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IR laser-induced modification of poly(vinyl acetate): Elimination of monomer and deposition of polar crosslinked films

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Abstract

IR laser-induced modification of poly(vinyl acetate) (PVAC) was examined through ablative and non-ablative thermal processing of bulk PVAC. Both laser-induced processes differ remarkably from conventional heating of PVAC, which yields acetic acid and non-polar carbonaceous residue. The non-ablative treatment at low-fluence irradiations results in the formation of volatile vinyl acetate and acetone and leaves the remaining irradiated polymer having an almost identical structure. The ablative treatment at high-fluence irradiations yields a multitude of volatile compounds (methane, ethane, vinyl acetate, acetone, acetic acid, benzene, H_2, CO and CO_2) and affords deposition of thin polymeric films that contain reactive conjugated C=C bonds and half of the initially present acetate groups. Residual reactivity of the C=C bonds leads to polymer crosslinking, substantial decrease in solubility and some increase in thermal stability. The low fluence-induced decomposition stands for the first example of the thermal decomposition of polyvinyls into the monomer and the high-fluence ablative deposition represents a one-step approach to crosslinked (intractable), thermally stable and polar polymeric films from linear-chain polymers with pending functional groups.

Keywords: Laser ablation; Laser irradiation; Poly(vinyl acetate)

1. Introduction

The conventional heating of polymers (through pyrolysis or thermogravimetry) was often applied in the past to identify the routes and products of polymer degradation (e.g. [1]). In this process, heterogeneous stages occurring on the hot reactor surface could not be entirely circumvented and the polymer heating was rather slow. These features made the polymer degradation to be thermodynamically controlled and affected by heterogeneous steps.

Conversely to many studies on the homogeneous gas-phase decomposition of organic monomers (using wall-less reactor, shock-tube and laser techniques), intentional examinations of polymer decomposition under wall-less conditions have not been carried out so far. One of elegant methods for such examination can be pulsed IR laser-irradiation of solid polymer target. Here, the laser radiation interacts only with a limited volume of polymer body and induces polymer decomposition far from vessel surface. Although the interaction of the pulsed IR laser irradiation with solid polymers was already reported, the studies aimed only at polymer ablation and deposition of thin polymer films [2–9]. This specific process occurs within a temperature jump and is controlled by kinetic rather than thermodynamic polymer degradation. It is feasible through multiple-photon absorption of energy-poor infrared photons, which leads to high vibrational excitation density in the polymer and high heating and cooling rates (respectively, $\sim 10^{6-11}$ and $\sim 10^{3-6}$ K s^{-1}) [10–12]. This ablative process yields polymer films whose structure differs or not from that of the initial target. For example, the IR laser ablative deposition (IRPLAD) of almost structurally

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identical films was demonstrated with irradiation of poly(ethylene glycol) [7,8] and poly(ethylene-alt-maleic anhydride) [9], whereas significant structural modifications (crosslinking) of the polymer was reported [6] upon irradiation of poly[oxy(tetramethyldisilane-1,2-diyl)].

We were interested in examination of homogeneous decomposition of poly(vinyls) whose conventional thermal degradation was recognized as a process in which pendant group is efficiently cleaved from the polymer backbone and which yields products not related to the monomer. The best known example is the thermal degradation of PVAC dominated [13–19] by elimination of acetic acid and formation of a carbonaceous residue possessing conjugated C=C bonds along with cyclic and aromatic units. In the present paper we report on a pulsed IR laser irradiation of PVAC and show that this irradiation induces thermal decomposition remarkably different from the conventional decomposition of PVAC. We report on several yet unobserved decomposition paths of PVAC and on the films deposited from the ablated PVAC.

2. Experimental

The irradiation of PVAC (0.5–0.8 g of a sample compressed in a tablet) with a TEA CO_2 laser (Plovdiv university) on the P(20) line of $00^01 \rightarrow 10^00$ transition (944.19 cm^{-1}) was performed using incident fluence 0.6–22.8 J cm^{-2} and repetition frequency 1 Hz. The laser beam was focused by Ge or NaCl lenses. The tablet was housed on a bottom of an evacuated (10^{-2} mbar) Pyrex vessel (Fig. 1, 42 ml in volume) equipped with a side arm with rubber septum, a PTFE valve and NaCl window and connected to a vacuum manifold furnished with a vacuum meter. The vessel also accommodated a holder for quartz, KBr and copper substrates. The properties of the films deposited on these substrates and nearby vessel surface (in total amounts of ~10–15 mg) were evaluated by FTIR spectroscopy, Raman spectroscopy, UV/vis spectroscopy (a Shimadzu UV/vis 1601 spectrometer) and electron microscopy.

The volatile products were identified through their mass spectra and were monitored by FTIR spectroscopy (a Nicolet Impact spectrometer), gas chromatography (a Shimadzu 14A chromatograph) and gas chromatography-mass spectrometry (a Shimadzu QP 1000 mass spectrometer) using 2 m long Porapak P columns, programmed (30–150 °C) temperature and sampling by a gas-tight syringe. The chromatograph was equipped with flame-ionization detector and connected with a Shimadzu CR 5A data processor.

SEM analyses were carried out by 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 O elements.

Raman spectra were recorded on a Renishaw (a Ramascope model 1000) Raman microscope with a CCD detector using the exciting beam of an Ar-ion laser (514.5 nm) 50 μW.

Gel-permeation chromatography measurements of molecular weight distribution in the deposited polymers was carried out in dry tetrahydrofuran (Aldrich, 99.9%, HPLC grade) using tandem HP Plgel columns and polystyrene standards. The initial and the deposited polymer were injected as solutions in dry acetone and the wavelength at 215 nm was used for the detection.

Solubility of the deposited films was determined by FTIR spectral measurements of the films (at 1737 cm^{-1}) before and after wash-up with acetone.

Thermogravimetric analysis of the solid deposit (sample weight 4–16 mg) were conducted by heating the sample up to 600 °C at the rate of 4 °C min^{-1}, using Cahn D-200 recording microbalances in a stream of argon. The composition of the outgoing gases was analyzed by an automatic sampling gas chromatograph Hewlett-Packard GC5890 (equipped with FID and TCD detectors) and a by quadrupole mass spectrometer (VG Gas Analysis Ltd, Middlewich, England). The original and the residual

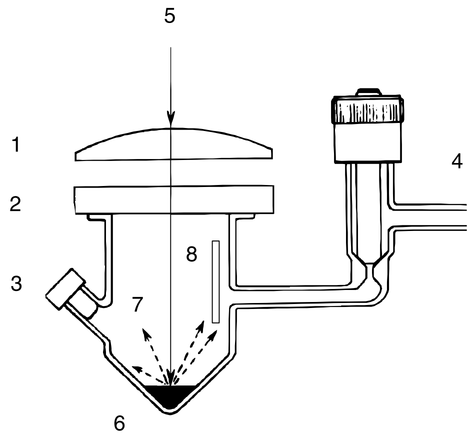


Fig. 1. Vessel for laser irradiation of PVAC. 1, NaCl lens; 2, NaCl window; 3, rubber septum; 4, P.T.F.E vacuum valve; 5, laser beam; 6, polymer target; 7, ablated currents; 8, substrate.

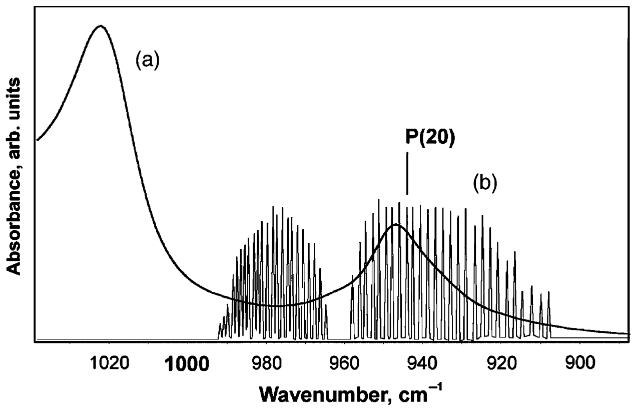


Fig. 2. Part of IR spectrum of PVAC (a) in the emission range of CO_2 laser (b).

samples were measured for their FTIR spectra by the KBr pellet technique.

PVAC (average M_w 167,000) was purchased from Aldrich.

3. Results and discussion

3.1. Irradiation features

PVAC shows absorption in the emission range of the CO_2 laser (Fig. 2) and can be resonantly ablated by tuning the TEA CO_2 laser radiation (the P(20) line of $00^01 \rightarrow 10^00$ transition, i.e. 944.19 cm^{-1}) into the band peaking at 945 cm^{-1} ($\delta_{C\text{–}H}$ out of plane vibration).

The pulsed IR laser irradiation of PVAC at low fluences (0.5–1.5 J cm^{-2}) results only in the formation of volatile products, while the irradiation at higher fluences (1.6–22.8 J cm^{-2}) leads to the formation of both volatile compounds and slightly yellow thin films deposited on the surface of the vessel and substrates. The irradiated PVAC target becomes glassy and remains transparent at 0.5–1.5 J cm^{-2} or yellowish at 1.6–22.8 J cm^{-2}. The distribution of volatile products differs depending on the irradiation conditions (Fig. 3) and its dependence on the used laser fluence is shown on Fig. 4.

The low fluence irradiations yield vinyl acetate as a major product along with acetone and small amounts of H_2 and hydrocarbons. Under these conditions, deposition of films on nearby surface was neither observed by the naked eye nor detected on KBr substrate by FTIR spectroscopy. Independent irradiations of PVAC films on KBr slices (instead of the PVAC tablets) revealed that the only change in the irradiated polymer is a continuous depletion of all IR bands, which leaves the total IR spectral pattern of the irradiated polymer virtually identical. The relative absorptivity of the acetate ν(C=O) (1737 cm^{-1}) and C–H stretch (2924 and 2972 cm^{-1}) bands—$A_{\nu(C=O)}/A_{\nu(C\text{–}H)}$—in the irradiated films remained constant (4.8) and this indicates that the formation of the gaseous products is accompanied by negligible (if any) structural changes in the irradiated (and depleting) PVAC.

The high fluence irradiations (2.5–22.8 J cm^{-2}) yield vinyl acetate, acetone, hydrocarbons (mostly methane, ethane and benzene) acetic acid, (main products) and CO and CO_2 together with hydrocarbons and H_2 (minor products). Under these conditions, slightly yellow films were deposited in ca. 20–45 wt% yield (consequently 80–55 wt% of volatile products). The yield of the solid films depends on the fluence and reaches its maximum at around 5 J cm^{-2} (Table 1).

3.2. Properties of deposited films

Morphology of the deposited films shows the same pattern—a rather smooth polymeric layer without large agglomerates—regardless of the low or high irradiation fluences used (Fig. 5).

The FTIR spectra of these films resemble that of the initial PVAC (Fig. 6). The only observed changes are four new bands. The week bands at 3020 and 968 cm^{-1} correspond [20] to the *trans*-CH=CH– configuration and indicate the absence of molecular elimination of acetic acid, the route well known [21] for the thermal decomposition of alkyl esters with β-hydrogen. The very weak bands at 1077 and 750 cm^{-1} being of less diagnostic value can be tentatively assigned to COC stretch and =C–H deformation. The relative absorptivity of the acetate ν(C=O) (1737 cm^{-1}) and C–H stretch (2810 and 3100 cm^{-1}) bands in the deposited

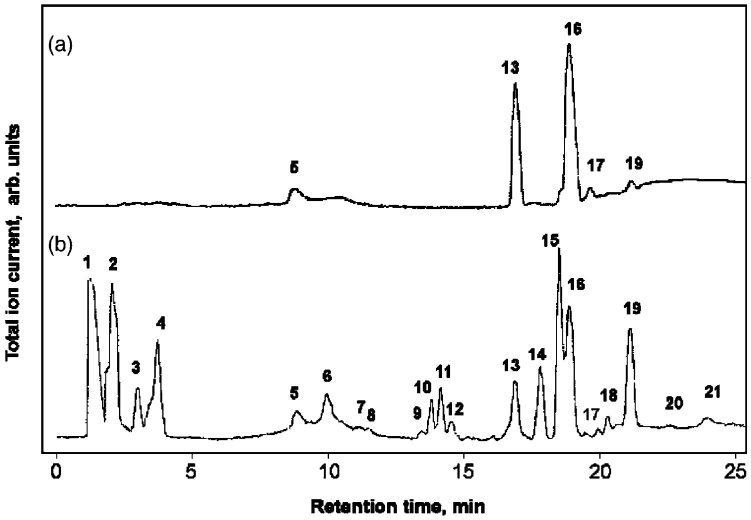


Fig. 3. Typical GC/MS traces of volatile products obtained upon irradiation of PVAC at fluence lower (a) or higher (b) than 2 J cm^{-2}. The given examples relate to the products distribution observed at 1.6 and 5.2 J cm^{-2}. Peak designation: 1, CH_4; 2, CO_2; 3, C_2H_4; 4, C_2H_6; 5, H_2O; 6, $CH_3CH{=}CH_2$; 7, $CH_3C{\equiv}CH$; 8, $CH_2{=}C{=}CH_2$; 9, CH_3CHO; 10, C_4H_8; 11, C_4H_6; 12, $CH_2{=}CH\text{–}C{\equiv}CH$; 13, $CH_3C(O)CH_3$; 14, cyclopentadiene; 15, CH_3CO_2H; 16, $CH_2{=}CHOC(O)CH_3$, 17, $C_2H_5OC(O)CH_3$; 18, C_6H_8; 19, C_6H_6; 20, C_6H_{10}; 21, $CH_3\text{–}C_6H_5$.

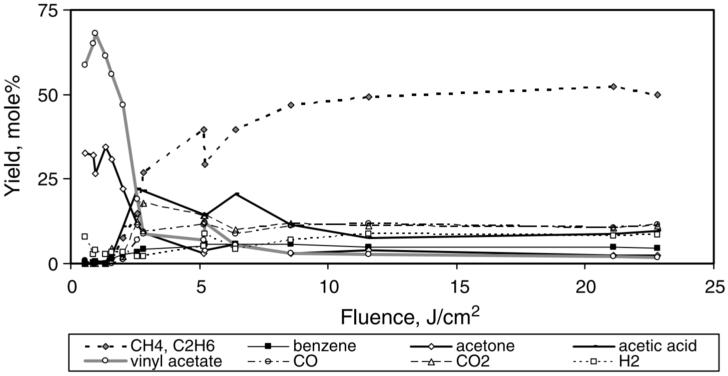


Fig. 4. Distribution of volatile products as dependent on laser fluence (After 1500 ($f<2$ J cm^{-2}), 900 (10 J cm^{-2} $<f>$ 2 J cm^{-2}) and 600 ($f>10$ J cm^{-2}) pulses).

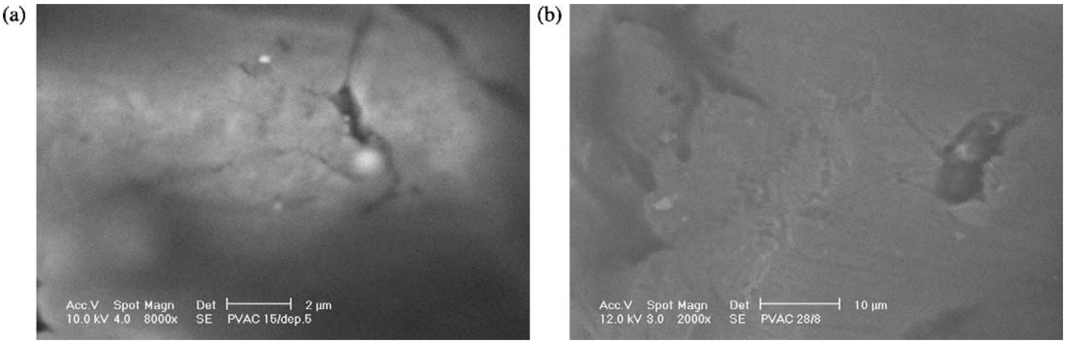


Fig. 5. SEM image of film deposited at 2.6 J cm^{-2} (a, bar = 2 µm) and 25 J cm^{-2} (a, bar = 10 µm).

films, expressed as the $A_{\nu(C=O)}/A_{\nu(C–H)}$ ratio, ranges between 1.9 and 2.4. The ratio decreases with increasing fluence and is roughly twice lower than the $A_{\nu(C=O)}/A_{\nu(C–H)}$ value for the non-irradiated PVAC (4.8). The unaltered position of the acetate band and the $A_{\nu(C=O)}/A_{\nu(C–H)}$ ratios are thus in keeping with a loss of ca. 50 percent of acetate groups and with the remaining 50% of acetate groups bonded in the same configuration.

The films are initially soluble in tetrahydrofuran and their elution profile (Fig. 7) determined by gel-permeation chromatography shows that their molecular distribution is different from that of the initial PVAC (Fig. 7(a), average M_w 167,000). The polymer fragmentation during the ablative process is indicated in all cases by a fraction at M_w of ca. 150,000 and lower molecular fractions (M_w even less than 10,000). The GPC profile corresponding to ablation at low fluences (2.6 J cm^{-2}, Fig. 7(d)) also includes a shoulder at lower retention times, which might be related to the formation of a fraction with molecular weight higher than that of the initial PVAC.

The unsaturated nature of the deposited films indicated by the FTIR spectra is confirmed by UV spectra of these films. They show a marked absorption at higher wavelengths, which gets slowly lost after prolonged staying of the films (Fig. 8). These features are in keeping with a

Table 1
Yield of the volatile and solid products

Fluence, (J cm^{-2})	Volatile products, (wt%)	Solid films, (wt%)
0.5–1.5	100	0
2.6	70	30
5.0	55	45
8.6	58	42
11.6	69	31
21	71	29
22.8	78	22

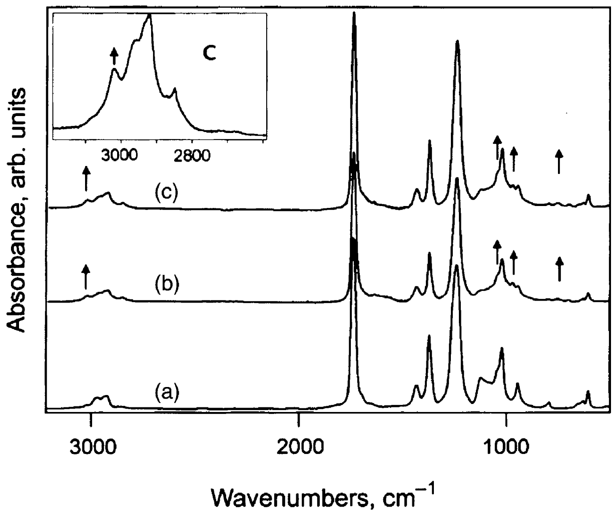


Fig. 6. FTIR spectrum of initial PVAC(a) and of films deposited at 2.5 J cm^{-2}, (b) and 21 J cm^{-2}, (c) the arrows show new bands (also in inset).

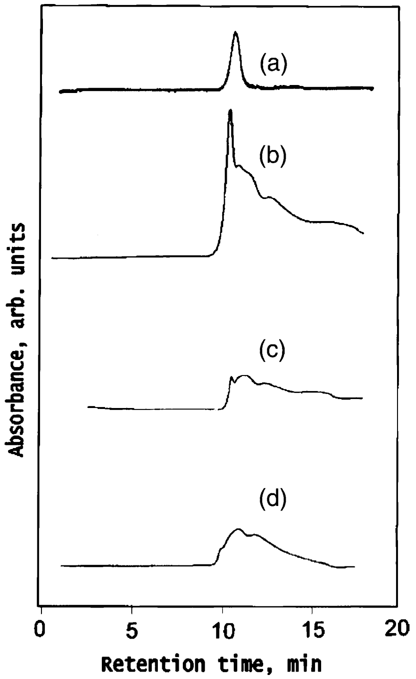


Fig. 7. Gel permeation chromatogram of the initial PVAC (a) and of the polymer deposited at 11 J cm^{-2}, (b) 22 J cm^{-2}, (c) and 2.6 J cm^{-2} (d).

conjugation of C=C bonds that disappear (Fig. 9) due to C=C bonds polymerization. This polymerization leads to crosslinking of the modified PVAC chains as confirmed by a decrease of film solubility with time (Fig. 10). It appears that the polymeric films obtained at low fluences are initially more crosslinked and that their solubility decreases much less than that of the films deposited at high fluences (Fig. 10).

The above data and interpretation gets strong support from the Raman spectra. The spectra of the initially deposited films show bands at 1132 and 1525 cm^{-1} that are, respectively, assignable [21,22] to the C–C and C=C stretch in polyenes. The empirical relationship [22] between the wavenumber of the C=C stretch and the number of the conjugated C=C bonds (n) allows us to estimate that $n = 11$.

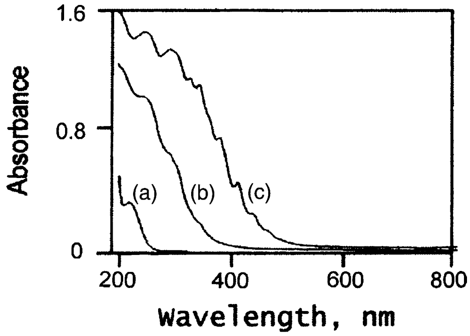


Fig. 8. Typical UV spectra of the initial PVAC (a), of the instantly measured deposited films (c) and of the deposited films measured after prolonged staying (b). The example given corresponds to the irradiation with fluence 2.6 J cm^{-2}.

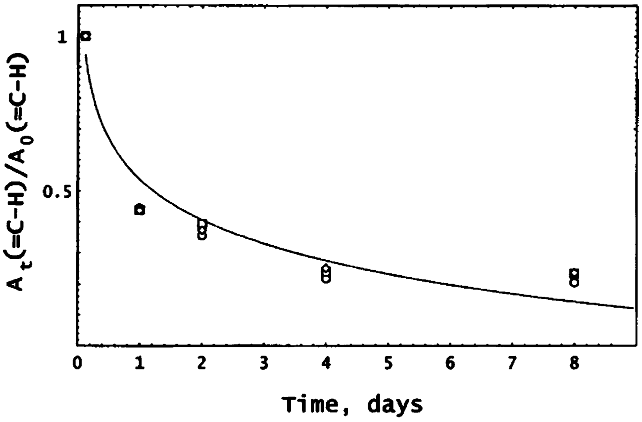


Fig. 9. Relative absorbance of ν(=C–H) band as dependent on time. The curve shown (corresponding to $f = 2.8$, 5.4 and 8.6 J cm^{-2}) was obtained for $f = 2.8$–22.8 J cm^{-2}.

After prolonged staying, the band at 1525 cm^{-1} gets lost and new bands—a dublet at 1607 and 1642 cm^{-1} (corresponding to C=C stretch of isolated C=C bonds) and a singlet at 2941 cm^{-1} (corresponding to H–C(sp^3) stretch)—appear. These changes clearly reveal that polyene system undergoes polymerization into an almost saturated hydrocarbon skeleton.

3.3. Chemistry involved

The observed gaseous and solid products reveal that the IR laser induced decomposition of PVAC differs remarkably from the conventional decomposition of PVAC, which is dominated by elimination of acetic acid and formation of non-polar carbonaceous residue [13–19]. The formation of vinyl acetate is the first example of the decomposition of poly(vinyls) into monomer and can be accounted for only by homolytic fissions of the near C–C bonds (1,2-splits). The formation of acetone, acetic acid, methane and ethane as well as that of CO, CO_2 and of H_2 is in keeping with

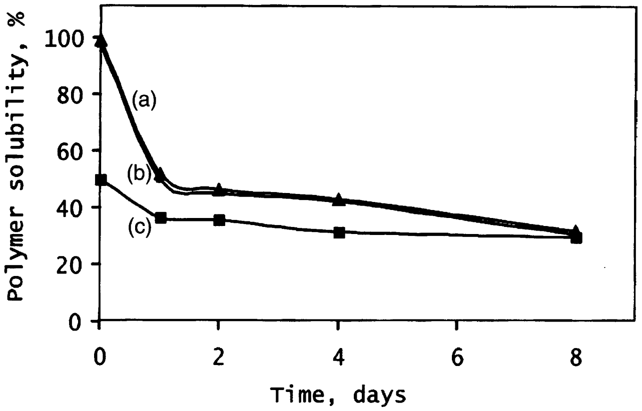


Fig. 10. Solubility of the polymer films as dependent on time. (a) and (b) common curve for $f = 8.6$–22.8 J cm^{-2}, (c) $f = 2.8$ J cm^{-2}.

cleavages in/of the acetate pending groups and of the C–H bonds. These homolytic steps result in the formation of an unsaturated polyalkene chain and yield $CH_3^{\cdot}$, $CH_3CO^{\cdot}$ $CH_3COO^{\cdot}$ and $H^{\cdot}$ transients that undergo the known decomposition, H-abstraction and recombination. The formation of benzene is compatible with aromatization reactions possibly involving formation of acetylene produced by decomposition of volatile vinyl acetate. The deposition of solid films can be only explained by cleavages of distant C–C bonds yielding macromolecular biradicals. The all plausible steps are given in Scheme 1.

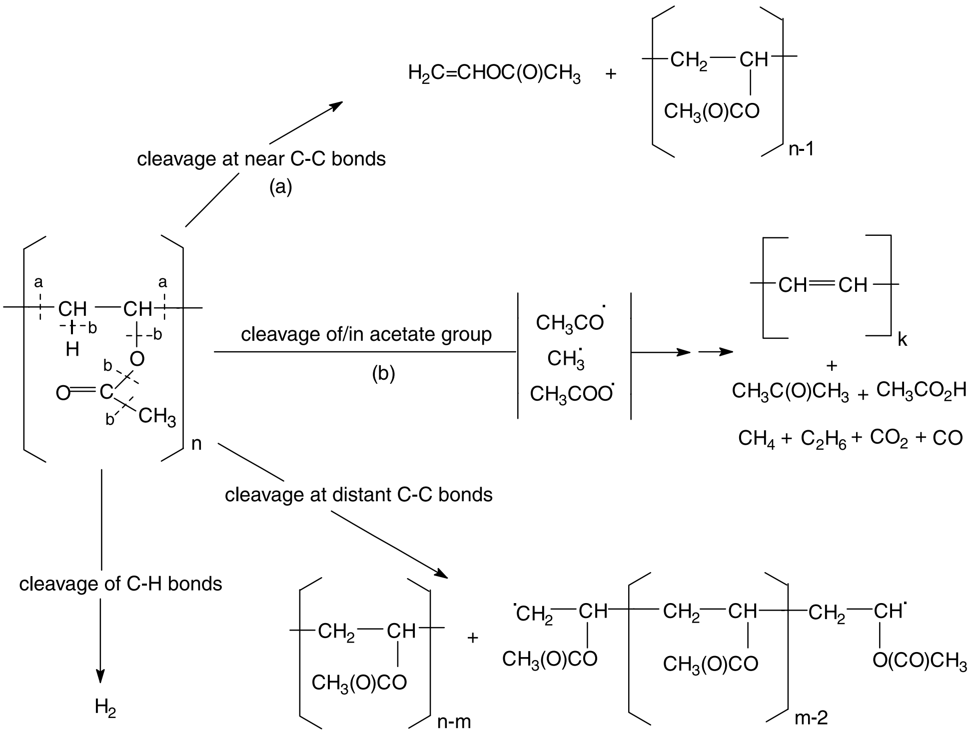
The IR laser-induced changes in the solid polymer are achieved through multiple-photon absorption leading to a high vibrational excitation density in the polymer. The absorption of a pulse leads to a temperature jump and high heating ($\sim 10^{-11}$ K s^{-1}) and cooling ($\sim 10^{3-6}$ K s^{-1}) rates [10–12]. The multitude of products at the higher radiation fluences and the rather selective decomposition at the lower radiation fluences are indicative of the occurrence of differently heated hot zones in the irradiated PVAC. The formation of vinyl acetate (a result of homolysis of the two near C–C bonds) appears a low energy pathway. The formation of H_2, hydrocarbons, acetone, and acetic acids (a result of the C–C and C–O splits in/of the pendant acetate group and of the C–H bond in the chain) and the deposition of the polymeric films are higher energy channels. These more feasible homolytic formation o vinyl acetate (and of acetone) over that of acetic acid at the low fluences reflect the differences in the bond dissociation energies (BDE) of the cleaved bonds (BDE: C–C ≤ C–O ≤ C–H) [22]. We assume that the deposition of the polar films (involving the same steps as the formation of vinyl acetate) requires higher energies, since the transfer of large biradicals needs sufficient amount of translational energy.

The great difference in the laser-induced and conventional pyrolytic routes of the PVAC decomposition is best explained by kinetic control of and the absence of heterogeneous effects in the laser-induced process, the features unavailable in the conventional decomposition. We note that the formation of acetic acid in the conventional decomposition was suggested [13,14] to occur as an unusual chain reaction accelerated by the proximal C=C bonds. The identification of the polyene moieties in the deposited films suggests that this acceleration is also important under the conditions of laser irradiation and proves that the removal of CH_3COO and H fragments does not occur from random centers of the chain but through stable allylic radicals (sequence *a*, *b* and/or *a*′, *b*′) (Scheme 2).

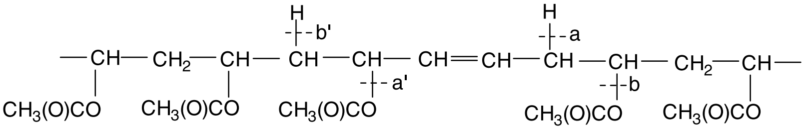
We note that the molecular elimination of acetic acid from gaseous alkyl acetates requires by ca. 80 kJ mol^{-1} less energy than the C–C bond homolysis [23,24] and suggest that the preference of the vinyl acetate formation (C–C homolysis) over feasible molecular elimination of acetic acid is related to conformational hindrance against the formation of the six-membered transition state in the solid state.

3.4. Thermal stability of the deposited films

Thermal behavior of the deposited films differs from that



Scheme 1.



Scheme 2.

of the initial PVAC. The comparison of the decomposition profiles reveals that the deposits lose less weight than the initial PVAC and that the deposits examined after prolonged staying lose less weight than those freshly prepared. Typical example is given in Fig. 11. This lower durability of the freshly prepared deposits is related to a lower extent of crosslinking. We note that the weight decrease is caused by evolution of methane, ethene, ethyne, 1-butene, acetic acid, carbon oxides (CO, CO_2) and also by sublimation. The residues do not possess any C=O group.

4. Conclusion

Three previously unobserved thermal paths of the IR laser-induced decomposition of PVAC were detected. These are the formation of vinyl acetate, the formation of acetone and the ablative deposition of polar polymeric films. The formation of vinyl acetate is the first example of thermal degradation of poly(vinyls) into monomer.

The specific features of the laser-induced decomposition of PVAC are attributed to kinetic control of the decomposition and absence of heterogeneous contributions of the decomposition.

The relative extent of these paths depends on the laser fluence. The low-fluence irradiation of PVAC yields vinyl acetate (main product) along with acetone and H_2. The high-fluence irradiations of PVAC result in the formation of a multitude of volatile compounds (vinyl acetate, acetone, acetic acid, CO, CO_2, methane, ethane and H_2) and leads to the ablative deposition of polymeric films containing conjugated C=C bonds and half of the initially present acetate groups.

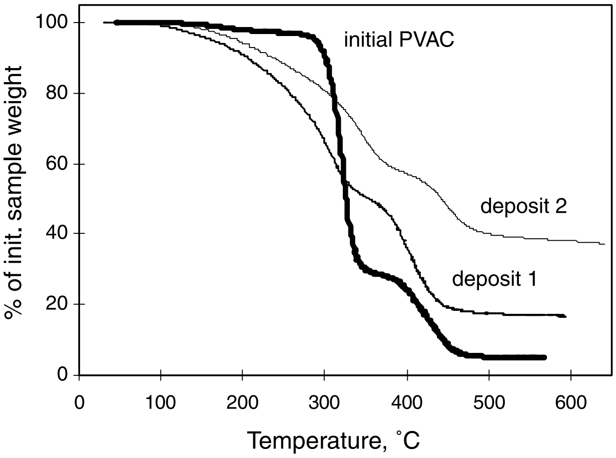


Fig. 11. Thermal decomposition of the initial PVAC, the freshly prepared deposit (deposit 1) and the deposit after prolonged staying (deposit 2) (The ablation conducted at 8.3 J cm^{-2}).

The deposited polymer films become intractable upon prolonged staying, which is explained by polymerization at the conjugated C=C bonds leading to crosslinking.

The ablative deposition of PVAC allowing fabrication of crosslinked (intractable) PVAC-based films suggests more use of the IR laser-induced treatment of the solid linear chain polymers with pending polar groups.

Acknowledgements

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