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Thermal degradation of poly(vinyl chloride-*co*-vinyl acetate) and its laser-derived analogue

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Abstract

Thermal behaviour of poly(vinyl chloride-*co*-vinyl acetate) and its laser-derived, partly crosslinked analogue having less pendant groups and some conjugated C═C bonds was examined by means of TGA technique and compared. The major degradation differences relate to the decomposition progress, evolution of volatile products and the yield of a carbonaceous residuum. The more feasible cleavage of acetate-and Cl-pendant groups and the higher yield of carbonaceous residuum observed with the laser-derived analogue are respectively explained by the accelerating effect of the conjugated C═C double bonds and crosslinking.

Keywords: Thermogravimetric analysis; Poly(vinyl chloride-*co*-vinyl acetate); Laser ablation; Crosslinked polymer

1. Introduction

Conventional thermal degradation of polymers is known as a process in which heat is slowly delivered from reactor walls and the decomposition paths are controlled thermodynamically and affected by wall effects. IR laser ablative degradation of polymers is a very different process in which decomposition steps are controlled kinetically rather than thermodynamically and in which ejected large macromolecules (and smaller fragments) are propelled in a stream of volatile decomposition products and recombine upon deposition to nearby surfaces. This ablative deposition allows formation of polymer materials very different from those produced by conventional heating (e.g. [1–6]).

The polymeric materials IR laser-ablatively deposited from poly(vinyl acetate) and poly(vinyl chloride) incorporate less pendant groups and initially contain conjugated C═C bonds. Slow polymerization at these conjugated C═C bonds leads to crosslinking and makes these materials become intractable upon staying for few days [5,6]. These crosslinked and less polar polymers represent novel polymeric systems, which can be of interest in various applications such as attachments of biological molecules and protective stabilization of reactive nanoparticles (e.g. [7–9]).

Thermal stability of these crosslinked and less polar poly(vinyl acetate)- and poly(vinyl chloride)-based materials was only briefly studied. We have revealed that the parental linear-chain poly(vinyls) with Cl- and acetate-pending groups and the laser-derived analogues degrade in different ways: while the degradation of the former occurs mostly in one stage, that of the latter takes place through several almost equally important stages and yields more carbonaceous residues [5,6].

An interesting model for a more detailed comparison of the thermal behaviour of the initial and the laser-derived polymer is poly(vinyl chloride-*co*-vinyl acetate) that contains two different pending groups. In this paper we prepared a laser-derived analogue of poly(vinyl chloride-*co*-vinyl acetate) and report on a comprehensive thermogravimetric analysis of this material and the parental poly(vinyl chloride-*co*-vinyl acetate). We reveal and explain differences in thermal behaviour of both materials by using thermogravimetric analysis, single ion monitoring

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and calculation of activation energy at different decomposition progress.

2. Experimental

2.1. Laser ablative deposition

The crosslinked laser-derived analogue of poly(vinyl chloride-*co*-vinyl acetate) was produced by a TEA CO_2 laser ablation of a bulk sample of a random ($[–CH_2CH(Cl)–]_x[–CH_2CH(O_2CCH_3)–]_y$, $x/y = 9$, $M_n \sim$ 44,000) copolymer purchased from Aldrich. The copolymer (0.3 g, compressed in a tablet) was irradiated with a pulsed TEA CO_2 laser (Plovdiv university) on the P(20) line of $0\,0^0\,1 \rightarrow 1\,0^0\,0$ transition (944.19 cm^{-1}) using incident fluence 13 $J\,cm^{-2}$ and repetition frequency 1 Hz. The tablet was positioned on a bottom of an evacuated (10^{-2} mbar) Pyrex vessel (42 ml in volume) equipped with a NaCl window and connected to a vacuum manifold. Its laser irradiation by 300 pulses yielded a solid product (ca. 13 mg) that was deposited on the vessel surface near the irradiated sample. The procedure was repeated and the deposited material scrubbed off from the vessel surface.

The vessel also accommodated a holder for quartz, KBr and copper substrates. Thin films deposited on these substrates were analysed by physical methods.

2.2. Thermogravimetry

Thermogravimetric analysis of the parental copolymer (weight 70 mg) and of the solid deposit (weight 15 mg) was conducted by heating the sample up to 700 °C at the rate of 4, 6 and 9 °C/min, using Cahn D-200 recording microbalances in a stream of argon (flow rate 100 ml/min). It was observed that the sample decomposition into volatile products and solid residuum was accompanied with partial evaporation/sublimation allowing deposition of a fraction of heated polymer on cold parts of the set-up. The composition of the outgoing gases was analyzed by an automatic sampling gas chromatograph Hewlett-Packard GC5890 (equipped with FID and TCD detectors) and by a quadrupole mass spectrometer (VG GAS ANALYSIS LTD Middlewich England) enabling multiple (16 channel) ion monitoring as time-dependent plot. Methane, ethane, ethene and ethyne were identified by gas-chromatography on the basis of knowledge of retention times of authentic samples. Other products were identified by mass spectrometry.

2.3. Physical methods for characterization of polymers

The properties of the deposited polymer were evaluated by FTIR (a Nicolet Impact spectrometer), Raman spectroscopy (a Renishaw Ramascope 1000 spectrometer) and UV/VIS (a Shimadzu UV/VIS 1601 spectrometer) spectroscopy and by electron microscopy.

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, Cl and O elements.

The XP spectra were measured using an ESCA 310 (Gammadata Scienta) electron spectrometer equipped with a high-power rotating anode, wide-angle quartz crystal monochromator, and a hemispherical electron analyzer operated in a fixed transmission mode. The measurements were performed using Al Kα radiation, an analyzer pass energy of 300 eV at pressure of residual gases 10^{-9} mbar and detection angle 90° (measured from the sample macroscopic surface). Quantification of the elements was accomplished by correcting photoelectron peak intensities for analyzer transmission function and for their photoionization cross-sections.

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.

Solubility of the deposited films was determined by FTIR spectral measurements of the films (at 2990–2810 cm^{-1}) before and after wash-up with dichloromethane.

2.4. Calculation of activation energy

The calculation of the activation energies of the thermal decompositions was conducted by using Friedman analysis [10], based on the Arrhenius equation. This method applies the logarithm of the conversion rate, d*x*/d*t* as a function of the reciprocal temperature at different degrees of conversion (Eq. (1)),

$$\ln\left(\frac{dx}{dt}\right) = \ln A - \frac{E(x)}{RT} + \ln(f(x)) \quad (1)$$

where *A* is the frequency factor, *R* the gas constant, *T* the thermodynamic (Kelvin) temperature, *E*(*x*) the activation energy, d*x*/d*t* the rate of reaction and the *f*(*x*) is the function dependent on the decomposition mechanism. In such complex processes as thermal decompositions, this function is not known a priori. For this reason, and because of limited amount of samples available, the simplified form of the analysis [11] was applied, where thermogravimetric decay curves were measured only at two values of the heating rate, namely, at 4 and 9 °C/min. The activation energy E(x) is then calculated according to Eq. (2),

$$E(x) = \frac{R[\ln(dx/dt)_2 - (dx/dt)_1]}{[(1/T_1) - (1/T_2)]} \quad (2)$$

where $(dx/dt)_1$ and $(dx/dt)_2$ are the conversion rates taken for the equal value of the conversion *x* from the both curves measured at the abovementioned different heating rates. In this simplified form of analysis, the *E*(*x*) is obtained with curves of only two values of the heating rate.

3. Results and discussion

3.1. Structure of poly(vinyl chloride-co-vinyl acetate) and laser-derived analogue

Morphology of the initial copolymer is smooth, whereas that of the deposited product is heterogeneous and consists of agglomerates and microfibers (Fig. 1).

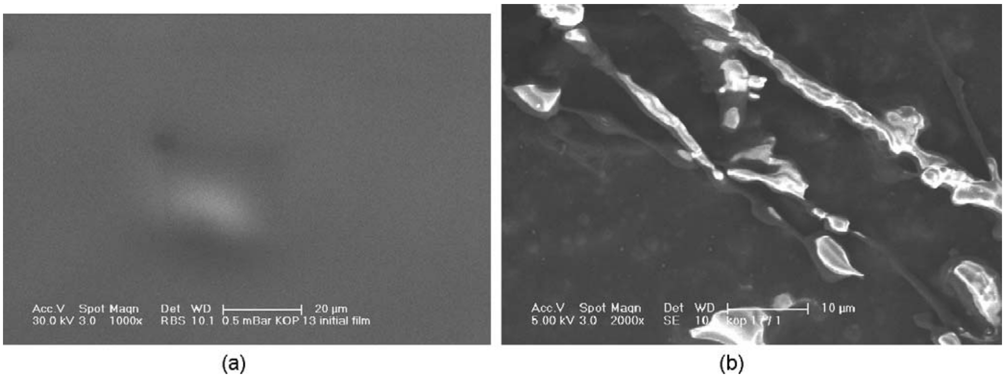


Fig. 1. SEM image of casted poly(vinyl chloride-*co*-vinyl acetate) (a, bar = 20 µm) and the laser-deposited product (b, bar = 10 µm).

Table 1
Composition of the initial copolymer and the laser-derived analogue

Sample	EDX analysis (at.%)			XPS analysis (at.%)		
	C	O	Cl	C	O	Cl
Initial copolymer[a]	77.9	4.8	17.0	66.7	10.0	23.3
Laser-derived analogue	89.2	2.2	8.6	83.3	5.8	10.8

[a] Theoretical values: 66.7%C, 6.0% O, 27.3% Cl.

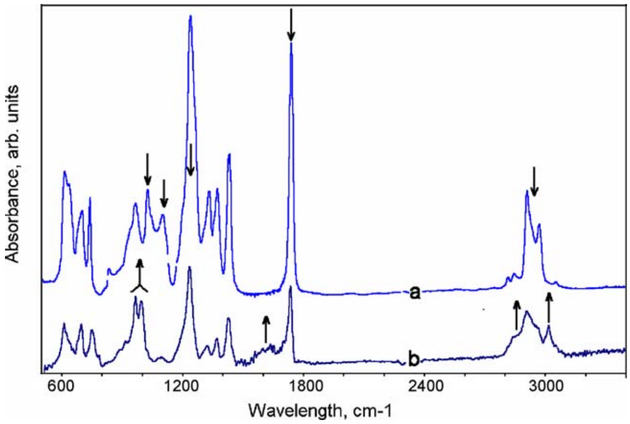


Fig. 2. FTIR spectrum of poly(vinyl chloride-*co*-vinyl acetate) (a) and laser-derived analogue (b). (Arrows show bands depleted in the initial copolymer and bands grown in the deposited product).

The EDX analysis of the bulk (0.5–1 µm) and the XPS analysis of the superficial layers of the initial copolymer and of the laser derived product (Table 1) show a pronounced decrease of the Cl and O elements in the latter and point out that the laser ablative deposition involves a substantial loss of both pending groups.

The depletion of Cl and acetate groups in the deposit estimated by both techniques is in fair agreement: the deposited material contains ca. 50% of the initially present Cl and and 50% of the initially present acetate groups. The XPS spectra of both samples assigned [10,11] in Table 2 show that the bonding environment of Cl and O atoms in both samples is virtually the same.

The FTIR spectral pattern (Fig. 2a) of the initial copolymer consists [12,13] of bands at 2970, 2910, 2843 and 2815 cm^{-1} (–C–H stretches), 1736 cm^{-1} (C=O stretch), 1424 and 1439 cm^{-1}, 1424 cm^{-1} (CH_3 rocking), 1372, 1330, 1237, 1100, and 1024 cm^{-1} (C–O stretch coupled with C–C vibrations), 966 cm^{-1} (skeletal vibrations) and 740, 700, 635 and 612 cm^{-1} (C–Cl stretches and skeletal vibrations). That of the laser-derived analogue (Fig. 2b) shows the bands at 3016 cm^{-1} (=C–H stretch), 2906 cm^{-1} (–C–H stretch), 1735 cm^{-1} (C=O stretch), ~1650 cm^{-1} (C=C stretch), 1426, 1366, 1320 and 1232 cm^{-1} (C–O stretch coupled with C–C vibrations), 994 and 967 cm^{-1} (the C–H out of plane deformation mode of *trans* –C(H)=C(H)–) and 750, 696 and 611 (the C–H out of plane deformation mode of *cis* –C(H)=C(H)–) together with C–Cl stretches. These spectra are in agreement with the above analyses: they show less C–Cl and –$OCOCH_3$ units in the laser-derived product. In addition, they reveal the presence of –C(H)=C<moieties. The unaltered position of the acetate band proves that the acetoxy group remains bonded in the same configuration. The relative absorptivity of the acetate ν(C=O) band and ν(C–H) band at 2910 cm^{-1}, ($A_{\nu(\mathrm{C=O})}/A_{\nu(\mathrm{C-H})}$), in the deposited films (1.6) and initial copolymer (2.8) is compatible with a greater (by ca. 43%) loss of acetoxy groups compared to that of the C–H bonds.

The Raman spectra of the deposited films show characteristic vibrations of C–C stretch at 1128 cm^{-1} (ν_1) and of the C=C stretch at 1518 cm^{-1} (ν_2) in conjugated polyenes [14,15] together with bands assignable [16] to higher harmonic

Table 2
XPS spectra: binding energies and half-widths of photoemission lines

Sample	C 1s			O 1s		Cl 2p$_{3/2}$
	$C_x H_y$	–C–O C–C(Cl)	–C–Cl	–C=O	–C–O	C–Cl
Initial copolymer	284.8 (1.4)	285.8 (1.4)	287.1 (1.4)	532.6 (1.6)	534.0 (1.6)	200.8 (1.3)
Laser-derived product	284.8 (2.0)	285.8 (2.0)	287.1 (2.0)	532.5 (2.2)	533.6 (2.2)	200.5 (1.5)

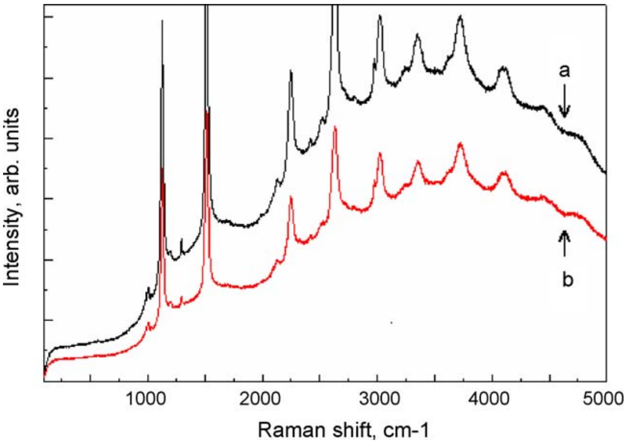


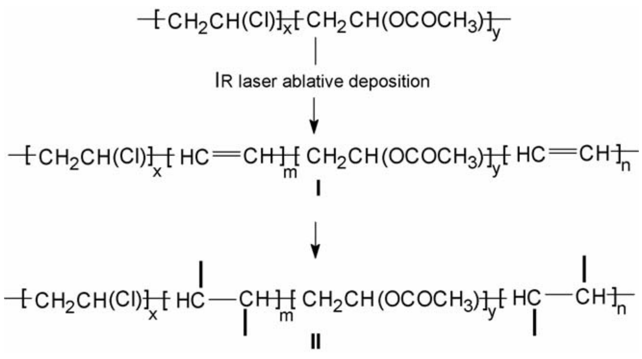
Fig. 3. Raman spectrum of the film deposited from poly(vinyl chloride-*co*-vinyl acetate) (a) and poly(vinyl chloride) (b, [6]).

and coupling modes at 2247 cm^{-1} ($2\nu_1$), 2630 cm^{-1} ($\nu_1 + \nu_2$), 3023 cm^{-1} ($2\nu_2$), 3350 cm^{-1} ($3\nu_1$), 3720 cm^{-1} ($2\nu_1 + \nu_2$), 4097 cm^{-1} ($\nu_1 + 2\nu_2$) and 4482 cm^{-1} ($3\nu_2$). (We illlustrate that these spectra are virtually identical to those of IR laser-ablatively deposited films from PVC [6]) (Fig. 3).

The above spectral analyses are in keeping with the formation of the laser-ablatively deposited product taking place via simultaneous elimination of HCl and acetic acid and a cleavage of the C–C bonds of the copolymer chain [5,6]. (Both compounds were identified as major volatile products). Some polymer crosslinking at the C=C bonds upon 2 days storage of the deposit (~30%) was proved by the identified decrease of the polymer solubility in chloroform. We thus infer that the structure of this laser-derived analogue is in keeping with a blend of contributions I and II (Scheme 1).

3.2. *Thermogravimetry*

The conventional decomposition of poly(vinyl chloride-*co*-vinyl acetate) is known [17–21] to occur through cleavage of both pendant groups and yields acetic acid and HCl as major volatile products. Further known facts are that (i) the side-group elimination is enhanced at similar content of the acetoxy- and Cl-groups, which was assigned [17,18] to an interunit facilitation of the initial acid loss, and that (ii) the proportion of acetic acid and hydrogen chloride corresponds to that in the copolymer [21] and remains constant during degradation [18].



Scheme 1.

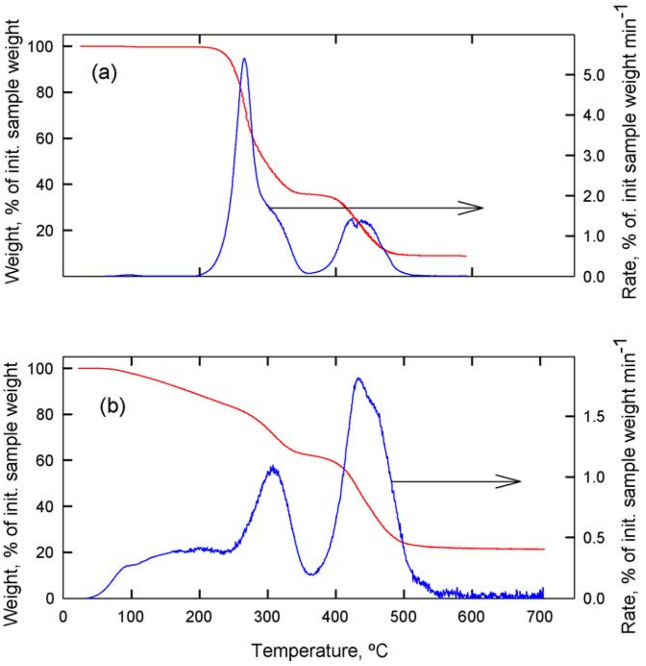


Fig. 4. Thermal decomposition of poly(vinyl chloride-*co*-vinyl acetate) (a) and laser-derived analogue (b).

Thermograms of poly(vinyl chloride-*co*-vinyl acetate) and of the laser-derived crosslinked product (Fig. 4) reveal that the decomposition progress of both samples is considerably different. The thermal decomposition of poly(vinyl chloride-*co*-vinyl acetate) begins at ca. 200 °C, it is a three-stage process with maxima at 270, 315 and 440 °C and the decomposition stages at 200–350 °C are more significant than that at ~400–500 °C. The thermal decomposition of the laser-derived analogue starts at a considerably lower temperature (below 100 °C), it is a three-stage process with maxima at 180, 310 and 440 °C and the two decomposition stages between 100 and 350 °C and that at 400–500 °C are roughly of equal importance.

The residual materials of both decompositions are black and do not have diagnostic IR spectral bands, proving that they are carbonaceous materials. Higher yield of the residuum in the thermal decomposition of the laser-derived analogue (20 wt.%) compared to that for the thermal decomposition of the parental copolymer (10 wt.%) is in line with crosslinked structure of the former.

Several main products, evolved from both samples in the course of heating, were detected through their characteristic mass spectral fragmentation. The diagnostic single ion traces at m/z 16, 28, 36, 44 and 60 due in the given order to CH_4, CO, HCl and CO_2 and CH_3CO_2H (Fig. 5) along with the GC traces of hydrocarbons (Fig. 6) allow characterize the individual decomposition stages with both samples in more detail.

For the initial copolymer, the first and second decomposition stage (200–350 °C) yield CO, HCl, CO_2 and CH_3CO_2H and the third stage (400–500 °C) yields CH_4, CO_2, CH_3CO_2H

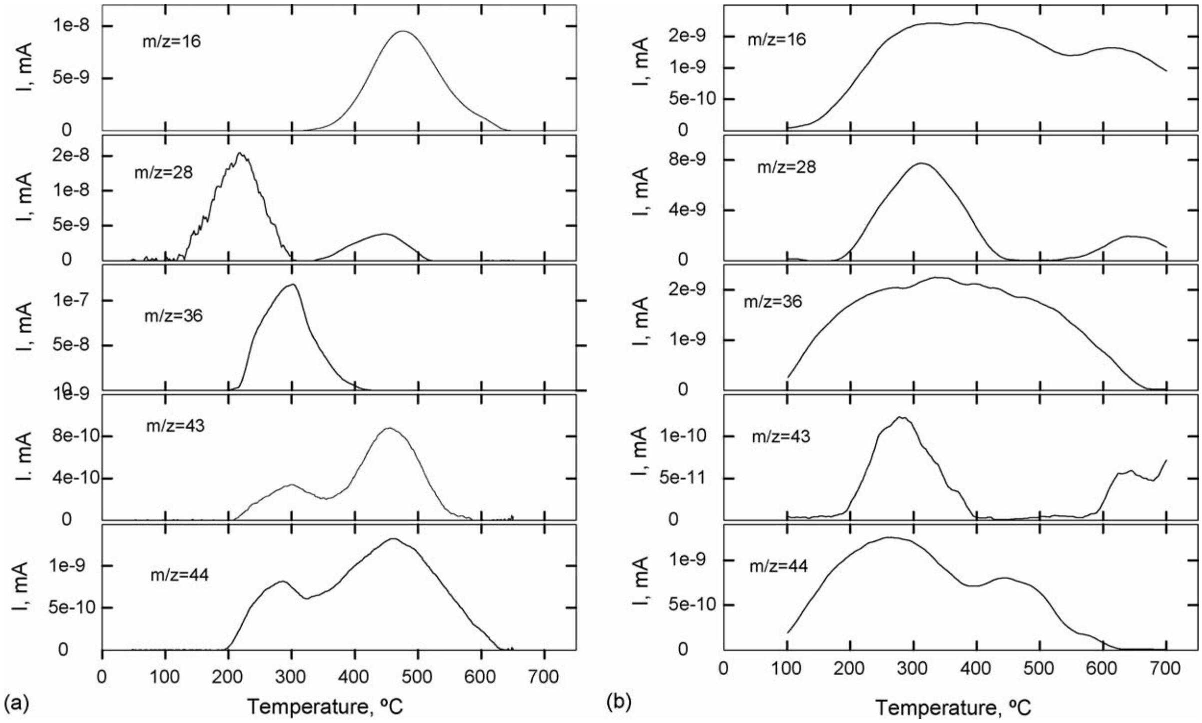


Fig. 5. Single ion traces of the main products from TGA of poly(vinyl chloride-*co*-vinyl acetate) (a) and laser-derived analogue (b).

and C_2H_2 (*m*/*z* 26, not shown). The hydrocarbons CH_4, C_2H_6 and C_2H_4 are evolved at temperatures between 400 and 580 °C, and CH_3CO_2H and CO_2 are also evolved at above 500 °C. The evolutions at above 500 °C are due to the decomposition of a sublimed portion of the heated sample.

For the laser-derived analogue, the early decomposition starting from below 100 °C is due to evolution of CO_2 and HCl, the second decomposition stage (250–350 °C) yields CH_4, C_2H_2 (*m*/*z* 26, not shown), CO, HCl, CO_2, CH_3CO_2H, and the third stage gives CH_4, HCl and CO_2. In addition, CH_4, C_2H_6 and C_2H_4 are evolved at 400–650 °C and CH_3CO_2H, HCl and CO are evolved above 500 °C. The compounds evolved above 500 °C are due to the decomposition of a sublimed material.

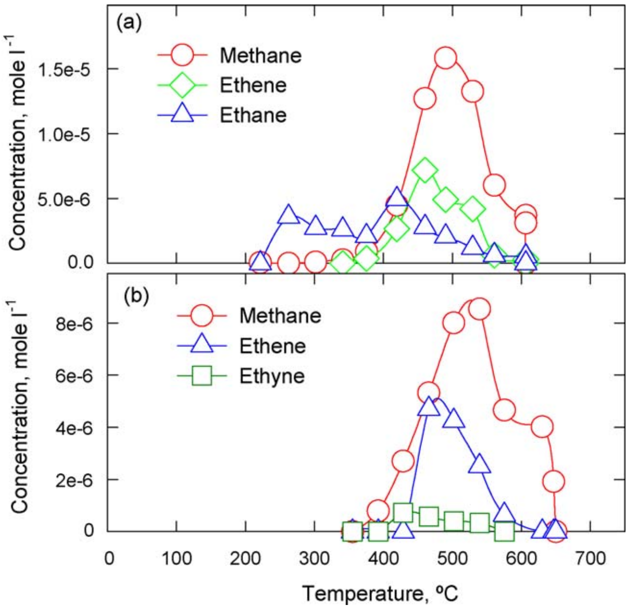


Fig. 6. Evolution of C_{1-2} hydrocarbons from poly(vinyl chloride-*co*-vinyl acetate) (a) and laser-derived analogue (b).

Total thermal degradation of the of the initially thermolyzed samples and their sublimed fractions is then described as follows: the parental copolymer eliminates HCl between 200 and 400 °C and removes the acetate group as acetic acid and CO and CO_2 between ~200 and 550 °C, whereas the laser-derived analogue eliminates HCl between 100 and 650 °C, acetic acid between 200 and 450 °C, CO between 200 and 750 °C and CO_2 between ~100 and 620 °C.

These features reveal that both samples dispose of their pendant groups with different feasibility and that the evolution of Cl is completed with the initial polymer at much lower temperature than with the crosslinked analogue. Different shapes of the curves at *m*/*z* 16, 28, 43 and 44 also suggest that both carbon oxides and methane may be produced not only from the intermediately produced CH_3CO_2H via the equally energy-demanding $CH_4 + CO_2$ and $CH_2CO + CO$ channels [22]), but also by different, yet unspecified paths.

The activation energies of the early decomposition stages (those peaking at 180–315 °C) are considerably lower (Table 3) than the known bond dissociation energies (BDE) of the cleaved C–Cl (~340 kJ/mole) and C–O (~380 kJ/mole) bonds [23] and are in keeping with the radical-chain routes [24,25] and acceleration of radical chains by proximal C=C bonds [26,27]. The observed more facile elimination of the both pendant groups from the laser-derived analogue is then in line with the presence of the conjugated bonds in this sample. (We emphasize that the

Table 3
Activation energy for the main decomposition stages

Parental copolymer		Laser-derived analogue	
°C	E_a (kJ)	°C	E_a (kJ)
270	202	180	198
315	272	310	187
440	421	440	59

calculation of activation energies, applied due to the very limited amount of sample, reflects only two values of temperature and may provide less reliable data.)

The activation energies of the late stages (those peaking at 440 °C) for both samples very differ (Table 3); that for the parental copolymer is close to the BDE values of the C–O bond and is related to the homolysis of the (residual) acetoxy groups bonded in saturated, C (sp^3)-structured moieties. The extremely low activation energy of the late decomposition stage with the laser-derived analogue is hardly explainable in another way than by the cleavage of both acetoxy-and Cl-substituents in sublimed portions of the samples accelerated by a conjugated system of the C=C bonds.

4. Conclusion

Thermal decomposition of poly(vinyl chloride-*co*-vinyl acetate) and of the polymeric product obtained by IR laser ablative deposition of poly(vinyl chloride-*co*-vinyl acetate) show different features that are ascribed to differences in their structure.

While the poly(vinyl chloride-*co*-vinyl acetate) is a linear-chain polymer with pendant polar groups, the laser-derived product possesses about half pendant groups, conjugated C=C bonds and partly crosslinked moieties.

Both thermal degradations are three-stage processes, but that of poly(vinyl chloride-*co*-vinyl acetate) is most significant at 270 °C and that of the laser-derived polymer is of similar importance at 180, 310 and 440 °C.

Elimination of both pendant groups is more feasible with the laser-derived product and is ascribed to accelerating effect of the neighboring C=C bonds.

The single ion traces of the main products together with calculated activation energy of the degradation at different temperatures are in line with radical-chain mechanism of the cleavage of the pendant groups at temperatures below 400 °C.

The observed elimination of pendant groups above 500 °C is attributed to degradation of sublimed fractions of the polymers.

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