# Kinetics of thermal degradation of poly(vinyl chloride)

## Thermogravimetry and spectroscopy

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**Abstract** Extensively studied thermal degradation of polyvinyl chloride (PVC) occurs with formation of free hydrogen chloride and conjugated double bonds absorbing light in visible region. Thermogravimetric monitoring of PVC blends degradation kinetics by the loss of HCl is often complicated by evaporation and degradation of plasticizers and additives. Spectroscopic PVC degradation kinetics monitoring by absorbance of forming conjugated polyenes is specific and should not be affected by plasticizers loss. The kinetics of isothermal degradation monitored by thermal gravimetric analysis in real time was compared with batch data obtained by UV/Visible absorption spectroscopy. Effects of plasticizer on kinetics of polyene formation were examined. Thermal degradation of PVC films plasticized with di-(2-ethylhexyl) phthalate (DEHP) and 1,2,4-benzenedicarboxylic acid, tri-(3-ethylhexyl) ester (TOTM) was monitored by conjugated double bonds light absorption at 350 nm at 160, 180, and 200 °C. Plasticizer-free PVC powder degradation kinetics and that of plasticized films were also obtained thermogravimetrically at temperatures ranging from 160 to 220 °C. Plasticizer-free PVC powder degradation and spectroscopically monitored degradation of plasticized PVC films occurred with the same apparent activation energy of $\approx 150$ kJ mol$^{-1}$. No difference in degradation kinetics of films plasticized with DEHP and TOTM was detected.

**Keywords** Poly(vinyl chloride) · Thermal degradation · Kinetics · Spectroscopy · Thermal analysis · Activation energy

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## Introduction

Poly(vinyl chloride) (PVC) is used in construction, medical devices, electrical insulation, rain gear, upholstery, and other products. The degradation mechanism of PVC and other halogenated polymers exposed to high temperatures or ionizing radiation has been extensively studied [1–5]. Halogenated vinyl polymers are relatively stable mechanically, however, darken easily. In consumer and medical products pleasant appearance that would not change over the time of use is as important as mechanical stability. It was found that formation of conjugated polyenes that absorb visible light was responsible for the change of appearance of halogenated polyolefines (Scheme 1) [1–20]. High extinction coefficients of conjugated polyenes ensured that darkening of the degrading polymer occurred long before any mechanical properties changes have been detected. Conjugated polyenes are formed by dehydrochlorination (Scheme 1). Naturally, PVC degradation can be monitored by the amount of hydrochloric acid released [20]. Monitoring PVC degradation by mass loss using thermogravimetric analysis became a classic example of polymer degradation studies [15, 21].

Pure PVC is a rigid fragile solid at room temperature. At chain length as low as 1000 (number average) the PVC glass transition reaches 80 °C [4, 22, 23] and on the average, non-plasticized PVC exhibits $T_g \approx 87$ °C [4]. Thus, PVC is heavily plasticized, to reduce its glass transition below room temperature for use in packaging, flexible tubing, films, upholstery and clothing. In monitoring degradation of these products using thermogravimetric analysis (TG) it is difficult to differentiate the mass loss due to plasticizer evaporation and the mass loss due to loss of hydrochloric acid.

Conjugated polyenes forming upon dehydrochlorination absorb light strongly above 320 nm [6, 9, 10, 13, 14, 21, 22,

**Scheme 1** Chain reactions of poly(vinyl chloride) degradation leading to formation of conjugated polyenes
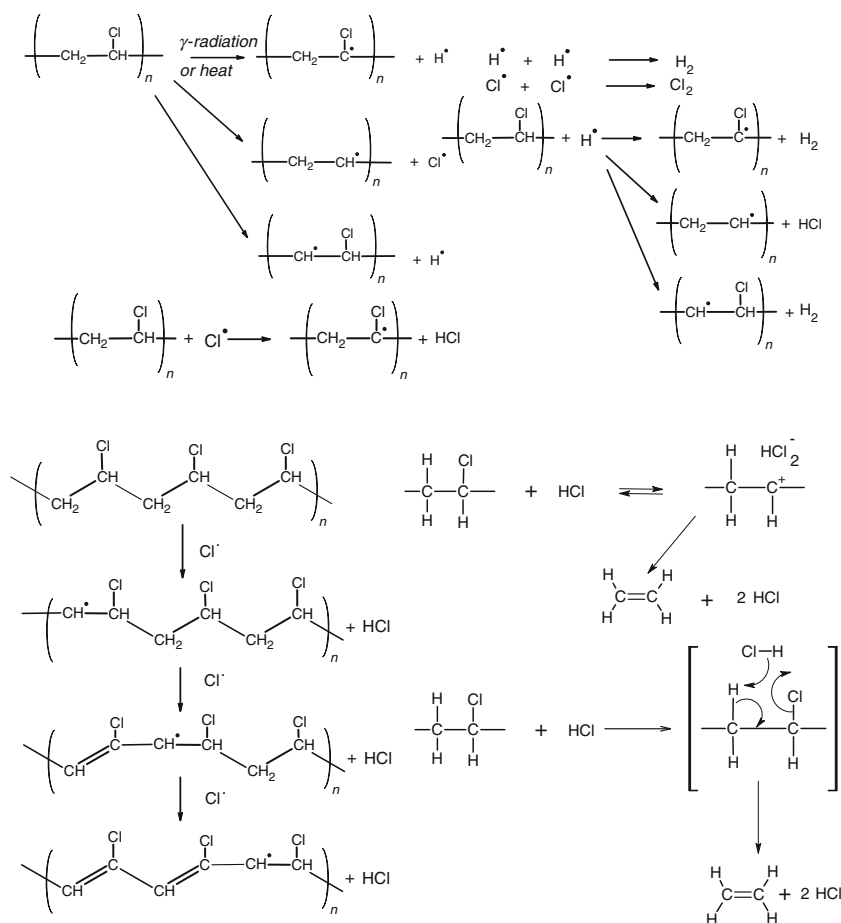


24], therefore, kinetics of PVC degradation can be monitored specifically using UV–visible spectroscopy. Some loss of conjugation may occur through Diels–Alder reaction converting two conjugated double bonds to one nonconjugated [25], and by the radicals reacting with double bonds [4, 22]. An extent of conjugation loss, to the best of our knowledge, was not quantified. Thus, it is not a priori clear whether degradation kinetics monitored by conjugated polyenes absorption will be close enough to the degradation kinetics obtained by hydrochloric acid release monitoring.

Wypych suggested in his book that it would be advantageous to monitor simultaneously HCl emission and color change caused by PVC degradation [22, p. 122]. In the current work we compared these processes.

Below we discussed the comparison of thermogravimetric and spectrophotometric monitoring of neat and plasticized PVC degradation kinetics.

## Experimental

A conventional poly(vinyl chloride) (suspension polymerized vinyl chloride, Oxyvinyl from Occidental Petrolium

Corp.) was used either in pure (powdered form) or as a di-(2-ethylhexyl)phthalate (DEHP) (Sigma-Aldrich), or tris (2-ethylhexyl) trimellitate (TOTM) (Eastman) plasticizer and PVC blend extruded as a 0.3 mm thick film at 170 °C. Small constant amount of epoxydized oils was present in DEHP and TOTM-plasticized samples. Thermogravimetric kinetic analysis was conducted using TGA Q500 (TA Instruments Co.) in isothermal mode. Temperature was initially increased at 20 °C min$^{-1}$ to achieve the desired isothermal conditions. The length of the isothermal degradation monitoring depended on the temperature and varied from 2 to 10 h. The TG of PVC degradation was conducted in air flow of 90 mL min$^{-1}$. The initial rate of thermal degradation was measured as a slope of the short-time linear portion of the kinetic curves of % mass loss dependence on heating time or light absorbance at 350 nm dependence on heating time.

Plasticized PVC film samples (15.0 × 45.0 × 0.3 mm) were heated at pre-set temperature (160–200 °C) in the oven for a pre-set time and degradation kinetics was reconstructed point by point by the absorbance at 350 nm. The films were wrapped in aluminum foil to reduce shape change during heating. Conjugated polyenes absorb at the

wavelengths ≥320 nm with absorption shifting to visible region with increase of the number of conjugated bonds, thus heat induced degradation kinetics was monitored by absorbance at 350 nm [6, 9, 10, 13, 14, 21, 22, 24]. Absorption spectra were measured in transmission mode using Cary 4000 (Varian Co.) spectrophotometer.

PSI Plot (PolySoftware International Co.) software was used to obtain linear fit and local slopes used as degradation rates in the intervals: from 20 to 50 min for all TG curves of powder PVC degradation, from 10 to 15 min and 30 to 45 min for plasticized PVC TG, and for spectrophotometric curves from 0 to 40 min for 200 °C, from 0 to 65 min for 180 °C, and from 0 to 220 min for 160 °C degradation.

## Results and discussion

Thermal discoloration of plasticized poly(vinyl chloride) films is noticeable in the visible portion of the spectrum and in the absence of a spectrophotometer color change can be used for semi-qualitative examination of the PVC blends stability (Fig. 1) [8–10, 26, 27]. Analysis of the samples yielded very clear temperature and time of thermal exposure dependent series of absorption spectra (Fig. 2).

The absorbance maximum of conjugated polyenes shifts to longer wavelengths with increase in number of conjugated bonds [8–10, 13, 26, 28]. All double bonds are formed due to hydrochloric acid elimination and, therefore, cumulative absorption is a good indication of the amount of



Fig. 1 Change in appearance of DEHP-plasticized PVC films upon exposure to 200 °C. Exposure time (minutes) indicated above each sample

HCl eliminated from PVC chain. PVC degradation kinetics monitoring at 350 nm was selected since low and high conjugation polyenes absorb at this wavelength (Fig. 3).

TG analysis of plasticized films and powders yielded a series of distinct kinetic curves (Figs. 4, 5).

Extraction of kinetic parameters from the thermogravimetric data is not trivial. Thus, even validity of the TG use in degradation monitoring was questioned [29–32] and a search for an acceptable approach is on-going [33–37]. The interpretation of TG degradation kinetics data may be complicated among other factors by diffusion of products out of the polymer matrix [37] as was reviewed elsewhere [28, 38].

There is a general consensus that in the analysis of reaction kinetics data obtained by thermal methods, the rate of reactions of the type "solid → solid + gas" may be represented by a kinetic equation separating temperature and concentration effects as was suggested by Kissinger in 1957 [33, 34, 39]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{1}$$

where $0 \leq \alpha \leq 1$ is a reacted fraction of the solid at after time $t$; $T$ is the absolute temperature; $k(T)$ is the rate constant, $f(\alpha)$ is a function that depends on a reaction mechanism, usually expressed through Gulbert and Waage's Law of Mass Action [40]; $E_a$ is an apparent activation energy; $R$ is the gas constant; $A$ is preexponential factor. The equation is adequate for representation of degradation kinetics of solids although the physical meaning of preexponential factor and activation energy is not defined through molecular properties and their temperature dependence is neglected. Eyring's transition state theory and its descendant, Rice–Ramsperger–Kassel–Marcus (RRKM) theory of chemical reactivity, that provided a molecular interpretation of the kinetic parameters and yielded temperature dependent activation energy and preexponential (frequency) factors [40–47], to the best of our knowledge, were not applied to analysis of the reactions of polymer thermal degradation. Equation 1 remained the most used equation in thermal analysis, although the numerous suggested modifications of Eq. 1 were tested [33, 48–52].

To obtain apparent activation energy of the *solid* → *solid* + *gas* reaction, temperature dependent portion of Eq. 1 is deduced from the experimental data. If concentration dependence of the reaction rate, $f(\alpha)$, is not known, the temperature dependence of the reaction rate is measured at the same degree of conversion, $\alpha$ [33–37, 39, 48–53]. In some cases, however, the overall reaction order and, consequently the form of $f(\alpha)$, are known. Thus, the sublimation of solids is zero-order reaction with $f(\alpha) \equiv 1$ and linear $\alpha$ dependence on the reaction time. Then, to
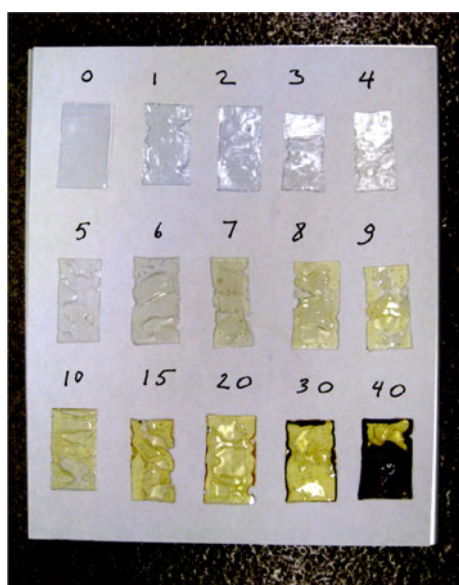
Fig. 2 Dependence of DEHP-plasticized PVC films absorption spectra on temperature and time of heating. Time increase change direction is indicated by an *arrow*.
a 200 °C, time/min: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 300, 40;
b 180 °C, time/min: 0, 5, 10, 15, 20, 30, 40, 60, 70, 80, 150;
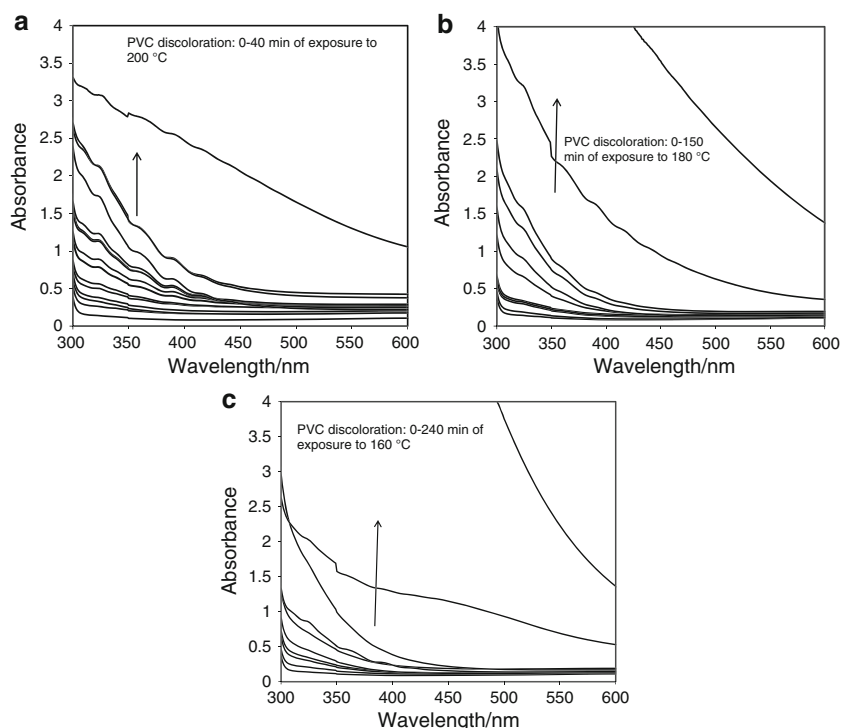c 160 °C, time/min: 0, 30, 60, 95, 105, 150, 195, 240, 300, 1080

Fig. 3 Kinetics of plasticized PVC degradation, spectrophotometric detection at 350 nm (scale expanded in the lower graphs to show early events kinetics): a DEHP-plasticized PVC films; b superposition of data for DEHP and TOTM-plasticized PVC films; c expanded DEHP-plasticized PVC films data; d expanded TOTM-plasticized PVC films data
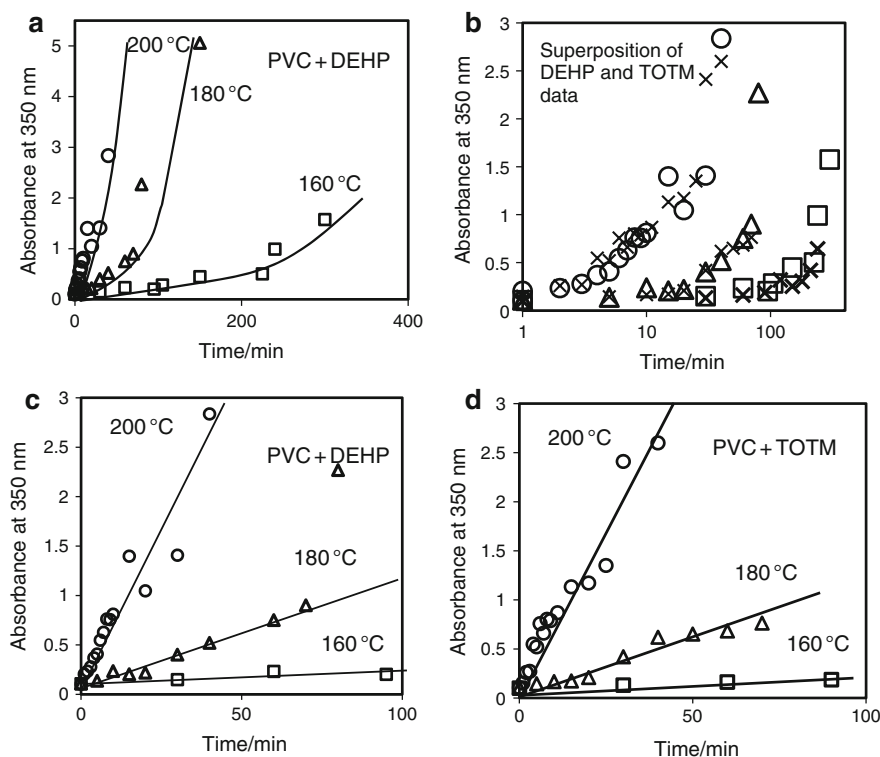
obtain $E_a$ the rate of reaction could be measured as a function of temperature at any $\alpha$ due to constant slope of kinetic curves [54 and ref. therein]. It was suggested to represent a concentration dependence of the polymer degradation rate, $f(\alpha)$, as a linear combination of zero-order reaction of monomer scission from polymer chain, or small molecules scission from a side chain or cyclization, first-order reaction of intramolecular scission of the main chain, and second-order reactions of crosslinking, radicals recombination, intermolecular chain disproportionation, autocatalysis, and so on [55]. Thus, for low $\alpha$ values $f(\alpha) \approx 1$ may be used.
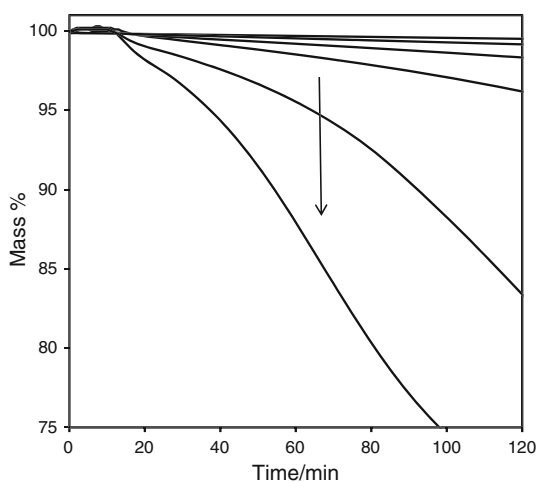
**Fig. 4** TGA-detected kinetics of PVC powder degradation at temperatures 443, 453, 463, 473, 483, and 493 K increasing in the direction of the *arrow*
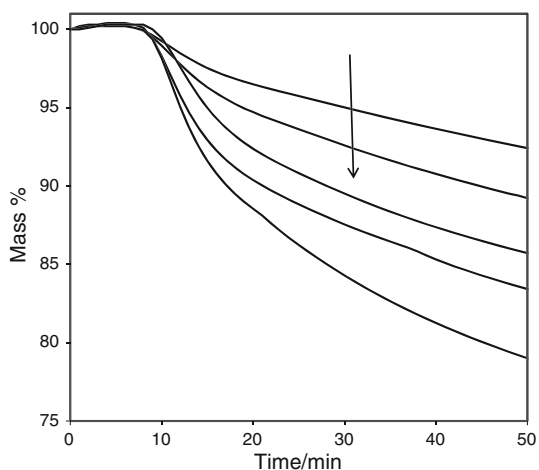


**Fig. 5** TGA-detected kinetics of DEHP-plasticized PVC film degradation at temperatures 433, 443, 453, 463, and 473 K increasing in the direction of the *arrow*

PVC degrades with formation of volatile hydrogen chloride (Scheme 1). Stromberg et al. [56] determined that $\geq 95\%$ of the volatile products of PVC degradation are hydrogen chloride, while the remaining products are non-volatile polyenes (Scheme 1). At temperatures ranging from 508 to 533 K they determined that overall isothermal PVC degradation kinetics was of the 1.5th order [56]. The data obtained by Oh et al. [57] confirmed that for $\alpha \leq 0.6$ the overall reaction of non-isothermal PVC degradation was a complex combination of reactions of zero-, first-, and second-order depended on heating rate. In a series of conclusive experiments Polozkov et al. [20] demonstrated that in the temperature interval from 438 to 463 K the isothermal PVC degradation was nearly perfect example of zero-order reaction.

Fisch and Bacaloglu also treated early kinetics of polyenes formation in PVC degradation as a zero-order process [58, 59]. Garcia et al. [60] and Woo et al. [46, 61] also considered PVC degradation at early times as zero-order. An approximation of PVC weight loss process as zero-order reaction appears to be a well accepted approach [62]. In general, Dickens and Flynn recommend using initial ($\alpha \leq 0.05$) TG detected degradation rates for deduction of activation energies of polymers degradation, since at low conversion the reaction rates are independent on the form of $f(\alpha)$, and reactions are $\approx$ zero-order [53]. Formal kinetics considerations confirm that the loss of HCl in thermal PVC degradation may be treated as a zero-order process (at early stages before HCl catalysis becomes dominant), since it is a monomolecular process with number of Cl and H on the vinyl groups remaining virtually constant relative to the number of formed HCl molecules [40, 53]. The degradation kinetics of polymers should be evaluated at early degradation stages for another reason: at advanced stages of degradation the polymer chains are crosslinked or cleaved, products of degradation are formed in different matrix and by a different mechanism [20, 28, 38, 63].

The thermal degradation rates in the present work ($T$ in the range of 433–493 K vs. Poloskov's 438–463 K) were obtained from the slope of the initial linear, zero-order regions of the kinetic curves based on the results of Polozkov et al. [20] and other researchers [46, 53, 58–62] (Figs. 3, 4, 5, 6).

Reaction rate of zero-order reactions is constant and is equal to reaction rate constant expressed by Arrhenius–Eyring type equation (Eq. 2) [40, 47, 64]. The slopes of the logarithm of the obtained degradation rates were plotted as
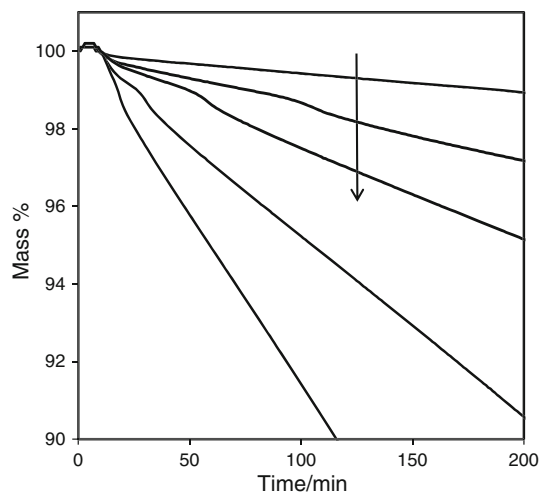


**Fig. 6** TGA-detected kinetics of TOTM-plasticized PVC film degradation at temperatures 433, 443, 453, 463, and 473 K increasing in the direction of the *arrow*

a function of the inverse absolute temperature at which the degradation reaction was conducted (Fig. 7).

Apparent activation energies of the observed overall reaction were obtained using slope of the best fitting lines obtained by a linear regression fit of the experimental data (Fig. 7) (Table 1)

$$k = A \exp\left(-\frac{E_a}{RT}\right) \qquad (2)$$

where $k/s^{-1}$ is an apparent rate constant, $A/s^{-1}$ is a pre-exponential or frequency factor, $E_a/J\ mol^{-1}$ is an apparent activation energy, $R/J\ mol^{-1} = 8.31$ is universal gas constant, $T/K^{-1}$ is absolute temperature. The apparent activation energies were deduced by a linear regression of the data using Eq. 1 (Table 1).

Degradation activation energies deduced from spectroscopic analysis of DEHP and TOTM-plasticized PVC and non-plasticized PVC powder by TG were remarkably close, $\approx 147$ and $153$ kJ mol$^{-1}$, respectively. The values of activation energy found by us were also close to those reported in the literature [19, 20, 53]. Especially good agreement was found with the data of Polozkov et al. [20], who monitored kinetics of HCl release and obtained $E_a = 146$ kJ mol$^{-1}$. On the other hand, activation energies of plasticizer loss $\approx 59$ and $\approx 114.0$ kJ mol$^{-1}$ were in a

good agreement with those observed specifically for solvent diffusion in polymers [65–70]. This indicated that TG detected mass loss during degradation of plasticized PVC can be attributed mostly to the loss of plasticizer in the early degradation stages, since the loss of HCl was <2% at comparable time of non-plasticized PVC degradation. Since activation energy detected by conjugated polyenes absorbance and by TG coincided, it appeared that the loss of plasticizer did not interfere with the conjugated polyenes formation. Apparent activation energy values for PVC degradation previously reported in the literature varied from 126 to 190.5 kJ mol$^{-1}$, and were dependent on the method of data processing [19, 20, 53].

Apparent activation energy of complex chemical reaction corresponds to the rate limiting, slowest reaction. Apparent activation energies obtained in the current work are of the same magnitude as that of zero-order dehydrochlorination reaction leading to double bond formation [22, p. 100] (Scheme 1).

Spectroscopically detected kinetics of formation of conjugated polyenes upon thermal degradation of PVC plasticized with DEHP and PVC plasticized with TOTM were virtually identical. Although DEHP and TOTM have substantially different viscosities at room temperature (58 mPa s for DEHP, vs. 194 mPa s for TOTM), above 373 K the viscosity of both plasticizers decrease below 10 mPa s [71, 72]. Therefore, if higher temperature (>150 °C) plasticized PVC degradation is controlled by hydrochloric acid diffusion, TOTM and DEHP plasticization effects would be similar. It is, however, remarkable that activation energy of degradation of plasticized and powdered neat PVC yielded virtually identical apparent activation energies, indicating that the rate controlling step in the chain process of PVC thermal degradation is not HCl diffusion [22, 73]. This conclusion contradicts to some extent that of Brown and co-workers who found a strong PVC film thickness dependence of apparent rate of PVC thermal degradation, indicating rate control by HCl diffusion [22, 73]. We believe that results observed by Brown can be explained by increased residence time of HCl in the thicker PVC sample resulting in higher HCl concentration in and consequent rate increase of PVC degradation through the secondary reaction with HCl (Scheme 1)
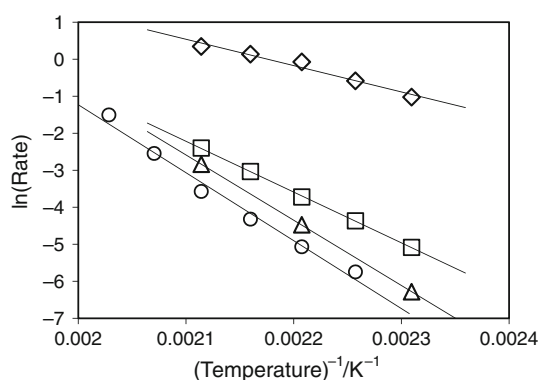


**Fig. 7** Arrhenius–Eyring dependence of poly(vinyl chloride) thermal degradation rate on inverse temperature: *diamond*—DEHP-plasticized film initial rates, TGA data; *square*—TOTM-plasticized film initial rates, TGA data; *triangle*—plasticized film (DEHP and TOTM) rate of light absorption change at 350 nm; *circle*—powder without plasticizer, TGA data, initial rates

**Table 1** Comparison of activation energies of poly(vinyl chloride) degradation

| PVC degradation detection method | Activation energy/kJ mol$^{-1}$ |
|---|---|
| Initial mass loss in thermal degradation of PVC films plasticized with DEHP (by TG) | 59.1 |
| Initial mass loss in thermal degradation of PVC films plasticized with TOTM (by TG) | 114.0 |
| Initial mass loss in degradation of PVC powder—no plasticizer (by TG) | 152.6 |
| Light absorption at 350 nm by PVC films plasticized with DEHP | 146.6 |
| Light absorption at 350 nm by PVC films plasticized with TOTM | 146.6 |

trapped in the PVC solid. This explanation is confirmed by the fact that control of degradation kinetics by the diffusion of degradation products out of polymer matrix was not found even in the case of thermal decay of highly cross-linked urethane acrylates [28, 38, 70]. The values of activation energy in the present work and in the case of urethane acrylate degradation [28, 38, 70] were higher than those characteristic for small molecules diffusion in polymer matrix. In turn, the independence of conjugated polyenes formation kinetics on products diffusion out of polymer matrix supported the previously published conclusions regarding rate limiting stage in kinetics of thermal degradation of polymers [28, 38, 70].

Independence of spectroscopically monitored PVC degradation kinetics on the presence and type of plasticizer confirmed that spectrophotometric detection is an acceptable and specific method of monitoring actual loss of HCl during degradation of PVC, while TG results may be biased by the presence of plasticizer or impurities in polymer matrix. Wypych stated that "many problems of degradation and stabilization would have been solved if there was a proper analytical methodology capable of measuring length distribution of growing polyenes, HCl emission, and color change in the same experiment" [22, p. 122]. We believe that the presented results indicated that spectroscopic monitoring of kinetics of polyene formation is equivalent to that of monitoring HCl emission kinetics. Considering different spectral regions corresponding to various conjugation levels, the same spectra can be used for analysis of kinetics of polyene chain formation [9, 10, 74].

In some processes leading to PVC degradation spectroscopy may be the only plausible method of evaluation the extent of degradation in real time, for example in monitoring degradation during PVC extrusion or molding into products or in environmental aging of PVC [75]. For non-transparent samples produced at different conditions, color or reflectance spectra may be used to derive an extent of thermal degradation during high temperature manufacturing. Thus we recorded the reflection spectra of DEHP-plasticized PVC films extruded at different temperature (Fig. 8). Clearly, extrusion at higher temperature leads to films with lower reflectance. This can be used to quantify and predict PVC degradation extent during storage or manufacturing.

We selected 350 nm to monitor degradation kinetics, although local absorption maxima shift to longer wavelength with an increase in the number of conjugated double bonds on the hydrocarbon chain [9, 10, 22, 74–76]. Salovey et al. [9, 10] and Broun [74, 75] correlated the number of conjugated double bonds forming during PVC degradation with the wavelength of the absorption maxima following a work by Sondheimer et al. [77]. Thus, 300 nm absorption maximum corresponds to polyene sequence with $\approx 4$
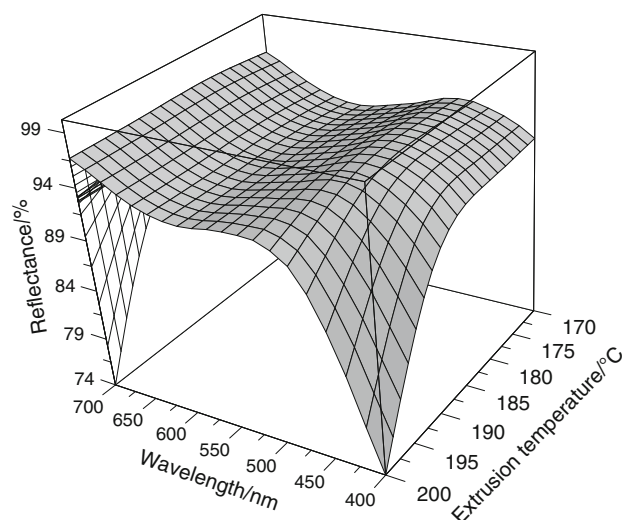


**Fig. 8** Change in reflectance spectra of plasticized PVC film with film extrusion temperature: just extruded films

double bonds, 350 nm to that of $\approx 7$ double bonds, 500 nm to that with 13 double bonds, etc. [74, 75, 77]. Rogestedt and Hjertberg proposed a PVC dehydrochlorination reaction mechanism leading to conjugation increase [76]. The absorption bands of different polyenes overlap, however, some information on the polyene sequence length can be obtained, since spectra of polyene with 5 double bonds do not overlap with that with 10 [77–80].

Our data on the change of the absorption spectra during PVC degradation indicated that there was a noticeable difference in kinetics of formation of shorter polyene sequences (3–7 double bonds at 300–350 nm) and longer ones (10 at 450 nm and higher) (Fig. 9). Kinetics of absorbance change at 450, 500, 650, and 800 nm (10, 13, and higher double bond sequences) were almost identical (Fig. 9). The shorter polyene sequences (3–7) started forming immediately with almost the same kinetics, while there was a substantial delay, induction period, or steady-state region in the kinetic curves of longer sequences (>10) formation at all of the studied temperatures (Fig. 9).

Rogestedt and Hjertberg also reported predominance of shorter polyene sequences in PVC degradation. They suggested that the formation of longer chains occurred with HCl autocatalysis [76] (Scheme 1), however, did not clarify why extent of formation of the sequences with >7 double bonds was lower. Braun also observed lower concentration of longer polyene sequences in the degraded PVC, however, did not evaluate the kinetics of the degradation [74]. In a series of publications Iván and co-workers reported that in PVC degradation in solutions short polyene sequences (≤4) were forming without "induction period" from the beginning of thermal degradation, while the longer sequences were forming with the delay and reversibly, leading to the maximum in the dependence of

**Fig. 9** Dependence of DEHP-plasticized PVC films light absorbance at different wavelengths on the time of films exposure to **a** 433 K, **b** 453 K or **c** 473 K
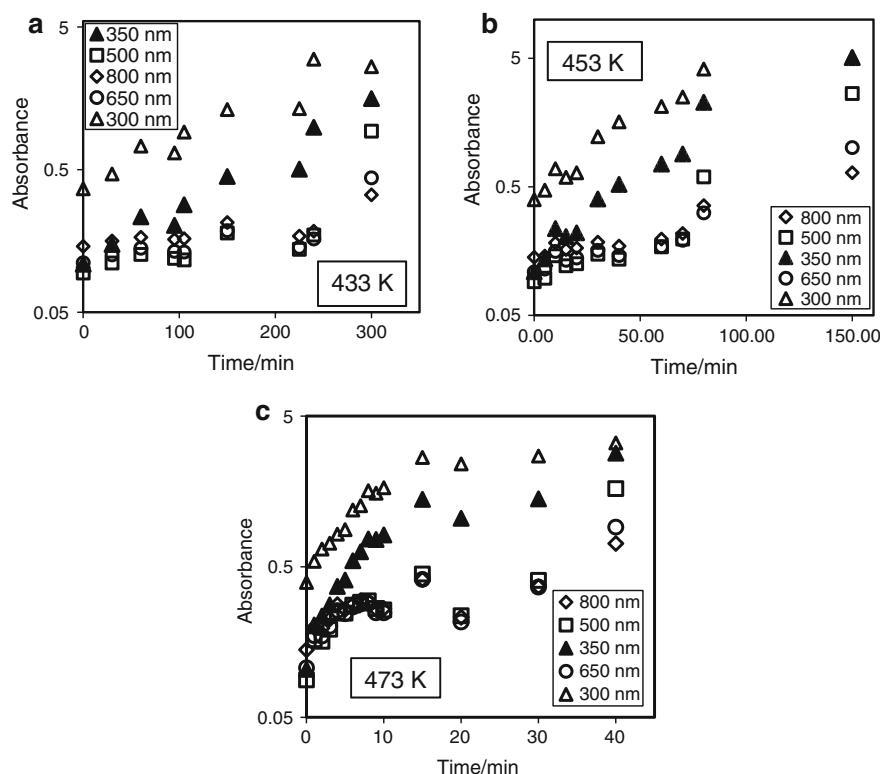
the polyene sequence length on the degradation time [78, 79]. These data are in agreement with conclusion of Tüdös et al. [80] that at the increased concentration of long-sequence (>4) polyenes cyclization by Diels–Alder reaction leads to spectral shift to short-sequence polyenes.

Iván and co-workers determined that most metal stearate stabilizers did not alter initiation rate of HCl loss. Similarly, we did not detect any plasticizer effect on polyene formation kinetics. These findings in conjunction with high apparent activation energy, O (150 kJ mol$^{-1}$), indicated control of conjugated polyene formation kinetics by slow dehydrochlorination at allylic chlorines, rather than by bimolecular HCl catalytic events that would occur with HCl diffusion rate. The detailed experimental and theoretical analysis of the formation kinetics of polyene chains during PVC thermal degradation at 160–230 °C was conducted by Tüdös et al. [80], who stated that longer polyene sequences may undergo intramolecular and intermolecular cyclization with formation of cyclohexadiene, thus shortening linear polyene sequence (Scheme 2). Indeed, with increasing chain length the number of rotational degrees of freedom and probability of cyclization increase [3, 38 and ref. therein]. Therefore, even after the longer polyene sequences are formed, their consequent cyclization would lead to light absorption in the region where the shorter ones absorb as shown by Tüdös et al. [80] and Yanborisov et al. [81]. The total absorbance at 350 nm should be proportional to the total number of HCl molecules eliminated

from the PVC chain. Therefore, detection of degradation kinetics at 350 nm was justified.

The quantum mechanical modeling of HCl elimination from polyenes of different length did not shed light on the different kinetics of longer polyene sequence formation, predicting dehydrochlorination activation energies and rates practically independent of the sequence length for polyenes with >2 double bonds [82]. The formal kinetics approach may explain the differences observed in this work (Fig. 9). Consecutive reactions of forming and decaying high length polyene sequences should exhibit a steady-state region, where the concentration is quasi-constant [40]. The experimentally observed kinetics of formation and disappearance of polyenes with the number of double bonds >10
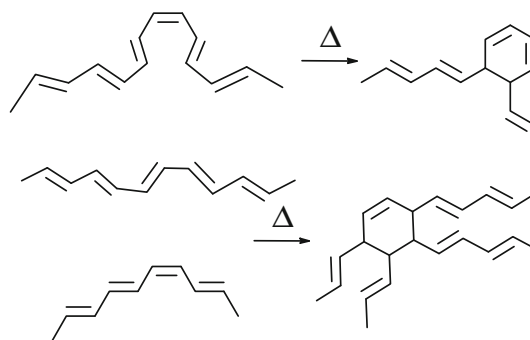


**Scheme 2** Intramolecular and intermolecular cyclization of polyenes [78]

yielded a steady-state region of constant concentration (Schemes 1, 2) (Fig. 9).

More detailed analysis of the polyenes formation kinetics lies outside the scope of this work, dedicated to comparison of spectroscopic and gravimetric detection of poly(vinyl chloride) thermal degradation kinetics.

## Conclusions

Kinetics of thermal degradation of pure powdered poly(vinyl chloride) and plasticized poly(vinyl chloride) films were monitored using thermogravimetric analysis and UV/Visible absorption spectroscopy.

Apparent activation energies of PVC degradation were deduced from the kinetic curves using Arrhenius–Eyring approach [40, 47, 64]. It was found that conjugated polyenes formation in plasticized film degradation monitored by absorbance at 350 nm occurred with similar activation energy as thermally induced mass loss of plasticizer-free PVC powder 147 and 153 kJ mol$^{-1}$, respectively. These results were in excellent agreement with the data based on monitoring hydrochloric acid release kinetics (146 kJ mol$^{-1}$) [20].

Independence of apparent activation energy of PVC degradation on plasticization and physical shape of the PVC sample (powder vs. thick film) indicated that kinetics of PVC degradation is not controlled by volatile products diffusion out of polymer matrix or bimolecular catalysis by HCl. This result was in agreement with the previously published data [28, 38, 53, 57, 70].

Spectroscopic measurements yielded degradation kinetics independent on poly(vinyl chloride) plasticization (neat PVC vs. DEHP-plasticized, vs. TOTM-plasticized) thus indicating that spectroscopy may be a preferred method for monitoring PVC degradation.

The PVC degradation kinetics monitored at wavelength corresponding to polyene sequences with double bonds number $\geq 10$ was different than kinetics of shorter sequences formation (Fig. 9). Clearly defined steady-state region in longer polyene formation kinetic curves may serve as an indirect confirmation of cyclization of longer polyenes during advanced stages of PVC degradation [78–81].

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