

## The Effect of Microwave Irradiation on Poly(vinyl alcohol) Dissolved in Ethylene Glycol

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**ABSTRACT:** Poly(vinyl alcohol) (PVA) dissolved in ethylene glycol is subjected to microwave (MW) irradiation for 1 h to determine possible degradation. Fourier transform infrared spectroscopy results show that MW treatment produces a minor effect on the solutions. Ultraviolet–visible spectroscopy suggests that PVA could undergoes loss of hydroxyl groups followed by formation of unsaturated conjugated bonds although the extent of degradation is limited, whereas size exclusion chromatography indicates that MW irradiation do not cause significant changes in PVA molar mass and neither chain cleavage nor crosslinking reactions are observed. Hence, polymer degradation induced by MWs in solution can be considered as negligible for prospective applications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

Nowadays, material science is interested in production of biodegradable, biocompatible, and workable polymers with a broad range of properties closely related to their advanced uses as multifunctional materials. One of those materials, widely known is poly(vinyl alcohol) (PVA). This polymer is used in adhesives, cosmetics, textile and pharmaceutical industry, paints, and even as a colloid protector in emulsion polymerization.<sup>1</sup> Numerous advantageous properties of PVA have lead to its broad practical applications due to its chemical resistance, favorable physical properties, and complete biodegradability.<sup>2</sup> Furthermore, it is water soluble and has broad industrial application as a result of its high capability of water absorption.<sup>3</sup>

During shelf life, polymers can be degraded by numerous ways including action of chemical substances, mechanical forces, and/or radiation. IUPAC has defined polymeric degradation as chemical changes in a polymeric material that usually result in undesirable changes in the in-use properties of the material.<sup>4</sup> In most of the cases, degradation is accompanied by worsening of physicochemical properties, such as a decrease in molar mass, whereas in some circumstances, degradation also includes changes in chemical structure of the backbone or elimination of polymer side groups. It can also be accompanied by crosslinking. Frequently,

degradation results in the loss of, or deterioration in, useful properties of the material.<sup>4</sup> This concept is valid for this study, in which degradation caused by microwave (MW) irradiation is examined. Thermal degradation of PVA on the other hand, has been investigated in more detail than other degradation ways. Thermogravimetry, thermal analysis Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry techniques have been used for this purpose.<sup>5</sup> The mechanism of thermal degradation of PVA comprises two steps. The first one involves elimination reactions, whereas the second is dominated by chain scission and cyclization. Additionally, highly hydrolyzed PVA shows a better thermal stability than PVA with a low degree of hydrolysis.<sup>6</sup> Degradation of PVA bulk material has been studied by several authors,<sup>1,2,5,6</sup> and it was concluded that the elimination of hydroxyl side groups is present and considerable amounts of isolated and conjugated polyenes in the degradation residue and small amounts of carbonyl groups could appear. Moreover, Ultraviolet–visible (UV–vis) spectroscopy has shown that the unsaturated double bonds produced by elimination do not lead to the formation of noticeable amounts of conjugation.<sup>5</sup>

In two related studies,<sup>7,8</sup> solid PVA films were heated by MW irradiation, and it was found that irradiation heating at moderate temperature (100–150°C) tends to cause polymer

dehydration with crosslinking formation through ether bridges, whereas heating to higher temperatures or by conventional heating cause formation of double bonds. Thus, the crosslinking is ascribed specifically to nonthermal MW effect. On the other side, another type of irradiation, for example, UV, does not cause crosslinking even after 10 h of treatment.<sup>3</sup> Although most of the studies have been carried out on bulk material, for particular applications, for example, electro spinning and casting PVA in form of solution in a suitable solvent is required.<sup>9–11</sup> The solutions are sometimes heated or even boiled to enhance the dissolution rate, and to overcome the relatively poor solubility of highly hydrolyzed PVA. The use of advantages of MW ovens is a good choice for polymer synthesis or for polymer-analog reactions.<sup>12</sup> There are also numerous reports describing that many slow or “difficult to run” reactions were suddenly made fast and easy by MW treatment.<sup>13–15</sup> Although MW application is an attractive alternative to convective heating, there are not enough reports about the resulting properties of PVA solutions after MW treatment, even though it is obvious that absorption of a quantum of MW radiation cannot directly induce chemical reactions, as its energy is too low to break chemical bonds.<sup>16</sup> Albeit MW was proposed to be used for accelerating chemical reactions by their efficient heating of the reactants, some difficulties could appear such as the reflection and absorption of MW by reactants, which does not allow a uniform MW heating.<sup>17</sup> The ability of a specific substance to convert electromagnetic energy into a heat at a given frequency and temperature is determined by the so-called loss factor  $\tan \delta$ . A reaction medium with a high  $\tan \delta$  value is required for efficient absorption and, consequently, for rapid heating. As ethylene glycol (EG) exhibits a high value of  $\tan \delta$  (1350 at 2.45 GHz),<sup>18</sup> it was chosen as the solvent in this study. Indeed, EG boils at 196–198°C and its use can provide homogeneous MW heating of the solution to relatively high temperature.

The objective of this study was to identify a possible degradation of PVA dissolved in EG when the solution was subjected to MW irradiation, and in case that degradation occurs, to investigate its mechanism. During the MW treatment, the process was monitored by UV–vis, FTIR spectrometry, and size exclusion chromatography (SEC).

## EXPERIMENTAL

### Materials and Sample Preparation

PVA ( $M_w \sim 47,000 \text{ g mol}^{-1}$ ), polymerization degree of 1000, 98% hydrolysis, and EG (99%) were supplied by Fluka (Sigma-Aldrich, Prague, The Czech Republic) and used without further purification.

PVA solution 5% w/w in EG was prepared at 120°C in a beaker covered by aluminium foil and it was stirred and heated for 1.5 h using a Heidolph MR Hei-Standard magnetic stirrer with heating (Heidolph Instruments GmbH., Schwabach, Germany). The solution was prepared by conventional heating because PVA could undergo crosslinking in solid state caused by MW irradiation at relatively low temperature (100–150°C) through ether bridges,<sup>7,8</sup> whereas conventional heating do not produce such effects. The prepared polymer solution was irradiated for 60 min by MWs in an open vessel reflux system. A CWR-Tech

MW domestic oven (M7017P-M, UK) with a standard frequency of 2.45 GHz and power of 700 W was modified toward this purpose and equipped with an external cooler to reduce the risk of explosion. Moreover, the temperature of the system was controlled by using a noncontact infrared digital thermometer GIM 1840 (Greisinger Electronic GmbH., Regenstauf, Germany) immediately whenever the cavity was opened. The temperature was always close to the boiling point of EG. Samples were taken at 4, 8, 12, 16, 20, 40, and 60 min and subsequently, the polymer solutions were diluted in water in 1 : 2 w/w ratios and they were allowed to cool to the laboratory conditions and used to obtain UV–vis spectra. For the same purpose, a blank sample of EG was subjected to MW irradiation for 1 h and no changes were detected by UV–vis absorption spectra. For FTIR analysis, the solutions were cast on polished silicon wafer substrate and dried in an oven at 28°C for 1 week. The obtained films had a thickness of about 200  $\mu\text{m}$ .

### Analytical Techniques

UV–vis spectra were taken with an AvaSpec-2048 spectrometer (Avantes, Eerbeek, The Netherlands). The apparatus for FTIR was a Scimitar FTS2000 (Digilab, Cambridge, MA, USA), and all FTIR absorption spectra were recorded by transmission mode at the resolution of 2  $\text{cm}^{-1}$  and plotted in absorbance scale. SEC analyses were performed using a setup consisting of a Waters 600E pump, a Waters 2414 differential refractometer (Waters GmbH, Eschborn, Germany), in-line degasser (Watrex, Prague, Czech Republic), and a Rheodyne 7725 injector. Analyses were carried out with a TSK GMPWXL column (7.8  $\times$  300  $\text{mm}^2$ ) (Tosoh Bioscience, Tokyo, Japan) at 30°C with a 100  $\mu\text{L}$  injection loop. Aqueous 0.1M solution of  $\text{NaNO}_3$  with 15% acetonitrile and flow rate of 0.8 mL/min was used as a mobile phase. The column was calibrated using narrow molecular weight pullulan standards (Polymer Laboratories Ltd., Shropshire, UK) with molar masses ranging from 677 to 788,000  $\text{g mol}^{-1}$ . Data processing was fulfilled with Cirrus Multi Detector Software (Polymer Laboratories Ltd., Shropshire, UK). Sample concentration of about 1.5  $\text{mg mL}^{-1}$  was used. Conventional calibration, relative to pullulan standards, was applied and weight average molar mass  $M_w$ , number average molar mass  $M_n$ , and polydispersity index  $P = M_w/M_n$  of the tested samples were determined. For SEC analyses, the samples were accurately weighed and dissolved in the mobile phase for  $\sim 10$  h at room temperature followed by dissolution at 70°C for 30 min under shaking. Before measurements, the samples were filtered through a 0.45  $\mu\text{m}$  Chromafil PP/PET filter (Millipore, Billerica, MA, USA).

## RESULTS AND DISCUSSION

### UV–vis Analysis

The presence of carbonyl groups in PVA arises from the production of the polymer. PVA is obtained by hydrolysis of poly(vinyl acetate), thus, the residual acetate groups resulting of incomplete hydrolysis process are always present as well as a small amount of degradation products as inevitable impurities caused by processing of the polymer. UV–vis spectra of the virgin and the irradiated PVA confirm the presence of residual carbonyl groups in all the samples as can be seen in Figure 1, where a time series of absorption spectra is plotted (graphs are vertically

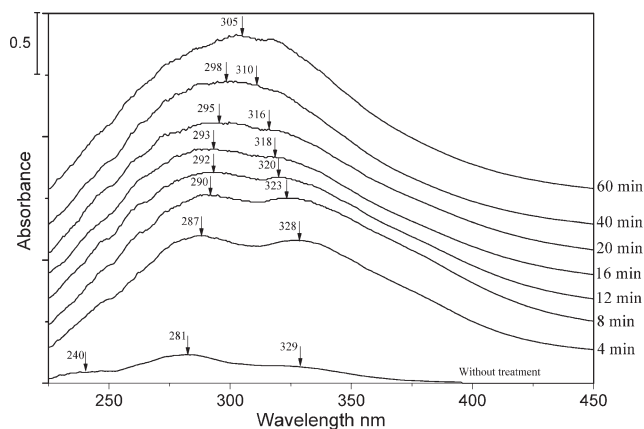


Figure 1. UV Spectra for PVA during the treatment.

shifted for better clarity). The low intensive band due to electronic transition related to carbonyl group appeared at a wavelength ( $\lambda$ ) of about 278 nm.<sup>3</sup> A second band at 330 nm due to carbonyl functionality was observed as well.<sup>19</sup> It has been also reported that the band at 280 nm is attributable to diene ketone  $-(CH=CH)_2-CO-$  and a shoulder or a peak of lower intensity at 330 nm to triene ketone groups  $-(CH=CH)_3-CO-$ .<sup>20</sup> The absorption peak centered at 240 nm can be interpreted as a manifestation of the monoene ketone. Hence, the degradation products are inevitably present to a small extent even in the raw material, possibly coming from its production and shelf ageing. The respective absorption bands are manifested in the spectrum of untreated material. On the other hand, no absorbance was present for the virgin material in visible light region. The biggest change in absorbance spectrum during MW treatment was manifested after 4 min as the steep increase of the signal. Then, the change in the shape of the spectra proceeded slowly, the two maximum at initial  $\lambda$  values of 281 and 329 nm merged smoothly into one broad band with a maximum at 305 nm within 60 min. A pale yellow discoloration of the solution was observed in later stages of irradiation which is attributable to the absorption peak shoulder exceeding wavelength 400 nm. The spectral band loss its structure and most probably a mixture of oligo- or polyene or polyene-carbonyl electron systems was manifested. It was described in the literature for solid PVA that the conjugated unsaturated system successively extends over more and more double bonds as the polymer undergoes to the thermal degradation. The absorption peak intervals in the same kind of transition are about 30–40 nm for small number of double bonds in conjugation, which means that for  $n = 4$  and 5 in  $-(CH=CH)_n-CO-$  maximum at 360–380 nm can be expected.<sup>21</sup> These values were observed for analogous polyenals  $CH_3-(CH=CH)_n-COH$  (where  $n = 2-5$ ) in solutions as well.<sup>22</sup> Similar features are observable also for sequences of  $-(CH=CH)_n-$  without being in conjugation with  $-CO-$  moiety in degraded PVA films, although the maximum in  $\pi \rightarrow \pi^*$  absorption are shifted toward to shorter wavelengths by 40–60 nm and resolved absorption bands are observable.<sup>21</sup> Discoloration, yellowish, red, and finally brown color appearance of the sample are generally experienced in the previously cited literature with the progress of solid sample conventional heating deg-

radation due to polyene or polyene-carbonyls formation. On the other hand, UV-vis spectra of bulk PVA irradiated with MW were described showing a strong absorption in the range 250–400 nm and the growth of absorption was observed to be more pronounced at the wavelength 330 nm for thermal heating and at 280 nm for MW heating, which were assigned to different polyconjugated unsaturated structures created by thermal degradation, but the extent of discoloration at higher wavelengths was suppressed for MW and the films become yellow and not brown. Crosslinking of the chains of PVA by ether (C–O–C) bridges was observed as the prevailing degradation mechanism in this case, in which interpretation requires dehydration via intermolecular reaction of hydroxyl groups eclipsing the intramolecular one due to a specific MW effect on polar groups.<sup>7,8</sup>

The time dependence of absorbance intensity during MW irradiation of PVA solution is shown in Figure 2 for selected wavelengths. It is clearly seen that conjugated double bond structures were formed by dehydration during first minutes of MW irradiation although their successive growth was stabilized after reaching maximum within 8 min, and the absorbance at the wavelength 360 and 380 nm remained nearly constant after 20 min, which means that the extent of conjugation did not exceed the length of four or five double bonds significantly. Similarly, the defects manifested by absorption at 260 nm were saturated after 20 min as well. The absorbance in the wavelength region around the maximum at 300 nm initially followed the same trend but after the 16th minute the course changed and it progressed again. A plausible explanation is that the degradation begins with dehydration and subsequent carbonyl group formation due to a rearrangement and continues by consecutive dehydrations, followed by conjugated double bond system propagation. According to all previously discussed literature, this is typical degradation pattern for PVA in solid state, which results into the intensive discoloration due to formation of polyene structures extended over multiple mer units. The behavior of PVA observed in Figure 2 testifies the presence of another mechanism which affects the process in opposite way, and thus, limits the polyene propagation. The defects grow up to critical

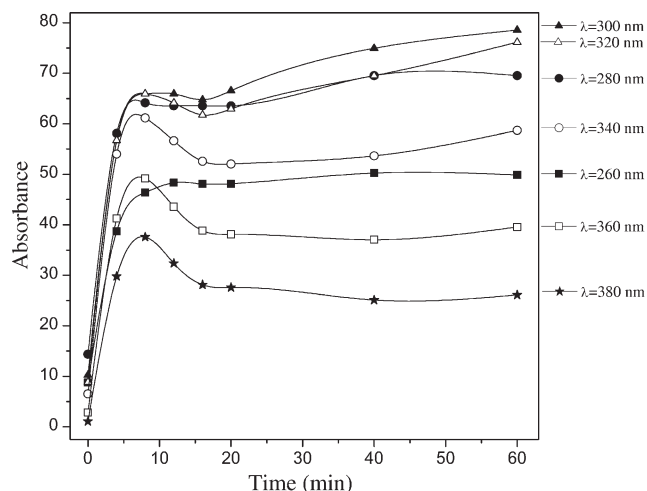
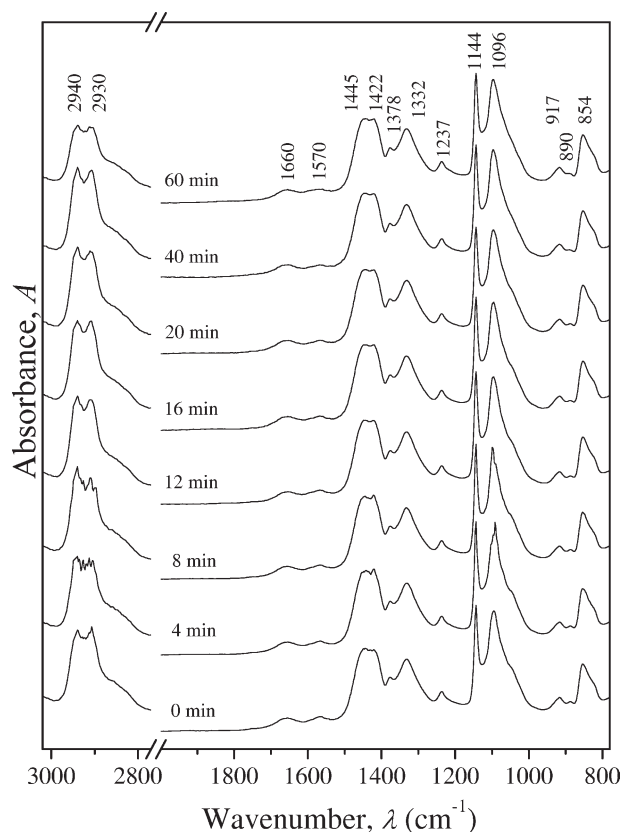


Figure 2. Time dependence of absorbance intensity during MW irradiation of PVA solution.



**Figure 3.** FTIR Spectra for PVA during the treatment.

size of approximately five double bonds in conjugation with C=O group and then, dissociate or regenerate back to defects which remain delocalized over few C=C or C=O bonds.

#### FTIR Analysis

The FTIR spectrum for virgin PVA has been elucidated in different studies.<sup>5,20,23</sup> In this work, the technique was used to monitor the possible degradation during MW irradiation and the most significant spectral regions of MW treated samples are shown in Figure 3. There is a strong broad absorption band centered at  $3336\text{ cm}^{-1}$  without any fine structure (not included in the graph for the sake of better presentation of the lower wavenumber region), which is characteristic for OH group. The bands at  $2940$  and  $2930\text{ cm}^{-1}$  are clearly associated with saturated C—H stretching, whereas the bands at  $1445$  and  $1422\text{ cm}^{-1}$  are related to  $-\text{CH}_2-$  bending.<sup>24</sup> The spectra do not show even weak bands for carbonyl group over  $1700\text{ cm}^{-1}$ , indicating that only small amount of acetate groups, below the detection limit, can be present in the polymer chain as the used PVA is highly hydrolyzed. Two peaks at  $1660$  and  $1570\text{ cm}^{-1}$  can be attributed to conjugated diones or single carbonyls in a conjugation with C=C double bonds in solid state, where peaks over  $1700\text{ cm}^{-1}$  are not manifested.<sup>23,25–27</sup> Bands in this region can be ascribed to conjugated C=C systems as well. Both interpretations are in agreement with observed UV–vis spectra; however, these bands do not vary with the time of MW irradiation which supports the idea that thermal degradation either does not occur or only small amount of carbonyl groups is formed

or the degradation proceeds without isolated carbonyl formation. In either of aforementioned cases, the degree of degradation is very low as these features can be observed by the means of UV–vis spectrometry only which is due to its higher sensitivity than that of FTIR. The peak at  $1144\text{ cm}^{-1}$  is connected with C—O stretching modes and a strong dependency of its intensity on crystallinity degree of the solid PVA material was observed.<sup>28,29</sup> Other authors<sup>7,8</sup> connect this band with C—O—C in ether bridges and crosslinking of PVA is deduced from increased in absorbance at this wavenumber. The bands at  $1378$  and  $1332\text{ cm}^{-1}$  can be attributed to combination frequencies of CH and OH.<sup>30</sup> A strong peak at  $1060$ – $1030\text{ cm}^{-1}$  is assigned for stretching C—O in C—O—H group,<sup>7</sup> but the band is shifted at  $1096\text{ cm}^{-1}$  due to interaction with unsaturated bonds.<sup>24</sup> The band related to  $\text{CH}_2$  rocking at  $917\text{ cm}^{-1}$  and a peak at  $854\text{ cm}^{-1}$ , which are associated to C—O stretching are manifested in the spectra as well.<sup>29</sup> FTIR spectra do not show any evidence of PVA degradation. The above discussed bands are present in the spectra of all the samples irrespective of treatment time. Neither increase in typical carbonyl absorption region (about  $1700\text{ cm}^{-1}$ ) nor increase of absorption in C—O—C region was observed ( $1144\text{ cm}^{-1}$ ). With respect to the UV analysis, the degree of degradation is very low, below the detection limit of the FTIR spectrometer, that is, less than 1% of changed hydroxyl groups and hence mer units.

#### SEC Analysis

PVA belongs to polymers whose composition plays important role in SEC analysis, when aqueous system is used. Although comprehensive studies describing chromatographic behaviors of PVA in aqueous solutions exist, determination of molar mass and molar mass distribution of this polymer are not a simple issue.<sup>31,32</sup> Thanks to various degree of hydrolysis, PVA can exhibit varying extent of hydrophobicity (caused by presence of vinyl acetate group) and hydrophilicity (caused by presence of vinyl alcohol group). Attention has to be, hence, paid to careful selection of columns and mobile phase to restrict nonsize exclusion effects during chromatographic separation. To eliminate these effects and suppress enthalpic interactions that might compete with size exclusion process, analyses were performed in aqueous mobile phase consisting of  $0.01\text{ M NaNO}_3$  and 15% (v/v) acetonitrile. Changes of  $M_w$ ,  $M_n$ , and polydispersity index  $P$  as a function of increased time of MW treatment are summarized in Table I. From the results, it is obvious that MW irradiation influenced PVA molar mass only to minor extent. Compared with starting material, weight average molar mass  $M_w$  of studied samples remained almost unchanged up to 20 min treatment. Molar mass reduction first occurred after 40 min of irradiation (decrease from  $38,500\text{ g mol}^{-1}$  to  $36,100\text{ g mol}^{-1}$ ) and continued further after 60 min of irradiation ( $M_w$   $34,400\text{ g mol}^{-1}$ ). Comparison of distribution curves recorded for the samples treated for 0, 12, and 60 min, depicted in Figure 4, corroborates the above given conclusions and clearly illustrates slight, but notable shift of entire polymer distribution to lower molar mass region. In addition to molar mass lowering, small but distinct peak with molar mass higher than  $5 \times 10^5\text{ g mol}^{-1}$  (labeled with arrow) was observed after a careful inspection of “zoomed” chromatogram (Figure 5). This peak was detected for

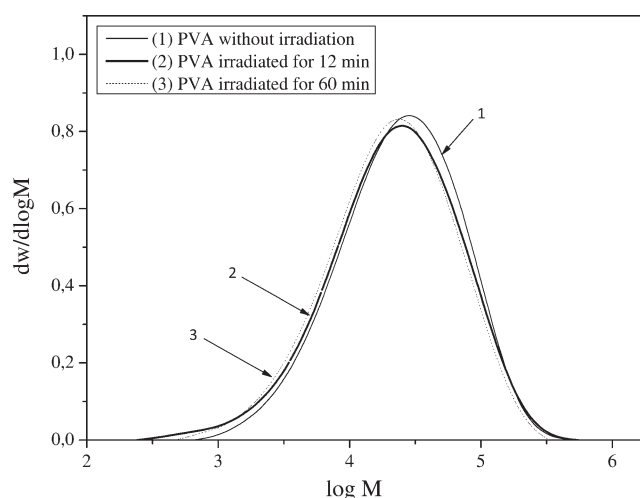
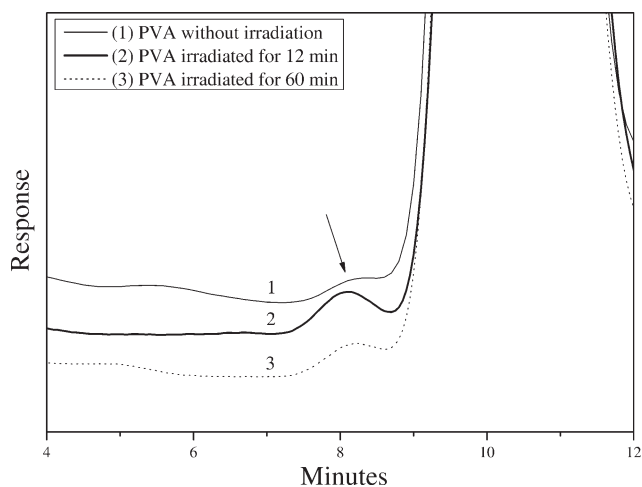
**Table I.** Values of  $M_w$ ,  $M_n$ , Polydispersity Index  $P$  Determined for PVA Samples Treated with Microwaves

Time of treatment (min)	$M_w$ ( $\text{g mol}^{-1}$ )	$M_n$ ( $\text{g mol}^{-1}$ )	$P = M_w/M_n$
0	38,500	11,000	3.5
4	38,300	10,300	3.7
8	37,700	10,300	3.7
12	38,000	10,400	3.7
16	38,800	10,100	3.7
20	38,500	10,200	3.8
40	36,100	9400	3.8
60	34,400	9300	3.7

all samples irrespective treatment time and indicates the presence of structures with higher molar mass than that of the main polymer. The presence of similar peak on PVA chromatogram was also reported by Lacík et al.<sup>31</sup> and it was attributed to the formation of aggregates.

## CONCLUSION

The aim of this work was to investigate the stability of PVA solution in EG under MW irradiation. The results have shown that MW treatment produces only minor changes of PVA. According to FTIR study, there are no evidences of significant presence of possible polymer degradation products, which can be considered as a manifestation of thermal stability under the given conditions. UV-vis spectra broadening testifies creation of low concentrated defects in form of conjugated double bond structures by dehydration during first minutes of MW irradiation although their propagation is stabilized after reaching maximum with prolonged time of irradiation. On the contrary, the defects remaining delocalized over few C=C or C=O bonds increase slowly with irradiation time, thus a degradation mecha-


**Figure 4.** Differential distribution curves obtained for (1) starting PVA material, (2) sample irradiated for 12 min, and (3) sample irradiated for 60 min.

**Figure 5.** Elution curves recorded for (1) PVA starting material, (2) sample irradiated for 12 min, and (3) sample irradiated for 60 min.

nism preferring their formation before consecutive polyene generation is concluded. In next, according to SEC study, MW heating does not cause crosslinking or other pronounced changes of molar mass namely due to chain cleavage of the polymer sample either. As a consequence, MW treatment within the investigated time scale can be recommended as an appropriate technique for heating of PVA solutions in EG because the results have shown that no significant changes have occurred during that part of the treatment. MW irradiation for 20 min did not cause any reasonable deterioration of the molar mass distribution. Moreover, the time span could be extended up to 60 min with the risk of negligible degradation, if needed. The MW-assisted heating of PVA in EG solution can, hence, bring benefits in shortening time and saving money consumed for the polymer processing.

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