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The thermal degradation of poly(vinyl acetate) measured by thermal analysis–Fourier transform infrared spectroscopy

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Abstract

The elimination process which occurs during the thermal degradation of poly(vinyl acetate) has been studied using thermal analysis–Fourier transform infrared spectroscopy. It was found that elimination of acetate groups initially began slowly, but increased as degradation proceeded due to an additional process. The increase in rate was found to depend on the concentration of unsaturated groups in the polymer chain. The activation energy for the initial step was found to be 190 kJ mol^{-1}, while that for the additional process was 130 kJ mol^{-1}. The additional process of elimination was considered to be due to a four-membered transition state, activated by double bonds adjacent to the acetate unit. © 2002 Published by Elsevier Science Ltd.

Keywords: Poly(vinyl acetate); Elimination; Spectroscopy

1. Introduction

Early studies of the thermal degradation of poly(vinyl acetate) (PVAc) [1] indicated that quantitative yields of acetic acid were produced by an elimination reaction, leading to a polyene residue. It was implied that the double bonds produced by the elimination of acetic acid could activate the elimination of adjacent acetate groups, leading to an increase in the rate of degradation. However, Ballistreri et al. [2] found that PVAc degraded in two stages. In the first stage, 240–310 °C, the thermal degradation of PVAc lead to production of a high proportion of acetic acid. Some aromatic hydrocarbons were also detected. In the second stage (320–370 °C), aromatic hydrocarbons were produced almost exclusively. It was concluded that the first stage of degradation was almost exclusively elimination of side-groups, and the second stage was due to the thermal degradation of the polyenic structure produced by the elimination reaction.

In this study, the technique of thermal analysis–Fourier transform infrared (TA–FTIR) spectroscopy [3] has been used qualitatively and quantitatively to study the thermal degradation of PVAc. Thermogravimetry (TG) was used to measure mass loss with time during degradation.

2. Experimental

PVAc was supplied by BDH, and had a molecular weight of 89,000. Ethyl acetate was used as a solvent.

TA–FTIR spectroscopy was carried out on thin films of PVAc deposited from solution onto KBr disks. The apparatus for TA–FTIR spectroscopy was a combination of a Nicolet 760 IR-Magna infrared spectrometer, and a Linkam 600 microscope hot-stage unit placed in the beam of the spectrometer. The hot-stage unit was fitted with BaF_2 windows suitable for infrared spectroscopy in the range 4000–740 cm^{-1}, and purged with argon (300 cm^3 min^{-1}) prior to each experiment. The same flow of argon was maintained throughout the experiment. The temperature of the hot-stage was calibrated with the melting points of KOH and NaOH. Isothermal temperatures between 240 and 290 °C were chosen, using a heating rate of 90 °C min^{-1}. This allowed the desired degradation temperature to be reached before significant degradation had occurred.

TG was carried out using a Stanton Redcroft STA 1000 thermogravimetric balance with a type R thermocouple placed close to a platinum crucible. Isothermal TG was carried out at temperatures between 260 and 300 °C, and

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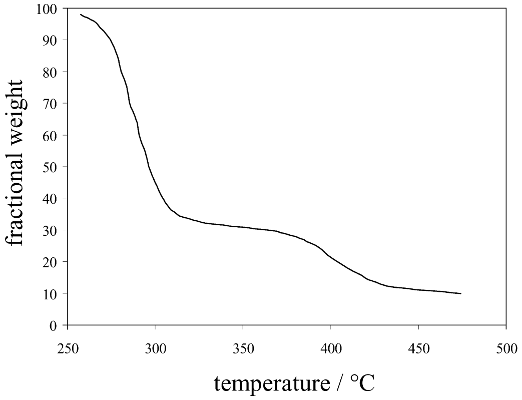

Fig. 1. Non-isothermal TG of PVAc at 0.5 °C min^{-1}.

non-isothermal TG was carried out at 0.5 °C min^{-1}. A sample size of 30 mg and a 40 cm^3 min^{-1} flow of argon gas was used.

3. Results and discussion

3.1. Thermogravimetric analysis of weight loss

PVAc was degraded thermally at a heating rate of 0.5 °C min^{-1}. The loss in weight with temperature is shown in Fig. 1 from which it can be seen that there was more than one degradation process. The majority of mass loss took place below 330 °C, but was followed by a further smaller mass loss between 360 and 450 °C. A non-volatile residue of approximately 10 wt% was formed. The results were consistent with the literature report of acetate group elimination [1,2] of polymer side-chains at the lower temperatures followed by a breakdown of the polymer backbone at the higher temperature, reported in the literature [2].

Isothermal TG of PVAc was carried out at temperatures between 260 and 300 °C. First order rate plots were non-linear and it was found that the rate of weight loss increased as the thermal degradation proceeded (see Fig. 2). The TG furnace at the end of each experiment smelled strongly of acetic acid, and it was considered possible that acetic acid could catalyse the degradation process, probably by ester hydrolysis. Double bonds in the polymer backbone, produced by elimination, may also activate the elimination and be responsible for the increased rate [1]. The thermal degradation of PVAc led to the formation of non-volatile residue (approximately 35 wt%). Complete elimination of all acetate side-groups would lead to a char of 30.2 wt%, and this was close enough to the yield observed to conclude that elimination of acetic acid was the predominant degradation process. For this reason, the weight loss data was corrected such that only 70% of the initial polymer weight was considered in calculating the first order rate constants (Fig. 2). The initial rate constants were plotted in an Arrhenius form (Fig. 3), and it was found that the initial slow degradation process had an activation energy of 190 ± 10 kJ mol^{-1}, and a pre-exponential factor of (1.39 ± 0.14) × 10^{14} s^{-1}. The rate constants at maximum rate were also determined and plotted in Arrhenius form (see Fig. 3). The additional degradation process was found to have an activation energy of 170 ± 10 kJ mol^{-1}, and a pre-exponential factor of (1.49 ± 0.15) × 10^{12} s^{-1}.

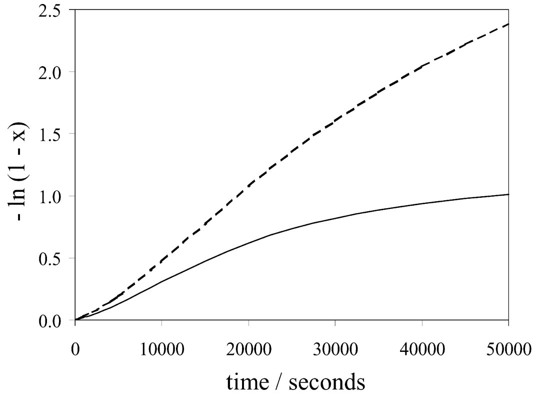

Fig. 2. First order rate plot for weight loss of PVAc during isothermal TG: (—) 260 °C uncorrected, (– – –) 260 °C corrected.

3.2. TA–FTIR spectroscopy

The thermal degradation of PVAc was investigated by TA–FTIR spectroscopy at temperatures between 260 and 290 °C. The evolution of infrared spectra from an experiment at 280 °C is shown in Fig. 4. The change in intensity of selected infrared bands during thermal degradation at 280 °C is shown in Fig. 5. Thermal degradation led to the production of new bands at 3070 and 1600 cm^{-1}. These bands are due to the formation of C–H bonds adjacent to unsaturated bonds and C=C double bonds along the carbon backbone, respectively, produced by the elimination of acetate side-groups. The infrared spectrum of the residue also contained infrared bands at 3450, 1740 and 1240 cm^{-1}, indicative of the presence of ketone groups in the polymer chains. Some hydroxyl groups, absorbing at 3450 cm^{-1}, were present at the start of the degradation process which

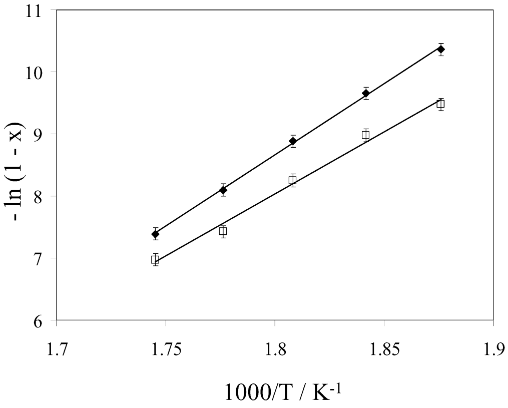

Fig. 3. Arrhenius plot for corrected isothermal TG data: (◆) initial rate, (□) additional rate.

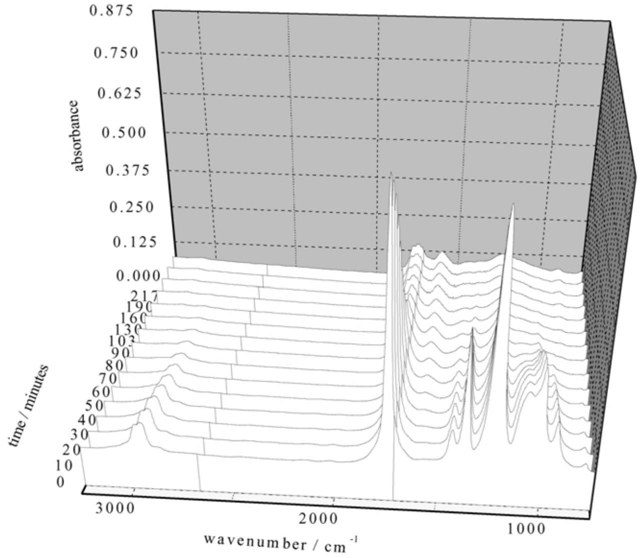

Fig. 4. Evolution of infrared spectra during the thermal degradation of PVAc at 280 °C.

may have been due to the presence of small amounts of water. Carbonyl groups may have been produced by a reaction between the acetate side-groups and acetic acid liberated by elimination (see Fig. 6(a), followed by migration of double bonds produced by elimination leading to carbonyl groups. Alternatively, migration of a double bond may have led to the elimination of an acetate side-group, leaving a carbonyl on the polymer chain (see Fig. 6(b).

A first order rate plot for the rate of loss of acetate side-groups at 280 °C is shown in Fig. 7. Consistent with TG results, the rate of loss of acetate side-groups was found to increase with time. If the rate of the additional degradation process depended on the concentration of double bonds, [C=C], then the rate of loss of acetate groups would be,

$$-\frac{\mathrm{d}[\mathrm{Ac}]}{\mathrm{d}t} = k_{\mathrm{init}}[\mathrm{Ac}] + k_{\mathrm{add}}[\mathrm{Ac}][\mathrm{C{=}C}] \quad (1)$$

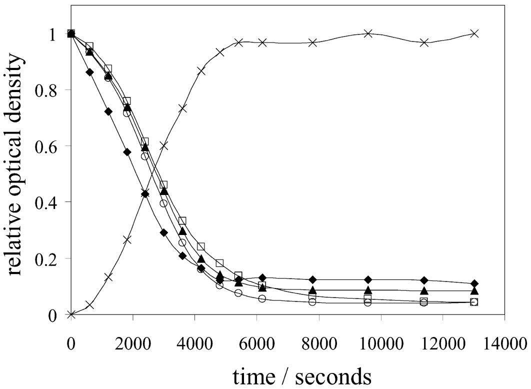

Fig. 5. Change in intensity of selected infrared bands during the thermal degradation of PVAc at 280 °C: (◆) 3450 cm^{-1}, (□) 2950 cm^{-1}, (△) 1740 cm^{-1}, (×) 1600 cm^{-1}, (○) 1240 cm^{-1}.

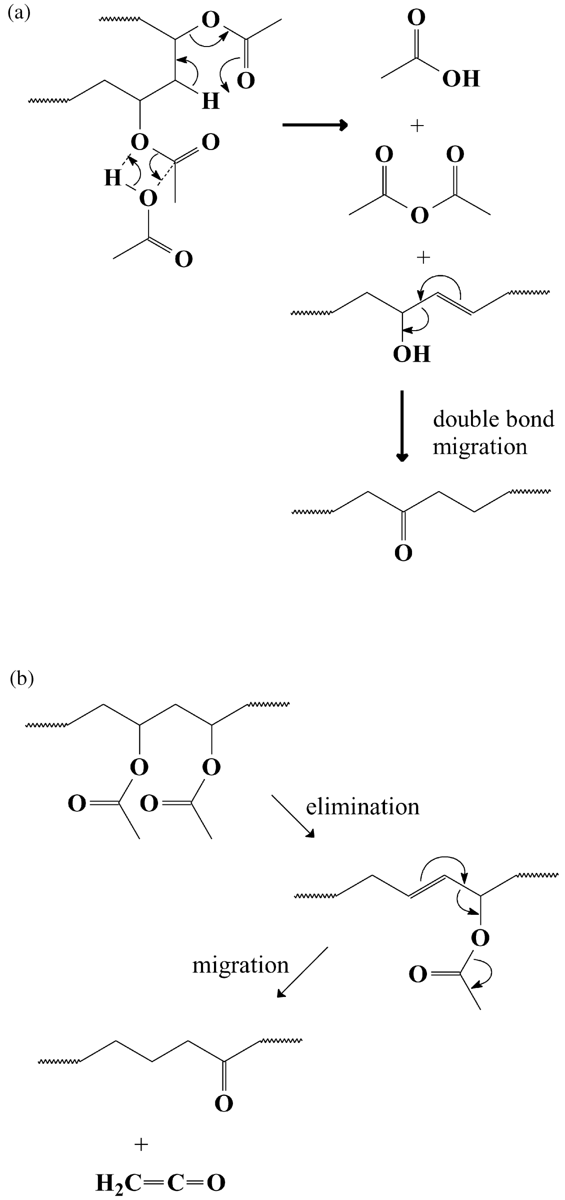

Fig. 6. Possible mechanisms for the production of carbonyl groups during the thermal degradation of PVAc: (a) by hydrolysis, (b) by double bond migration.

where [Ac] is the concentration of acetate groups, k_{init} is the first order rate constant for the initial degradation process and k_{add} is the first order rate constant for the additional degradation process. Eq. (1) can be rearranged into the following form:

$$-\int \frac{\mathrm{d}[\mathrm{Ac}]}{[\mathrm{Ac}]} = \int \{k_{\mathrm{init}} + k_{\mathrm{add}}[\mathrm{C{=}C}]\}\mathrm{d}t \quad (2)$$

which following integration becomes

$$-\ln[\mathrm{Ac}] = \{k_{\mathrm{init}} + k_{\mathrm{add}}[\mathrm{C{=}C}]\}t \quad (3)$$

which can be rearranged to

$$-\frac{\ln[\mathrm{Ac}]}{t} = k_{\mathrm{init}} + k_{\mathrm{add}}[\mathrm{C{=}C}] \quad (4)$$

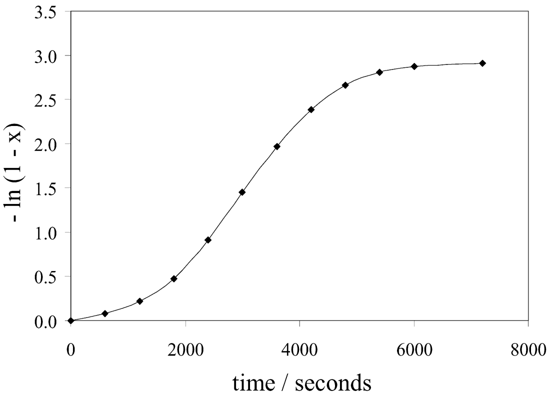

Fig. 7. First order rate plot for the loss with the infrared band at 1230 cm^{-1} of PVAc at 280 °C.

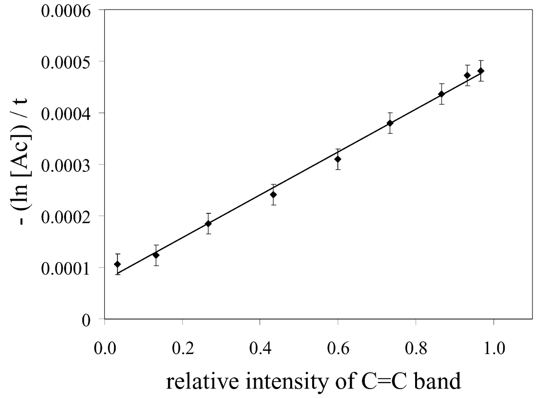

Fig. 8. Determination of $k_{(init)}$ and $k_{(acc)}$ for the thermal degradation of PVAc at 280 °C.

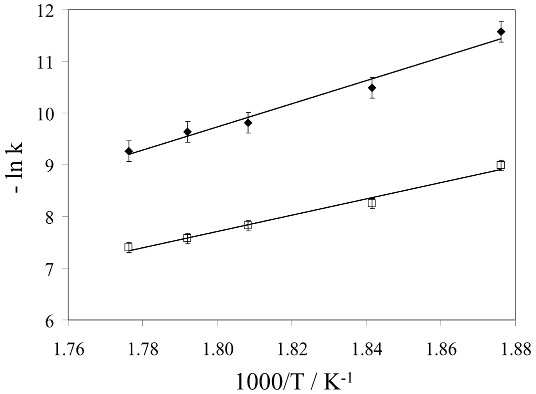

Fig. 9. Arrhenius plot for the elimination of acetate side-groups from PVAc: (◆) initial rate, (☐) additional rate.

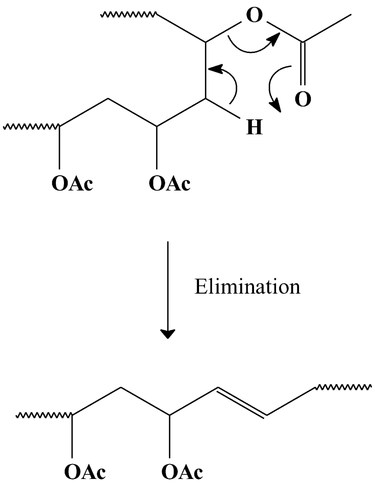

Fig. 10. Six-membered transition state by which acetate side-groups are eliminated from PVAc.

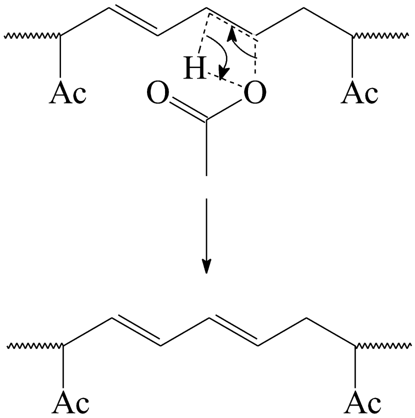

Fig. 11. Four-membered transition state by which acetate side-groups are eliminated from PVAc.

Therefore, a plot of $-\ln[Ac]/t$ versus [C=C] should be linear with a slope of k_{add} and an intercept of k_{init}. The relative intensity of the infrared band at 1240 cm^{-1} was used for [Ac], and the relative intensity of the band at 1600 cm^{-1} was used for [C=C]. A plot of $-\ln[Ac]/t$ versus [C=C] for thermal degradation of PVAc at 280 °C is shown in Fig. 8. This type of plot was found to be linear at all degradation temperatures within experimental error, which was a strong indication that the rate of loss of acetate side-groups depended upon the concentration of C=C double bonds. The effect of residual acetic acid on the rate of elimination can be disregarded, because if this were the case the rate of elimination would be governed by the steady state concentration of acetic acid. The first order rate constants were determined and plotted in Arrhenius form (Fig. 9). For the initial degradation process, the activation energy was 190 ± 10 kJ mol^{-1} and the pre-exponential factor was $(1.60 \pm 0.16) \times 10^{13}$ s^{-1}. The pre-exponential factor was consistent with a six-membered transition state [4] (see Fig. 10), from which a positive entropy change of 2 ± 1 J K^{-1} mol^{-1} at 573 K was calculated. The small positive entropy change indicated that the pre-exponential factor may have been convoluted with other factors, and that the entropy change calculated may not be meaningful.

The additional degradation process had an activation

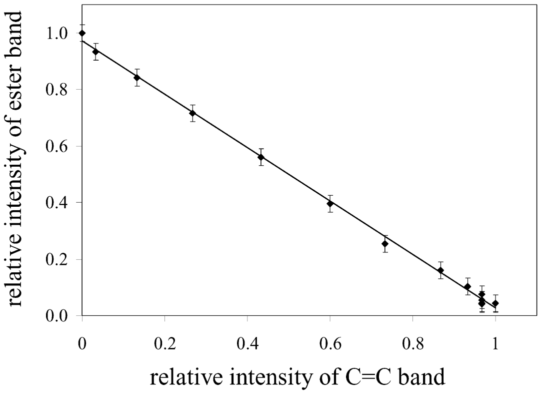

Fig. 12. Correlation between the loss of acetate side-groups and gain in C=C double bonds during the thermal degradation of PVAc.

energy of $130 \pm 10\ \mathrm{kJ\ mol^{-1}}$ and a pre-exponential factor of $(8.98 \pm 0.90) \times 10^8\ \mathrm{s^{-1}}$. The value of the pre-exponential factor was much lower than was found for the initial degradation process, and was consistent with a four-membered transition state for side-group elimination such as that shown in Fig. 11, which is promoted in the presence of adjacent C=C double bonds. The rate constant for the additional process depended on both [Ac] and [C=C], and given that $[\mathrm{C{=}C}] = 1 - [\mathrm{Ac}]$ (see Fig. 12), then the rate of loss of acetate side-groups:

$$-\frac{\mathrm{d[Ac]}}{\mathrm{d}t} = k_{\mathrm{init}}[\mathrm{Ac}] + k_{\mathrm{acc}}([\mathrm{Ac}] - [\mathrm{Ac}]^2) \tag{5}$$

contained a second order term in acetate concentration. A second order term in the rate constant could convolute the form of the pre-exponential factor. It was evident that the process of elimination of PVAc was activated by C=C double bonds produced by previous elimination reactions.

4. Conclusions

The thermal degradation of PVAc below 330 °C led to the elimination of acetic acid, and the production of double bonds in the polymer chain. The rate of loss of acetate side-groups was found to increase as degradation proceeded. This was considered to be due to the presence of C=C double bonds from previous elimination events, which activated the degradation process. Residual acetic acid produced by the elimination process was not thought to affect the rate of degradation.

It was found that the non-volatile residue formed by degradation of PVAc consisted of a polyenic backbone punctuated by ketone groups. This is not consistent with 100% conversion of side-groups to acetic acid. This may have been caused by migration of a C=C double bond into a side-group position, leading to production of a ketone group, and the liberation of ketene. Alternatively, residual acetic acid may hydrolyse an acetate side-group, leading to a hydroxyl side-group, which in the presence of an adjacent C=C double bond can lead to formation of a ketone group, as is the case for poly(vinyl alcohol) [5]. However, the relatively low boiling point of acetic acid (118 °C) infers that only a small amount of acetic acid is present in the polymer at the temperatures used.

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