution: 3-(2-hydroxyethyl)thiophene + acetochloride = 3-(2-acetoethyl)thiophene;
2. copolymerisation: 3-(2-acetoethyl)thiophene + 3-nonylthiophene (or 3-pentylthiophene);
3. substitution of acetate groups in copolymer by hydroxyl groups;
4. functionalisation of copolymer—substitution of hydroxyl groups by methacrylate or acrylate groups.

The products were identified by IR and NMR spectroscopy. Details of synthesis and physical properties (including conductivity) of obtained copolymers will be soon described elsewhere [41].

2.2. NMR spectroscopy

^1H and ^{13}C NMR spectra of polythiophenes were recorded in Varian 2000 200 MHz spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard.

2.3. Conditions of UV-irradiation

Thin polymer films were obtained by a casting from tetrahydrofuran solutions onto quartz plates or on KBr windows and then they were vacuum dried for 24 h. Such films were exposed to a high-pressure mercury lamp (HPK 125 W, Philips, Holland) at 10 cm distance in air atmosphere. The emission range of the lamp was 254–578 nm. The integral intensity of incident light measured by IL 1400A radiometer (International Light, USA) equalled 58.0–62.5 mW/cm^2. The temperature at film position was 40 °C.

2.4. *Analysis of irradiated samples*

The course of photooxidative degradation of copolymers was examined (monitored) by FT-IR and UV–VIS absorption spectroscopy using Genesis II (Mattson, USA) and UV-1601PC spectrophotometer (Shimadzu, Japan), respectively. For each IR spectrum 100 scans at 400–4000 cm^{-1} were done (resolution was 4 cm^{-1}). Electronic spectra were recorded in 200–800 nm range with 2 nm resolution.

The quantitative analyses of photoproducts were made by calculation of the height of chosen absorption peaks or their integral intensities. The comparison of the rate of photodegradation of copolymers was done by calculation of percentage changes of absorbance (or integral intensity) and plotting them versus irradiation time.

3. Results and discussion

3.1. *Characteristics of PT copolymers*

All three PT copolymers were black powders. Their solutions in THF and thin polymeric films prepared for spectrophotometric measurements were yellow.

The ^{1}H NMR spectrum of P[MET-co-3NT] (Fig. 1) shows the signals of aliphatic protons characteristic for a side chain of comers in the high-field range. Two pronounced peaks at 2.55 and 2.79 ppm assigned to α-methyl protons give insight into the head-to-tail (HT) and head-to-head HH diad sequences in the fragment of chain where two (or more) 3NT mers are linked together or in those parts of chain where 3NT units are separated only by one 3MET “unfamiliar” mers [42].

The nature of signals at about 2.80 and 2.55 ppm were previously confirmed by analysis of the NMR spectra for HH configuration only (∼2.55 ppm due to poly(3,4-thiophene)) [43].

Consequently, the contents of HT configuration (calculated on the basis of the integral intensity of these two peaks) for P[MET-co-3NT] was, respectively, 80 and 70% for the second comers in copolymer. Moreover, the sum of integrals for 3NT and 3MET comers gives the percentage composition of the copolymer. However, residual NMR signals at 3.96 and 3.81 ppm indicate incomplete reaction between the hydroxyls and methacryloyl chloride. The final composition of copolymers under study is depicted in Scheme 2.

The FT-IR spectra were done to support NMR data in regard to the structure of the copolymers in each step of modification. The strong bands at ∼820 cm^{-1} in the spectra of all copolymers, attributed to 2,3,5-trisubstituted thienylene rings, show that the thienylene moieties are α–α coupled (2–5′) what is important from the conducting point of view. The band characteristic for α–β coupling [44] is absent in the spectra of our samples.

Fig. 2 shows the example of IR spectra for chemically modified P[MET-co-3NT] copolymer and their second derivatives in the range of 1000–1800 cm^{-1} on each step of modification. Loss of the band at 1736 cm^{-1} due to the carbonyl stretching vibration of acetyl group (see Fig. 2A) shown in Fig. 2B is related to the formation of hydroxyl copolymer (it is confirmed by simultaneous formation of hydroxyl band). Formation of the methacrylate ester in the last step of the synthesis forms a new carbonyl band at 1718 cm^{-1} (Fig. 2C).

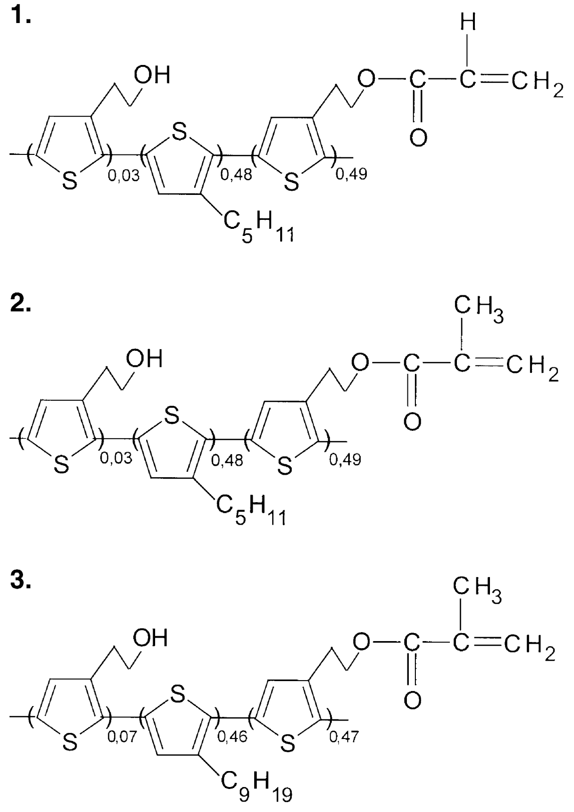
The main IR bands of PT copolymers and their assignments are collected in Table 1.

In electronic spectra of all copolymers, similar broad band in 340–640 nm range with slightly different maximum positions at 431 nm (copolymer **1**), 425 nm (copolymer **2**) and 419 nm (copolymer **3**) occurs. These differences result from different length of conjugated double bond sequences as well as from different substituents in our copolymers.

3.2. *The influence of UV-irradiation on PT copolymers*

UV-irradiation of PT copolymers causes the great changes in both IR and UV–VIS spectra, which are the evidence of photochemical reactions.

Analysis of IR spectra of UV-irradiated PT copolymers indicates the development of broad bands in hydroxyl and carbonyl region with simultaneous decrease of bands due to methyl/methylene groups and bands corresponding to



Scheme 2. Structure of thiophene copolymers used: P[AET-co-3PT] (**1**); P[MET-co-3PT] (**2**); P[MET-co-3NT] (**3**).

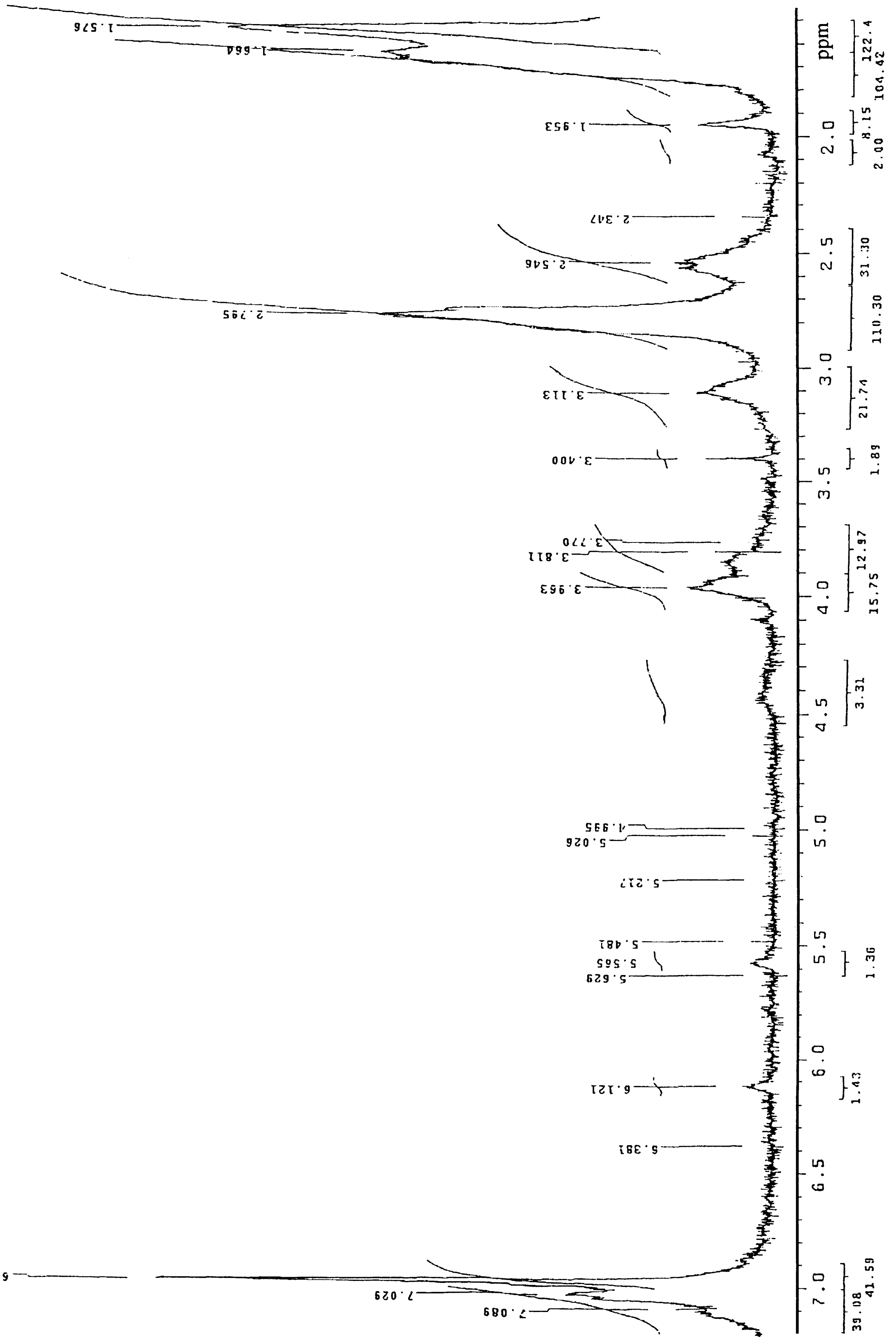


Fig. 1. ^{1}H NMR spectra of P[MET-co-3NT] (**3**).

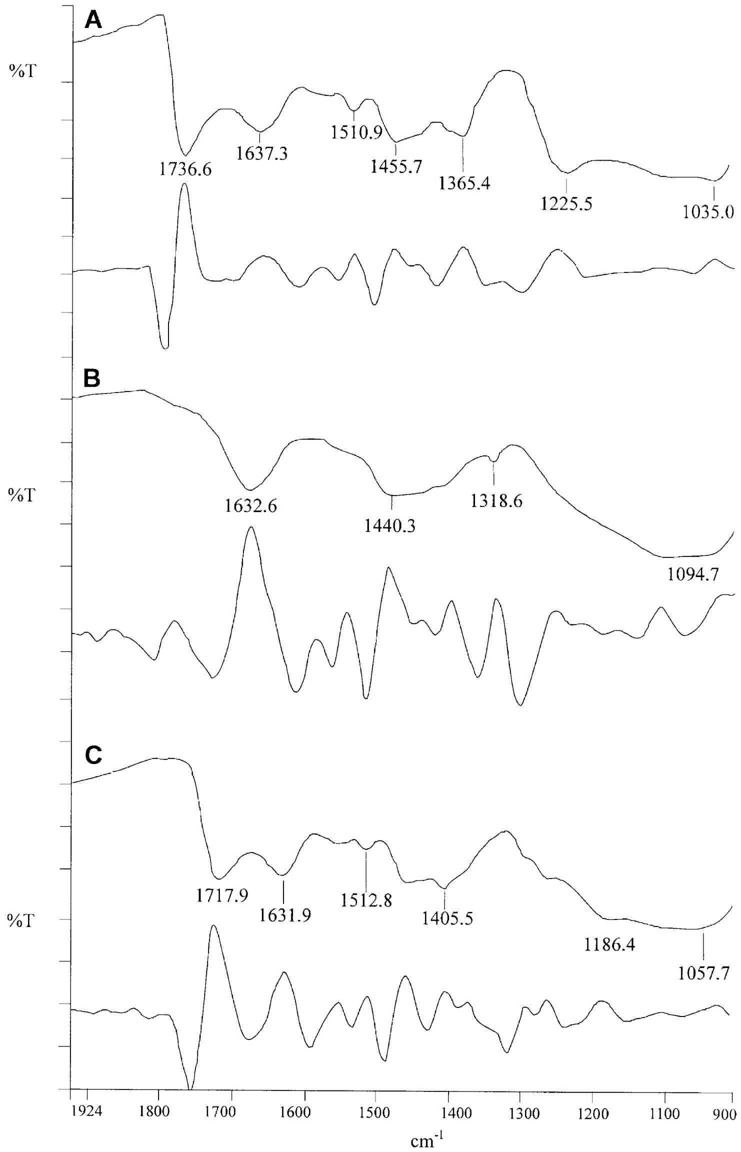


Fig. 2. FT-IR spectra and their second derivatives of copolymer **3** during three steps of modification: (A) P[ACET-co-3NT]; (B) P[HET-co-3NT]; (C) P[MET-co-3NT].

Table 1
Vibrational assignment of thiophene copolymers

Absorption band (frequency, cm^{-1})			Assignment of vibrations [45]
Copolymer **1**	Copolymer **2**	Copolymer **3**	
2960[a]	2962[a]	2960[a]	CH_2 stretching (symmetric and asymmetric)[b]
2923	2920	2919	CH_2 stretching (symmetric and asymmetric)[b]
2853	2853	2851	CH_2 stretching (symmetric and asymmetric)[b]
1722	1718	1718	CO stretching
1652	1651	1652	C=C in acrylic or methacrylic substituent
1560	1559	1543	C=C stretching in thiophene ring
1459	1458	1459	C=C stretching in thiophene ring or CH_2 deformation
1376	1376	1376	CH_2 deformation
1271	1261	1261	C=C stretching in thiophene ring
1151	1120	1157	C–O (ether) in acrylic or methacrylic
1067	1037	1037	C–O (ether) in acrylic or methacrylic
824	820	823	C–H bending out-of-plane

[a] Branch of band.

[b] With overlapping CH and CH_3 vibrations.

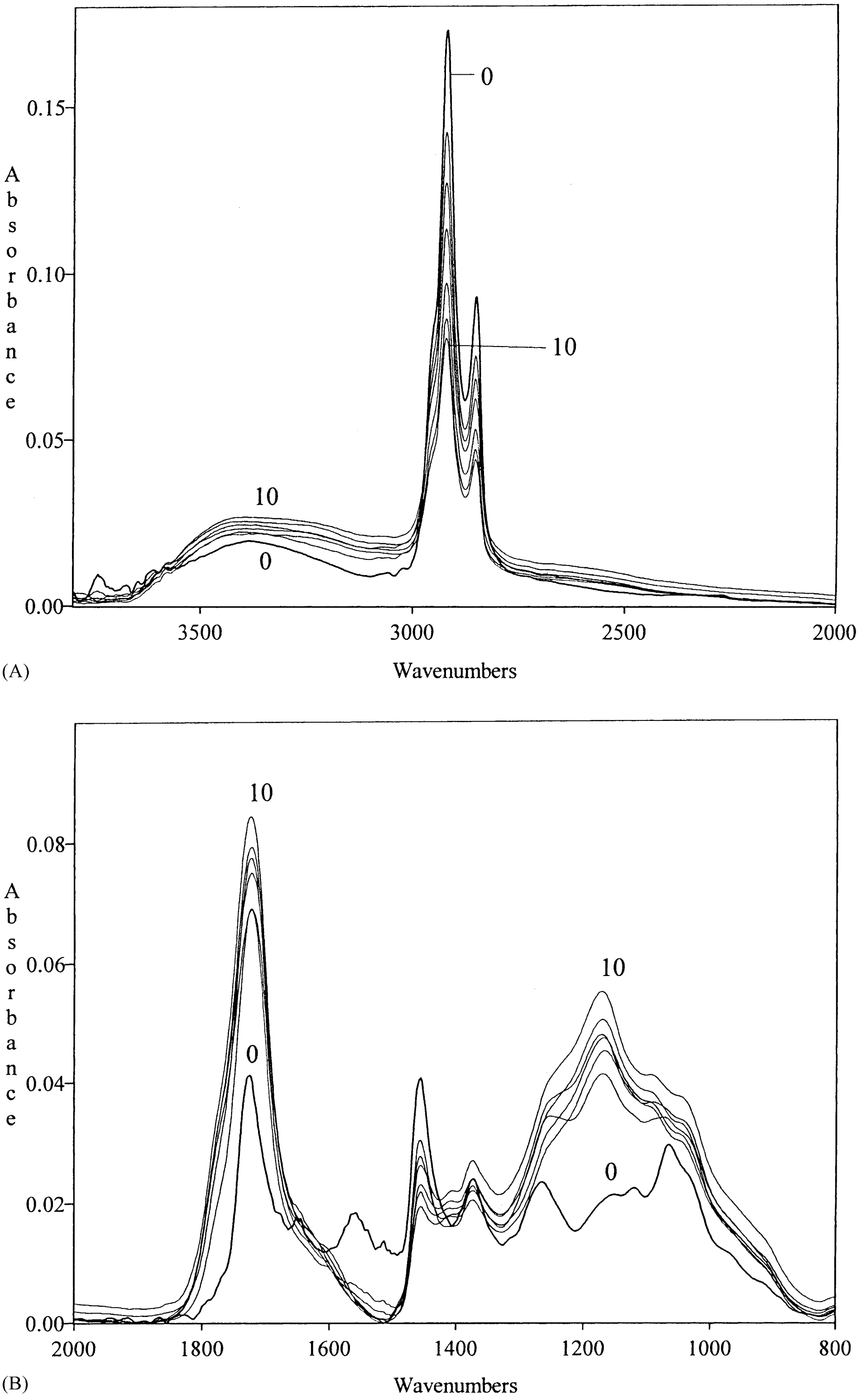


Fig. 3. Changes in FT-IR spectra in copolymer **2** during 0–10 h UV-irradiation: (A) 2000–4000 $\mathrm{cm^{-1}}$ range; (B) 800–2000 $\mathrm{cm^{-1}}$ range.

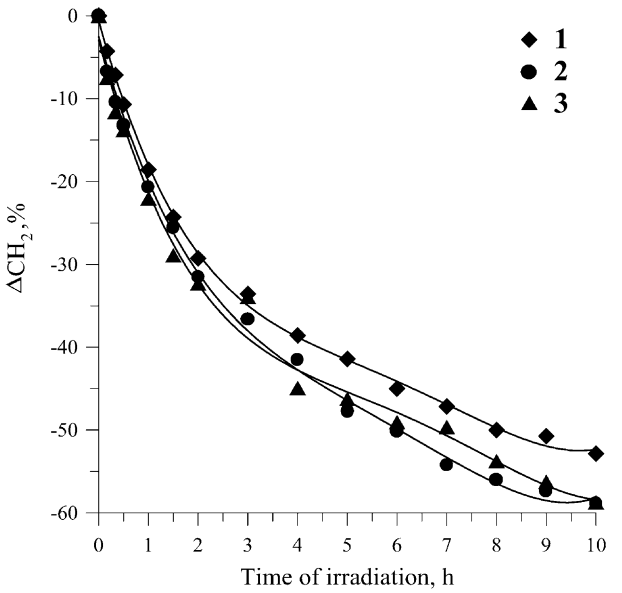


Fig. 4. The changes of methyl/methylene group amount in UV-irradiated copolymers **1**–**3** vs. irradiation time (calculated as changes in integral intensity of 2700–3010 cm^{-1} band).

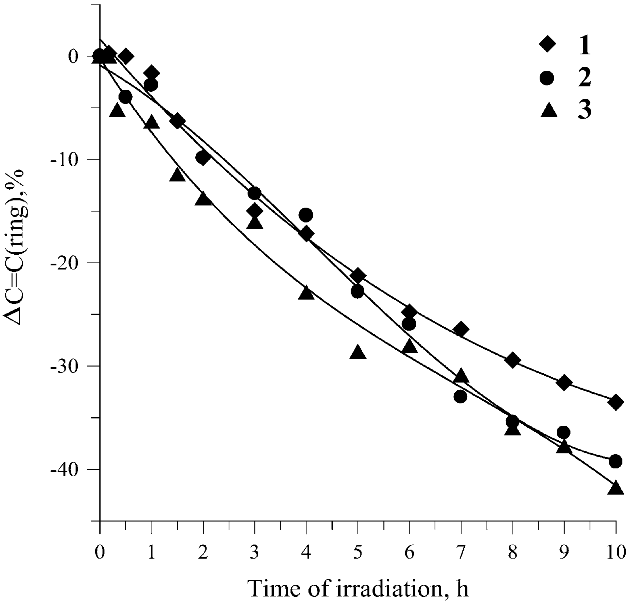


Fig. 5. The changes of conjugated double bonds in copolymers **1**–**3** during UV-irradiation (calculated as percentage changes of absorbance at 1458 cm^{-1}).

double bonds. An example of spectral changes in UV-irradiated copolymer **2** is shown in Fig. 3.

The changes of the integral intensity of band at 2700–3010 cm^{-1} range, corresponding to the stretching vibrations of methyl/methylene groups, in function of irradiation time show fast decomposition in the first hours and the lower rate of the reaction during further steps of exposure in all PT copolymers (Fig. 4).

The kinetic curves indicating the loss of conjugated double bonds (obtained by plotting absorbance at 1458 cm^{-1} versus irradiation time) also continuously drop (Fig. 5). One can say that copolymer **1** is only slightly more resistant to photodegradation when compared to copolymers **2** and **3**.

The variations of hydroxy/hydroperoxy group absorbance measured in peak maximum (Fig. 6) as well as the changes of integral intensity of 3040–3700 cm^{-1} band (not shown here) are irregular, which indicate that formation and destruction of these groups occur alternately. Copolymer **1** shows the greatest resistance on photooxidation leading to the formation of OH/OOH groups; copolymer **3** was found to be the most unstable in this process.

Considering the changes of integral absorbance at 1600–1800 cm^{-1}, due to carbonyl groups, we can say that photooxidation process is fastest in 1–2 h of UV-irradiation. Then, after irradiation time longer than 2–3 h, the concentration of carbonyl groups is approximately constant or even decreases (Fig. 7). The efficiency of photooxidation is much lower in copolymer **1** than those in copolymers **2** and **3**. It is necessary to remember that carbonyl groups are incorporated in macromolecules and processes of their destruction are accompanied by the formation of new type of carbonyls due to photooxidation. Therefore, two opposite processes take place in photodegraded PT copolymers. The fast development of carbonyl band clearly indicates that photooxidation predominates the destruction of acrylic (methacrylic) groups.

Electronic spectra show systematic decrease of absorbance in the whole UV–VIS region during UV-irradiation of samples (Fig. 8). These changes are caused by decay of conjugated double bonds. The dependence of changes of absorbance in maximum as well as absorbance at the same

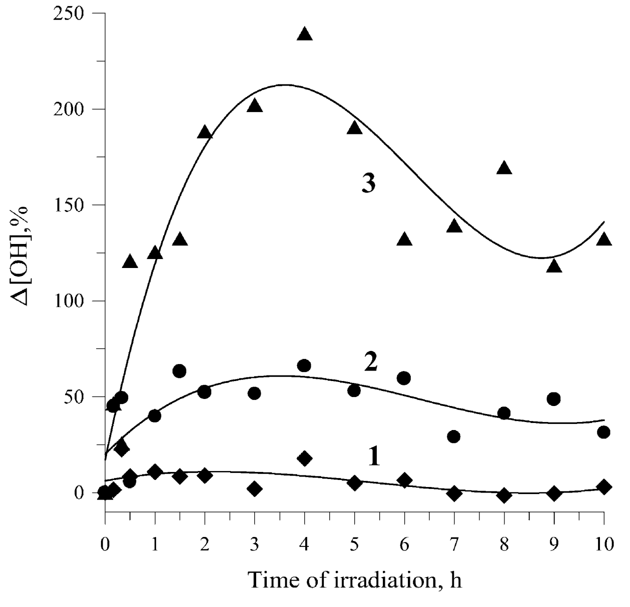


Fig. 6. The dependence of hydroxy/hydroperoxy group amount (measured as absorbance at 3400 cm^{-1}) vs. irradiation time in copolymers **1**–**3**.

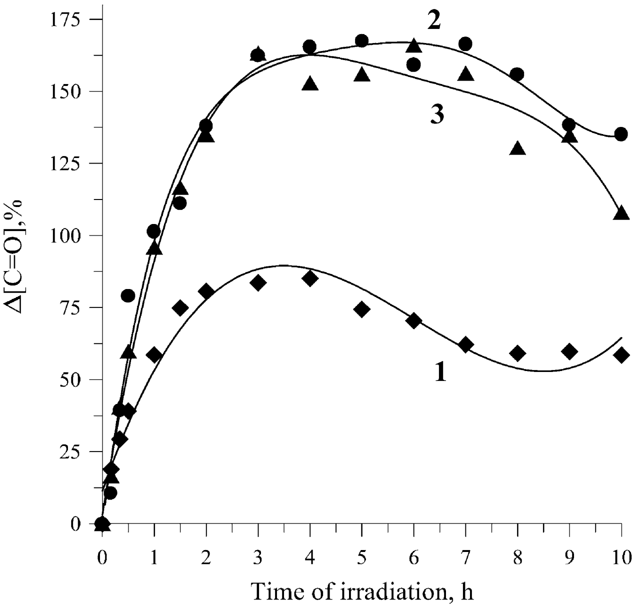


Fig. 7. The dependence of carbonyl group amount (measured as integral intensity of 1600–1800 cm^{-1} band) vs. irradiation time in copolymers **1**–**3**.

point (e.g. 400 nm; chosen for comparison) versus irradiation time shows similar trend. The fastest decrease of absorbance was observed in the first stages of degradation but there are no differences between the slope of kinetic curves of copolymers **1**–**3** until 1 h exposure (Fig. 9). Such differences occur only after 2 h of UV-irradiation and in consequence, the efficiency of decomposition of copolymers **2** and **3** is higher than that in copolymer **1** after longer degradation (2–10 h).

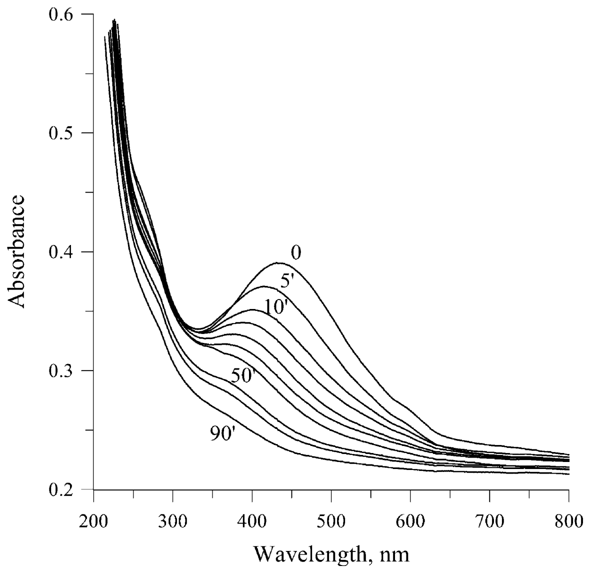


Fig. 8. UV–VIS spectra of copolymer **1** UV-irradiated during 0, 5, 10, 15, 20, 25, 30, 50, 60 and 90 min.

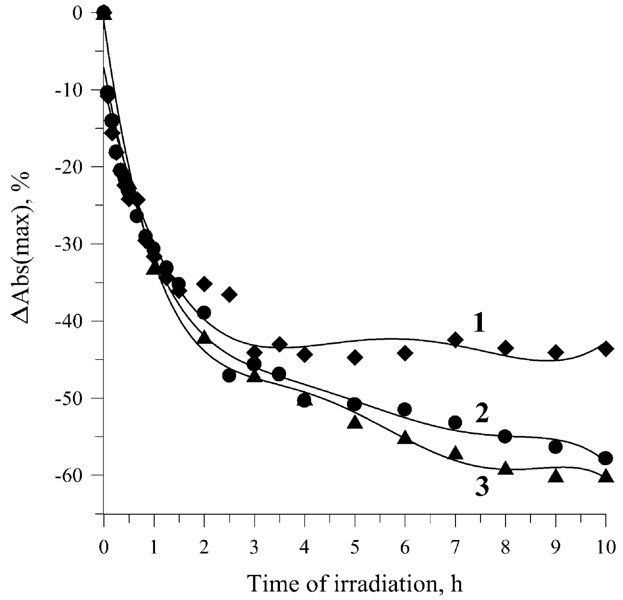


Fig. 9. The percentage changes of absorbance at maximum in UV-irradiated copolymers calculated from UV–VIS spectra at 431 nm (copolymer **1**), 425 nm (copolymer **2**) and 419 nm (copolymer **3**).

3.3. Mechanism of photooxidative degradation of PT copolymers

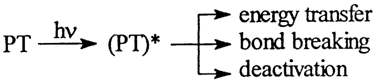
Chemistry of thiophene copolymers is considered on the base of electronic configuration of macromolecules. In thiophene rings, four π-electrons of carbon atoms and two electrons of sulphur atom form delocalised sextet characteristic for aromatic compounds. Thus, thiophene ring, in which all the carbon atoms as well as sulphur atoms are sp^2 hybridised, is stabilised by resonance and this is more reactive than benzene (its resonance energy (122 kJ/mol) is somewhat lower than that of benzene). Thiophene derivatives easily undergo substitution reactions (position 2 is especially favourable).

We propose the mechanism of photodegradation of thiophene copolymers on the base of photoreactions occurring in polythiophene, acrylic (methacrylic) methacrylate as well as in polymer containing side double bonds [46].

Chemical changes caused in PT copolymers during UV-irradiation, which were monitored by spectroscopic methods are explained as follows.

The absorbed light causes excitation of macromolecules. The excitation energy can be transferred to another macromolecule or chemical species (e.g. oxygen molecules) present in the system (reactions (4) and (5)) and can be used in primary reactions leading to formation of free radicals (reactions (6)–(8)). Energy of irradiation emitted by polychromatic lamp used in our experiment is high (short wavelength photons have especially high energy) and it is enough to break down the chemical bonds in thiophene copolymers, thus, main chain scissions (reaction (6)) as well as abstractions of side substituents (reactions (7) and (8)) take place.

Excitation:



(1)
(2)
(3)

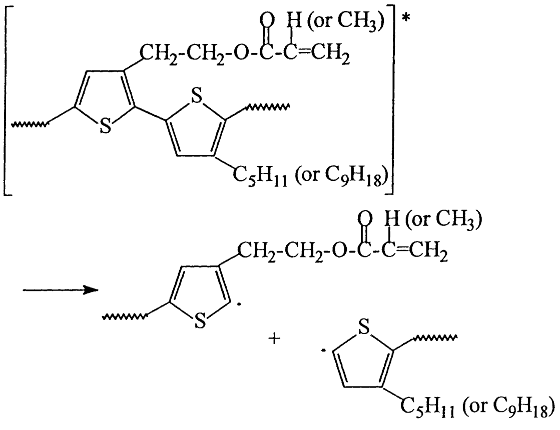
Energy transfer:

$$(PT)^* + PT' \rightarrow PT + (PT')^* \qquad (4)$$

$$(PT)^* + {}^3O_2 \rightarrow PT + {}^1O_2 \qquad (5)$$

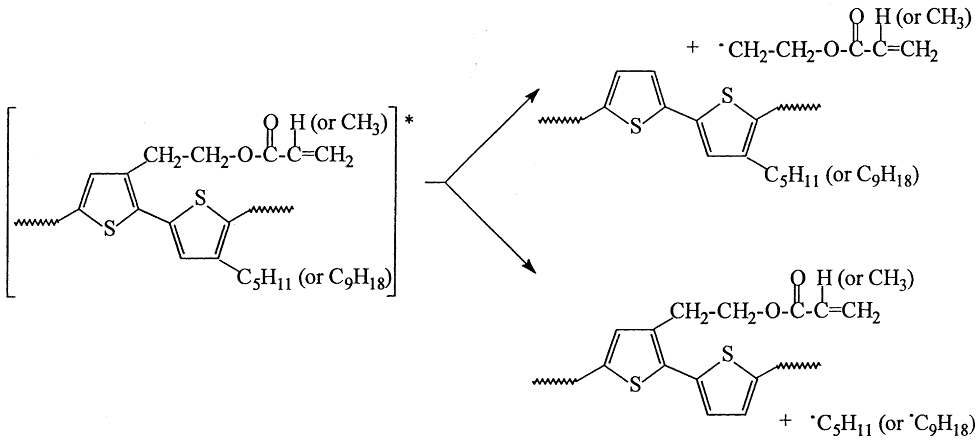
Bond breaking:

- main chain scission:



(6)

- side group abstraction:



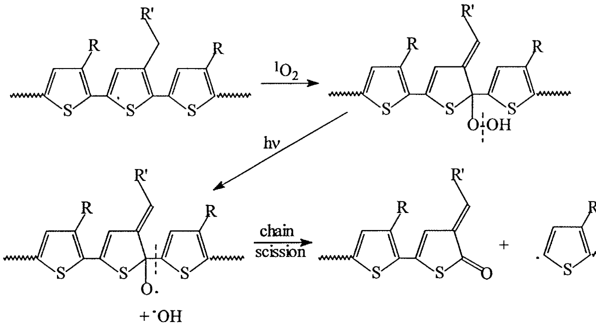
(7)

(8)

As was suggested by Holdcroft [47], excited polythiophene macromolecules can lead to the formation of singlet oxygen ($^1O_2$) by energy transfer (reaction (5)). This reactive form of oxygen easily attacks the thiophene rings in favourable α-position and photochemically unstable hydroperoxides are created (reaction (9)). Further, irradiation causes their photolysis to macroalkoxy and hydroxyl radicals, and finally, to the chain breaking (reaction (10)). Small hydroxyl radicals can abstract hydrogen atom from next macromolecule, then, they are responsible for the chain decomposition occurring even in dark (reaction (11)).

Second possibility of singlet oxygen addition to PT resonance form is reaction (12), in which intermediate dioxetane ring is formed. Their unstability leads to the chain scission and formation of ketonic groups in thiophene ring.

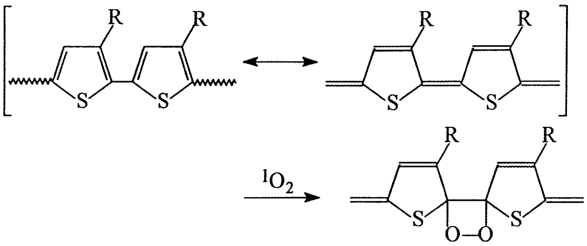
Reaction with singlet oxygen:



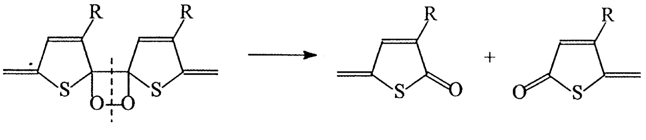
(9)

(10)

$$PT + HO^\bullet \xrightarrow[\text{abstraction}]{\text{hydrogen}} PT^\bullet + H_2O \qquad (11)$$

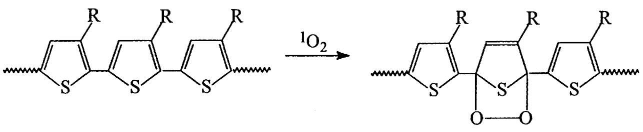


(12)

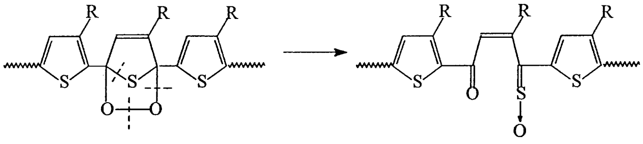


(13)

The 1,4-Diels–Alder addition of singlet oxygen was also proposed [47]. The result of this reaction is opening of thiophene rings, which leads to the deep decomposition of PT backbone (reactions (14) and (15)).



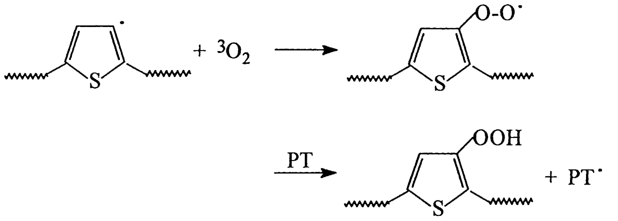
(14)



(15)

Our experiment was carried out in air atmosphere, thus, the classic oxidation must be taken into account (reaction (16)).

Oxidation:



(PT• is polythiophene macroradical)

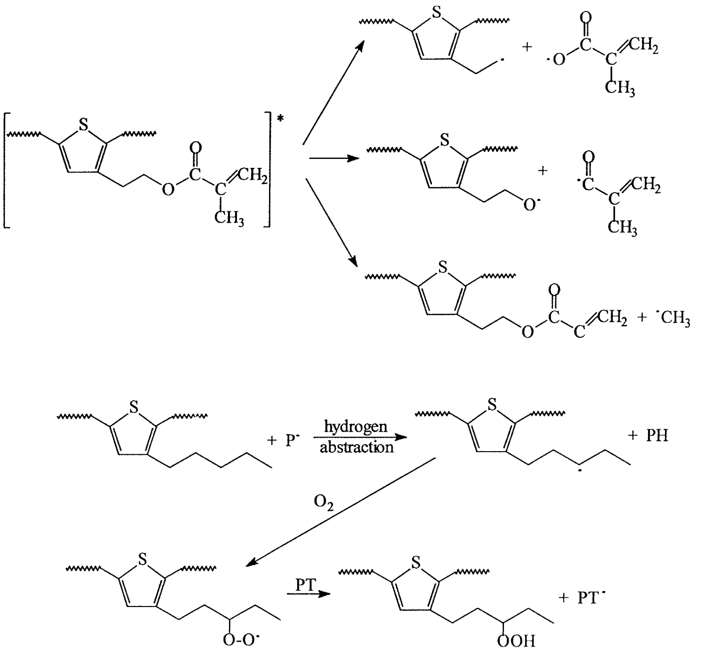
(16)

We should also consider the destruction of acrylic (methacrylic) groups (reactions (17)–(19)) as well as the oxidation of alkyl side substituents (reactions (20) and (21)) during UV-irradiation of PT copolymers in air atmosphere. A large amount of different carbonyl groups formed indicates the occurrence of such competitive reactions in our case.

Destruction of side groups:

Addition of singlet oxygen to double bonds in side acrylic (or methacrylic) groups as a competitive reaction to reactions (9), (12) and (14) can be also expected:

Destruction of side groups:



(17)

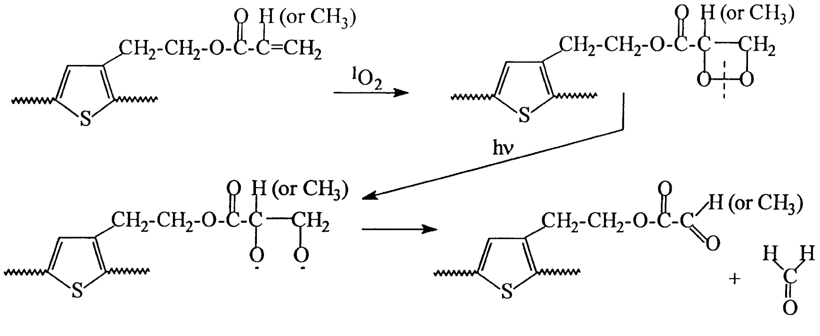
(18)

(19)

(20)

(21)

(where P• is any radical)



(22)

(23)

Typical feature of radical mechanism of photooxidative degradation is the occurrence of secondary reactions even after switching off the light (in dark). Radical recombination (reaction (24)) or disproportionation leads to termination.

$$\mathrm{PT}^{\bullet} + \mathrm{PT}^{\bullet}(\text{or } \mathrm{R}^{\bullet}) \rightarrow \text{non-radical products} \quad (\text{linear, branched or crosslinked}) \qquad (24)$$

where $\mathrm{R}^{\bullet}$ is a low molecular radical.

4. Conclusions

New conducting thiophene copolymers were characterised by enhanced chain mobility and relatively good solubility owing to alkyl substituents. Their sensitivity to light increases due to acrylic (methacrylic) groups containing double bonds.

We can conclude that all three copolymers exhibit different photochemical properties dependent on side group introduced to polythiophene chain. The large differences in their photooxidation were observed, whereas the main chain scission and ring opening process occurs with similar efficiency and rate.

Copolymer **1** was more resistant on photooxidation than copolymers **2** and **3**. It is confirmed by much lower efficiency of carbonyl and hydroxy/hydroperoxy groups formation in polythiophene. Copolymers **2** and **3** containing methacrylic groups were much more sensitive on photooxidation. Copolymer **3** showed especially high yield of photooxidation leading to OH/OOH formation.

The chain oxidation causes the decrease of the conjugated double bonds amount, for example, by singlet oxygen addition or ring opening, which is the reason for the lowering of optical density. This was confirmed by the changes observed in UV–VIS spectra.

It seems that decisive influence on photochemical stability of thiophene copolymers has acrylic substituent. Lower photostability of PT containing methacrylic groups in side chain is probably caused by easy abstraction of methyl groups (reaction (19)), by analogy to poly(methyl methacrylate). Small labile $\mathrm{CH_3}^{\bullet}$ radicals are able to abstract hydrogen atoms from other units or macromolecules. This way, chain polymer degradation is reinitiated.

Size of alkyl group bonded to PT chain has no significant influence on the course of photochemical reactions in copolymers studied.

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