

The Study of the Thermal Stability of Poly (Vinyl- Chloride) with Different Molecular Weight

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Abstract

This study investigated the influence of the molecular weight on the thermal stability of poly (vinyl chloride) (PVC) under nitrogen atmosphere was studied by bromometry titration at various temperatures (160-190°C). The extent of dehydrochlorination (%conversion) was calculated from the ratio of the HCl evolved to the amount available in the polymer. The intrinsic viscosities of solutions to deduce the effect of the molecular weight on the degradation of polymer were calculated. In addition to the course of the dehydrochlorination, the spectral changes in the visible and infrared regions have been investigated. It was found that the number- average molecular weight (45,000, 104,000) slightly affected the thermal dehydrochlorination. The experimental results also indicated the relationships between molecular weight and structural defects.

Keywords: Poly (vinyl chloride), Thermal degradation, Dehydrochlorination, molecular weight.

Introduction

The degradation and dehydrochlorination of PVC have been widely studied since the 1940s (Marvel & Horning 1943). Heating PVC above 100°C causes the polymer to degraded (Grassie 1981). In most of the early experiments, dehydrochlorination at temperatures up to 300°C was studied, mainly with the aim of improving the thermal stability of PVC. Thermal degradation of PVC occurs by an autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds (Bacaloglu & Fisch 1994, Simon 1992, MC Neill *et al.* 1995, Simon 1990).

This results in an unacceptable discoloration of the polymer and a change in physical and mechanical properties together with a decrease or an increase in molecular weight as a result of chain scission or cross- linking of the polymer molecules, respectively (Patel *et al.* 1992, Hellemans *et al.* 1993, Meier & Kip 1992).

Thermal degradation occurs due to the presence of labile sites in the polymer chains, such as allyl chlorine (Braun *et al.* 1986; Hjertberg & Sorvik 1983), tertiary hydrogen and chlorine atoms (Hjertberg & Sorvik 1983), terminal end groups such as double bonds (Hjertberg & Sorvik, 1980), oxygen- containing groups (Panek *et al.* 1985), peroxide residues (Bauer & Sabel 1975, George & Garton 1977), head-to- head structures (Crawley & Mc Neil 1978) and the steric order of the monomer

(Martinez *et al.* 1983, Martinez *et al.* 1985). This requires stabilization of the polymer for practically all technical applications.

Of particular interest is the observation that the molecular weight influences the thermal stability of PVC. It has already been pointed out that low molecular weight has an effect on the thermal stability of PVC (Zegelman *et al.* 1980). However, the dehydrochlorination of PVC is not a function of the molecular weight when the number- average molecular weight exceeds about 30,000 (Abbas & Sorvik 1976). It is known that the structural defects (particularly double bonds) of PVC depend on the molecular weight and considerably increase the initial rate of PVC degradation. Therefore study of the influences of molecular weight on the thermal stability is actually a study of the influences of structural defects on PVC.

About the influences of structural defects on the thermal stability, there are the effects of terminal double bonds on the thermal stability. The following is a brief review:

- (1) The terminal double bonds reduce the intrinsic thermal stability of PVC (Geddes 1967, Talamini & Pezzin 1960, Geddes 1967).
- (2) The terminal double bonds do not affect the thermal stability of PVC (Bengough & Onozuka, 1965, Minsker 1972).
- (3) PVC containing either more or less terminal double bond has lower thermal stability than PVC

containing a moderate amount (Onozuka & Asahina 1969). This paper will present results about relations between molecular weight and thermal stability of PVC.

Experimental parts

Materials:

Poly vinyl chloride (PVC) samples, high molecular weight with K-value 69-71 and low molecular weight with K-value 55-57, from Fluka Company, tetrahydrofuran (THF), 1,2-dichloroethane ($C_2H_4Cl_2$), cyclohexanone ($C_6H_{10}O$), acetone (C_3H_6O) were purchased from Merck Chemical Company.

Purification of PVC:

PVC was purified by solution in THF/acetone and precipitated with constant stirring in a large excess of methanol. The precipitated polymer was filtered off after 24 h, washed with methanol, and air-dried ($60^\circ C$) (Mohamed et al. 2001).

Degradation of PVC: rates of dehydrochlorination

Degradation studies were carried out using PVC powder at $180^\circ C$ under nitrogen atmosphere. The PVC sample (1.5 g) Transferred into a degradation tube. The tube was connected to a source of nitrogen maintained at a flow rate of 180 ml/min. The degradation tube was then immersed in a thermostat oil bath. The amount of HCl evolved was established after various periods of time by titration. The extent of dehydrochlorination (% conversion) was calculated from the ratios of HCl evolved to the amount available in the polymer (Okemien & Sogbaike, 1996).

Determination of unsaturation:

The degraded PVC (0.05 g) was swollen in 15 ml 1, 2 dichloroethane solution for 15 min. The resulting mixture was heated to $100^\circ C$ with continuous stirring.

2 ml of bromine solution in carbontetrachloride and 1 ml of mercuric acetate in glacial acid were added. The mixture was gently agitated for 1 hr.

After remaining for 24 hr in darkness at ambient temperature, the unreacted bromine was estimated by adding 25 ml of 10% w/v KI solution and measuring the iodine liberated by titration with sodium thiosulphate (0.001 N) and the end point determined with starch (Gallo et al. 1948), the

results are quoted as mol/g polymer in the results section.

Intrinsic Viscosity Measurements:

The degraded PVC (0.05 g) was purified by solution in cyclohexanone and precipitated in a large excess of methanol. The precipitated polymer was filtered off, washed several times with methanol, dried in vacuum at room temperature and stored in the dark.

The viscosity measurements in cyclohexanone solution were made with an ubbelohde viscometer at $30 \pm 0.01^\circ C$. The intrinsic viscosities and relative and specific viscosities of solutions were calculated by means of the following equations (Ping *et al.* 1989).

$$[\eta] = \frac{[\eta_{sp} + 3L\eta_{rel}]}{4C} \quad (1-2)$$

$$\eta_{rel} = [\eta]/[\eta_0] = t/t_0 \quad (2-2)$$

$$\eta_{sp} = \eta_{rel} - 1 \quad (3-2)$$

Where $[\eta]$, η_{sp} and η_{rel} are the intrinsic, specific and relative viscosities, respectively. C is the concentration of the solution (g/ml). In these expressions, t is the time of flow of polymer solution and t_0 , the time of flow of solvent at the temperature of measurement.

The ratios of the intrinsic viscosity of PVC samples degraded to the intrinsic viscosity of undegraded sample ($[\eta]/[\eta_0]$) was used to deduce the effect of the molecular weights on the degradation of PVC.

UV- visible Absorption by Degraded Samples:

UV – visible spectra of degraded polymer samples in 1, 2 dichloroethane solution for conjugated double bonds were obtained by using a Shimadzu 120-02 uv/ visible spectrophotometer: The degraded PVC samples dissolved readily in warm 1, 2 dichloroethane. The extent of discoloration of the degraded polymer samples was measured colorimetrically at $\lambda = 360$ nm as a function of the degradation time.

FT-IR Analysis:

IR spectra were recorded by Fourier transform infrared spectrophotometer using the FT-IR Shimadzu model 4300 Japan in the range $650-4000$ cm^{-1} at $25^\circ C$. All the samples were mixed with KBr for these analyses.

Results and Discussion:

The UV/ visible Absorption Spectra of PVC Samples Degraded:

The absorption bands were characterized using the maximum wavelength values of Marks et al. (Marks *et al.* 1967).

The extent of discoloration was determined colorimetrically by measuring the absorbance at $\lambda = 360$ nm for the various samples as a function of the degradation time. The results, as shown in Figure 1, reveal the lower discoloration of PVC samples stabilized with high molecular weight compared with the low molecular weight.

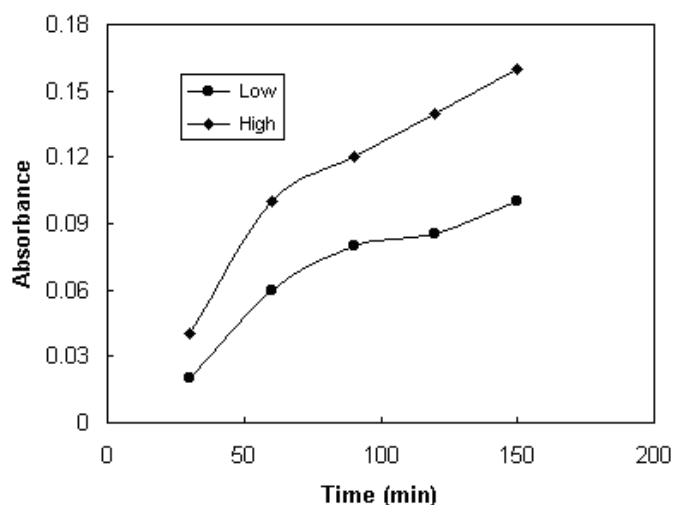


Figure1. UV-Visible spectra of PVC thermally degraded in N₂ at 180°C for 60 min

FT-IR Spectra of Degraded PVC Samples:

The FT-IR spectra of undegraded PVC and degraded PVC at 180°C for different time intervals (30, 60, 90, 120, 150 min) are represented in Figures 2, 3, 4.

In this study attention was focused on the range in the absorption pattern in two main regions:

(a) Stretching vibration of the C=C conjugated group between 1600- 1680 cm⁻¹ and (b) The C=C in conjugated group stretching vibration between 1610-1620 cm⁻¹.

It indicated that (Figures 2, 3, 4) when the time of degradation increased absorption by C=C would increase.

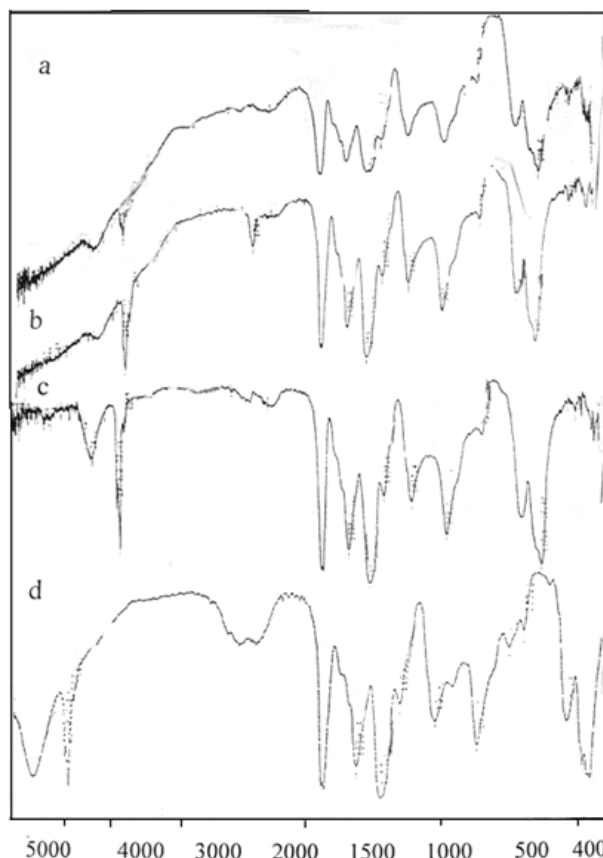


Figure 2. Variation of FT-IR spectra of thermally degraded rigid PVC, with low molecular weight at 180°C in N₂ as a function of degradation time: (a) 0 min: (b) 30 min: (c) 60 min: (d) 90 min.

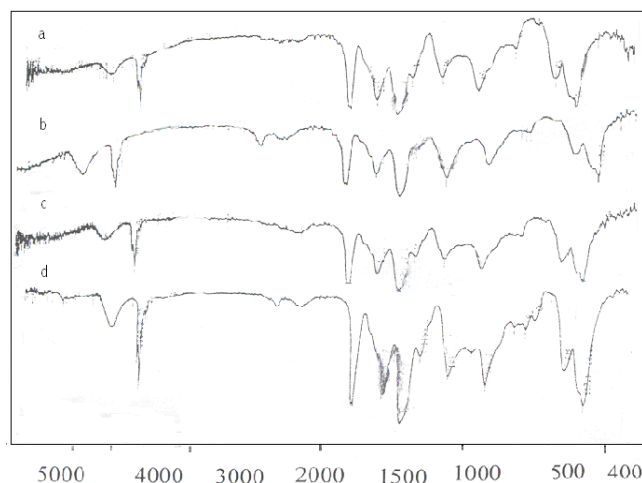


Figure 3. Variation of FT-IR spectra of thermally degraded rigid PVC with high molecular weight at 180°C in N₂ as function of degradation time (a) 0 min: (b) 30 min: (c) 60 min: (d) 90 min.

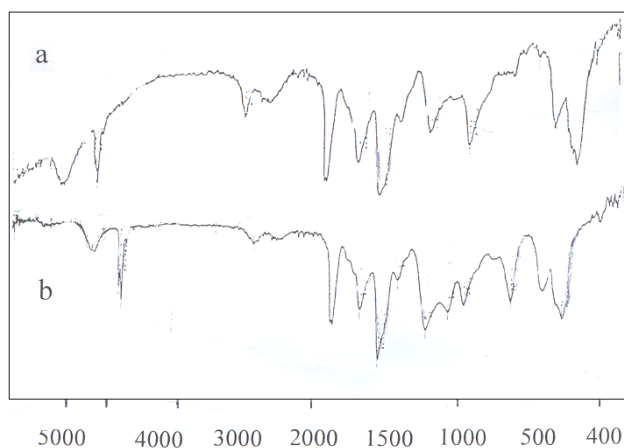


Figure 4. Variation of FT-IR spectra of PVC samples degraded at 180°C in N₂ for 60 min: (a) low molecular weight (b) high molecular weight.

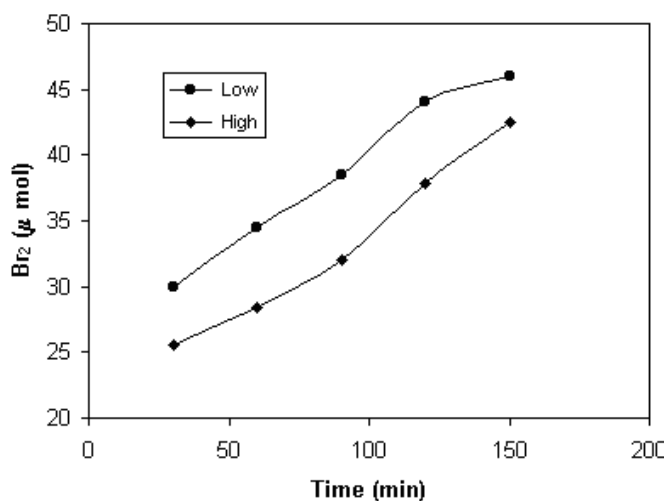


Figure 5. Bromine value consumed by double bonds in the PVC degraded as a function of degradation time in N₂ at 180°C.

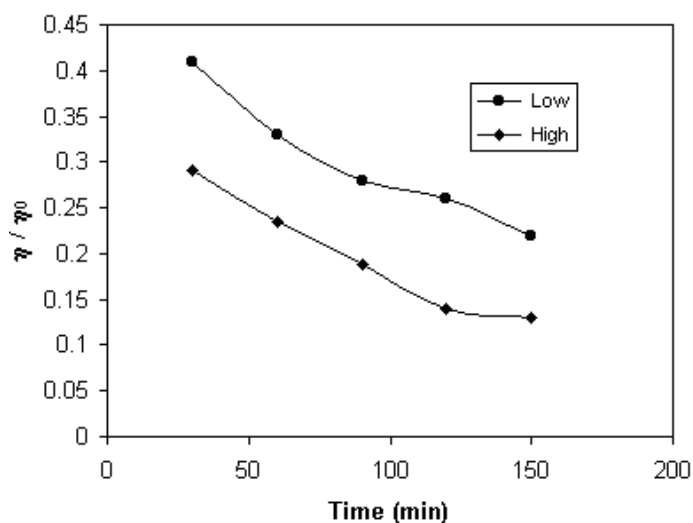


Figure 6. Intrinsic viscosity for PVC degraded in N₂ at 180°C

In comparison with PVC alone, PVC degraded with different molecular weight show that when the molecular weight increased absorption by C=C would decreased. So the thermal stability of low molecular weight polymer is less than high molecular weight polymer.

The results in Figure 6 show that the values of intrinsic viscosity obtained for PVC samples degraded with high molecular weight are much higher than the values for low molecular weight samples. These results are indicative of a stabilizing effect of the molecular weight on the thermal degradation of PVC.

Levels of Unsaturation in Degraded PVC Samples: Bromometry:

The evolution of HCl during thermal degradation of PVC leads to the formation of double bonds in the polymer, provided that the double bonds formed during the initial stage of dehydrochlorination do not undergo further reaction, measurement of bromine value consumed of degraded PVC samples estimate the extent of degradation.

The numbers of double bonds in the degraded polymer samples were worked out from the bromine values consumed as a function of degradation time (Fig.5). The results show that the amount of Br₂ consumed in the polymer degraded with high molecular weight is smaller than the polymer degraded with low molecular weight.

Extent of Thermal Degradation: Intrinsic Viscosity:

The variation in values of relative intrinsic viscosities ($[\eta]/[\eta_0]$); where $[\eta_0]$ is the intrinsic viscosity of undegraded polymer; and $[\eta]$ is the intrinsic viscosity of the degraded PVC samples with degradation time is shown in Fig.6. It has been reported that the intrinsic viscosity of PVC undergoing degradation decreases with further increase in the number of double bonds in the polymer with increase of degradation time (Shindo *et al.* 1972), probably due to reduced flexibility along the main polymer chain.

Effect of PVC Concentration on Degradation:

Data of dehydrochlorination of PVC with various amounts are shown in Figures 7, 8. These data indicate that the rate of dehydrochlorination increase with increasing the amount of PVC.

Temperature Effect on the Rate of Dehydrochlorination in Degradation of PVC:

The extents of degradation of PVC at various temperatures are shown in Figures 9, 10. It can be seen that the extent of dehydrochlorination at temperatures between 160-180°C is linear. The rates of dehydrochlorination at 1% conversion (R_{DH}) were of the same order of magnitude but at 190°C the initial rate of evolution of HCl was relatively slow and gradually increased after about 75 min. Figures 9, 10 shows that the values of R_{DH} increase with increasing in temperature.

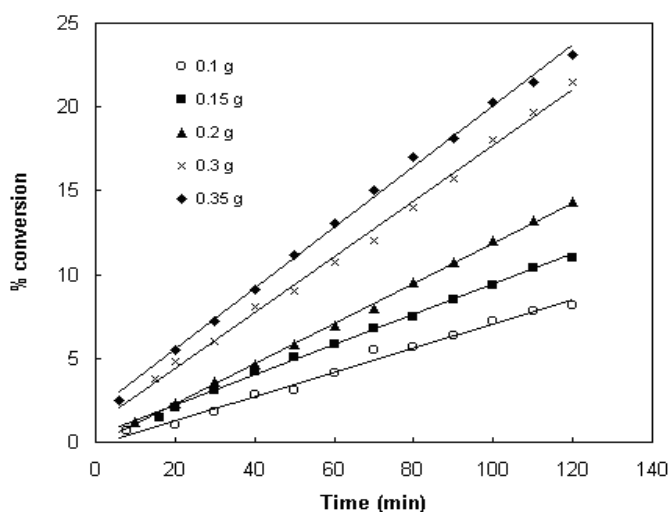


Figure 7. Conversion (%) of PVC in N₂ at 180°C for various amounts of PVC with high molecular weight

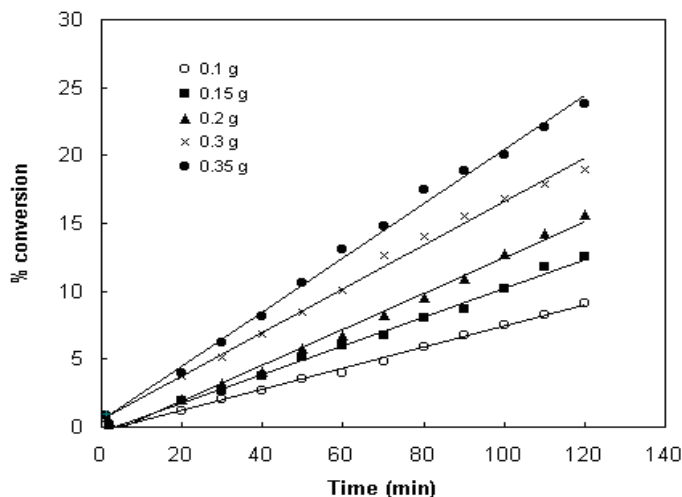


Fig.8. Conversion (%) of PVC in N₂ at 180°C for various amounts of PVC with low molecular weight.

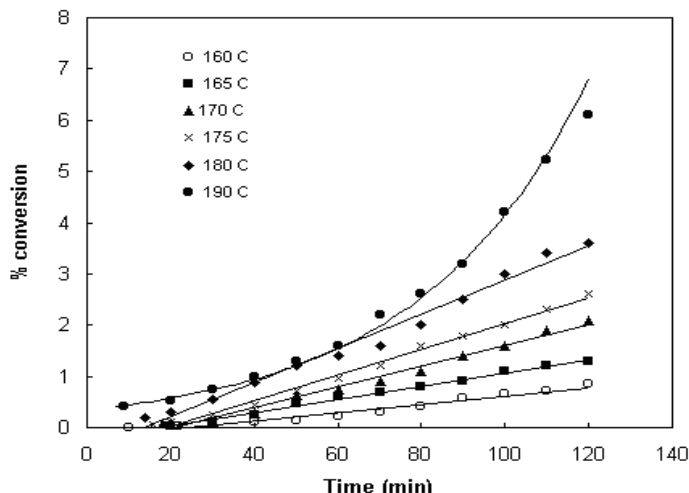


Fig.9. Conversion (%) of PVC with high molecular weight at various temperatures.

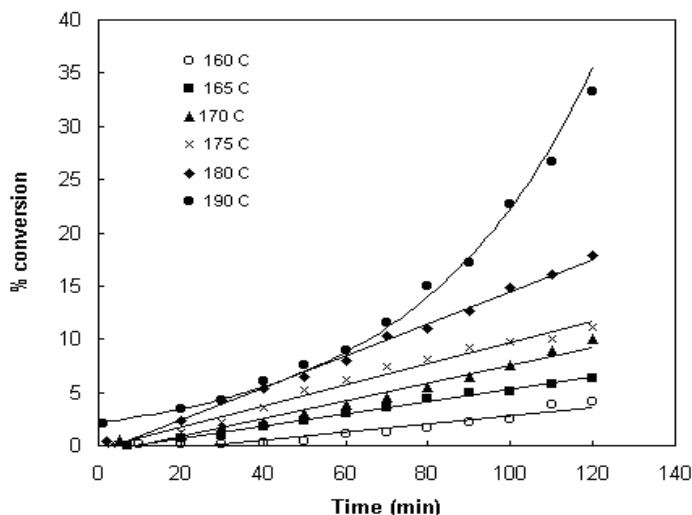


Figure 10. Conversion (%) of PVC with low molecular weight at various temperatures.

Table 1. the value of t_{DH} for PVC in various molecular weight

T (°C)	t_{DH} (min)	
	PVC (48000)	PVC (104000)
160	55	130
165	25	90
170	17	82
175	15	60
180	8	50
190	1	30

The values of the required time for dehydrochlorination to attain 1% conversion, t_{DH} are shown in Table 1.

The results in table 1 show that molecular weight exerts stabilizing effect on the degradation of PVC. The values of t_{DH} for PVC (104000) ranged from 30 min at 190°C to 130 min at 160°C that compared with the values obtained for degradation PVC in low molecular weight.

These results indicate that the molecular weight has a deleterious effect on the stability of PVC, increasing t_{DH} (table 1) and reducing the R_{DH} value.

Stabilization of Thermally Degraded PVC with different molecular weight:

Results of the dehydrochlorination (% conversion) of PVC against degradation time are represented in Figure 11.

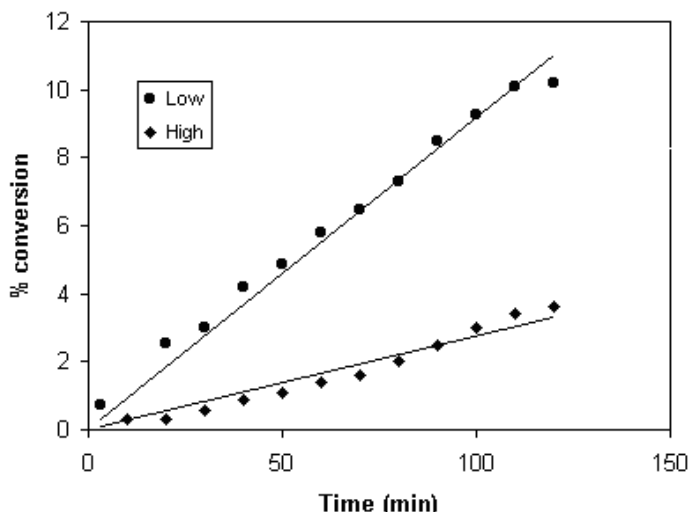


Figure 11. Dehydrochlorination of PVC (% conversion) in the different molecular weight in N_2 at 180°C.

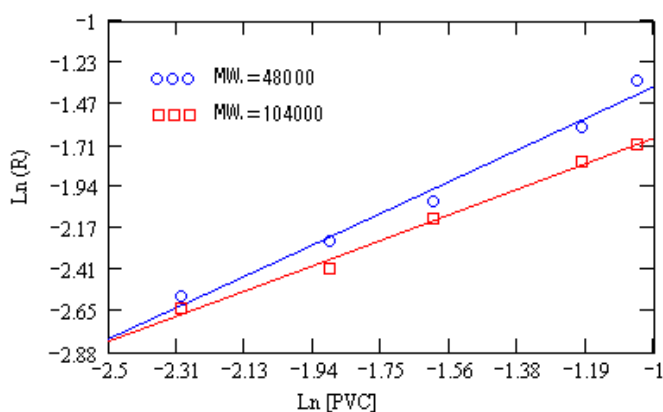


Figure 12. $\ln(R)$ vs. $\ln(PVC)$ with various amount of PVC (\square) High M.W Low M.W (\circ) high M.W.

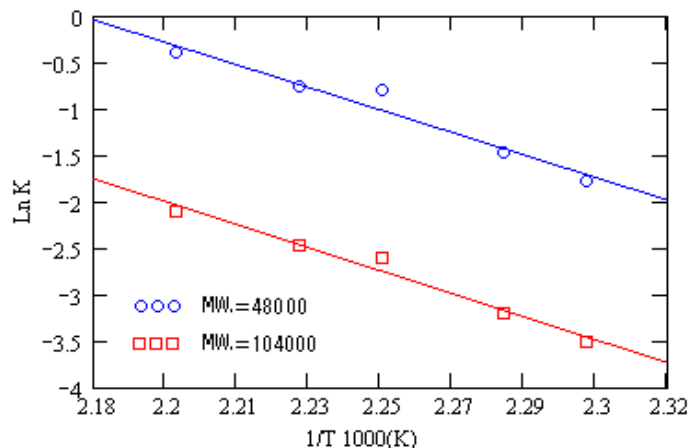


Figure 13. $\ln K$ vs. $1/T$ for degraded PVC (\square) High M.W Low M.W (\circ) high M.W.

It can be seen from this figure that the investigated high molecular weight exhibits a greater stabilizing efficiency compared to that of PVC in low molecular weight. The greater stabilizing efficiency is illustrated not only by lower rates of dehydrochlorination during the subsequent stage of degradation reaction, but also by the longer induction periods (T_s), during which no detectable amounts of hydrogen chloride gas are liberated (Table 2).

The effect of molecular weight resulted in an appreciable improvement in both t_s and the rate of dehydrochlorination.

This fact confirms the important role played by molecular weight in the stabilization mechanism.

Table 2. The induction period is obtained in different temperatures.

T (°C)	Induction period (min)	
	Low M.W	High M.W
160	10	22
165	7	20
170	5	18
175	3	16
180	2	14
190	1	9

Kinetics of Dehydrochlorination of PVC:

Determination of reaction order:

Results of dehydrochlorination of PVC with various amount of PVC are depicted in Figures 7, 8. The

results indicate that the rate of dehydrochlorination increase with the increasing of the amount of PVC.

The experimental values of dehydrochlorination of PVC are given in Table 3.

In these conditions the rate equation is as follows:

$$R=K [PVC]^{\alpha}$$

The plot of $\ln R$ vs. $\ln [PVC]$ is linear and presented in Figure 12.

The slopes of the plots are 0.94 and 0.76, respectively which suggest that the orders of reaction with respect to low and high molecular weight of PVC.

Therefore, the following rate equations were obtained.

$$R_{\text{low M.W}}= K [PVC]^{0.94}$$

$$R_{\text{high M.W}}= K [PVC]^{0.76}$$

Table 3. Effect of amount of PVC on the rate of dehydrochlorination of PVC at 180°C

PVC (g)	$R \times 10^2$ (%conversion/ min)	
	Low M.W	High M.W
0.10	7.71	7.2
0.15	10.57	9.0
0.20	13.21	12.0
0.30	20.18	16.6
0.35	26.18	18.2

Table 4. the effect of temperature on the rate coefficients of dehydrochlorination of PVC.

T (°C)	K(rate coefficient) (mol g ⁻¹ min ⁻¹)	
	Low M.W	High M.W
160	0.17	0.030
165	0.23	0.041
170	0.45	0.074
175	0.47	0.085
180	0.67	0.122

References

- Abbas K.B., Sorvik E.M. 1976: Poly styrene degradation induced by stresses resulting from the freezing of its solutions: *J. appl. Polym. Sci.* **20**: 2395–2401.
- Bacaloglu R., Fisch M. 1994: Degradation and stabilization of poly(vinyl chloride). II. Simulation of the poly (vinyl chloride) degradation processes initiated in the polymer backbone: *Polym. Degrad. Stab.* **45**: 315–324.
- Bauer J., Sabel A. 1975: Der einfluß von sauerstoff auf die polymerisation von vinylchlorid am beispiel der suspensionspolymerisation :*Angew Makromol. Chem.* **47**: 15–27.

Calculation of Activation Energy:

The dehydrochlorination of PVC was carried out at different temperatures (Figures 9, 10). It was observed that the dehydrochlorination of PVC increases with increasing temperature. The degradation rate coefficients were determined from the rate of dehydrochlorination.

The effect of temperature on the rate coefficients of dehydrochlorination are given in table 4.

According to the Arrhenius equation, $\ln (K)$ vs. $1/T$ yields a straight line which the activation energy determined from its slope (Figure 13).

The activation energies of the degradation of the PVC with low and high molecular weight are 25.99 and 29.37 (Kcalmol⁻¹), respectively. Results observed in our laboratory are consistent with the investigative works (Shindo et al. 1972). The calculated activation energies and the data of table 4 show that the rate coefficients are lower and the activation energies are higher for the PVC with high molecular weight. This daringly indicates that the polymer with high molecular weight is more stable than the polymer with low molecular weight.

Conclusions

The results from this study have provided qualitative and quantitative, data on the stability effect of molecular weight on the thermal degradation of PVC.

In this work, we studied degradation of PVC at various molecular weights. The length of the induction period, T_s , the rate of dehydrochlorination at 1% degradation to attain 1% conversion (t_{DH}) was used to compare the stability efficiency. From the rate of dehydrochlorination as measured by bromometry on one hand, and the extent of discoloration of thermally degraded PVC on the other. The experiment shows that the molecular weight slightly affects the rate of thermal dehydrochlorination of PVC. From the kinetics study, suitable rate equation is proposed. The results reveal the higher stabilizing efficiency of the investigated molecular weight as thermal stabilizer for PVC.

- Bengough W.I., Onozuka M. 1965: Abnormal structures in polyvinylchloride I—a method of estimating labile chloride groups in polyvinylchloride: *Polym.* **6**: 625–634.
- Braun D., Bohringer B., Ivan B., Kelen T., Tudos F. 1986: Structural defects in poly(vinyl chloride)—IV. Thermal degradation of vinyl chloride/acetylene copolymers: *Eur. Polym. J.* **22**: 1–4.
- Braun D., Bohringer B., Ivan B., Kelen T., Tudos F. 1986: Structural defects in poly(vinyl chloride)—V. Thermal and photodegradation of copolymers of vinyl chloride with various acetylene derivatives: *Eur. Polym. J.* **22**: 299–304.
- Crawley S., Mc Neil I.C. 1978: Preparation and degradation of Head-to-Head PVC: *J. Polym. Sci.: Polym. Chem. Ed.* **10**: 2593–2606.
- Gallo S. E., Wiese H. K., Nelson J. F. 1948: Unsaturation in Isoprene- Isobutylene Copolymers: *Ind. Engn. Chem.* **40**: 1277–1280.
- Geddes W.C. 1967: The thermal decomposition of poly (vinyl chloride). I. Kinetics of dehydro chloriation. *Rubber Chem. Technol.* **40**: 177–184.
- Geddes W.C. 1967: The thermal decomposition of polyvinylchloride—I. Kinetics of dehydrochlorination: *Eur. Polym. J.* **3**: 267–281.
- George M.H., Garton A. 1977: Effect of oxygen on the polymerization of vinyl chloride: *J. Makromol. Sci. Chem. A.*, **11**: 1389–1396.
- Hellemans J.P.H.M., Colemonts C.M.C.J., Meier R.J., and Kip B.J. 1993: An in situ Raman spectroscopic study of the degradation of PVC: *Polym. Degrad. Stab.* **42**: 323–333.
- Hjertberg T., Sorvik E.M. 1980: On the influence of hydrogen chloride on the thermal degradation of poly(vinyl chloride): *Report, IUPAC working party on PVC. Cleveland, ohio.*
- Hjertberg T., Sorvik E.M. 1983: Formation of anomalous structures in PVC and their influence on the thermal stability: 2. Branch structures and tertiary chlorine: *polym.* **24**: 673–684.
- Hjertberg T., Sorvik E.M. 1983: Formation of anomalous structures in PVC and their influence on the thermal stability: 3. Internal chloroallylic groups: *polym.* **24**: 685–692.
- Marks G.C., Benton J.L., and Thomas C.M. 1967: Thermal degradation of poly (vinyl chloride) in nitrogen atmosphere. *Sci. Monograph.* **26**: 204.
- Martinez G., Mijangos C., Millan J. 1983: Influence of tacticity on thermal degradation of PVC. V. Relation between the nature of labile conformations and the polyene distribution in the degraded, polymer *J. Appl. Polym. Sci.* **28**: 33–43.
- Martinez G., Mijangos C., Millan J. 1985: Correlation between tacticity and thermal stability in comparison with other defect structures in PVC. *Eur. Polym. J.* **21**: 387–391.
- Marvel C.S., Horning E.C. 1943: *Organic Chemistry*. 2nd Ed. New york: Wiley.
- Grassie N. 1981: Applied Science publishers.
- MC Neill I.C., Menetea L., Cole W.J. 1995: A study of the products of PVC thermal degradation: *polym. Degrad. Stab.* **49**: 181–191.
- Meier R.H., Kip B. J. 1992: A quantum chemical study of the degradation and the maximum polyene length in PVC: *Polym. Degrad. Stab.* **38**: 69–84.
- Minsker K.S. 1972: Stabilization of poly (vinyl chloride) with organotin compounds: *Khimiya, Moscow.* 272–280.
- Mohamed N.A., Sabaa M.W., Khalil Kh.D., Yassin A.A. 2001: Organic thermal stabilizers for rigid poly (vinyl chloride) III. Contonal and cinnamal thiobarbituric acids. *Polym. Degrad. Stab.* **72**: 53–61.
- Okiemien F.E., Sogbaïke C.E. 1996: Stabilising effect of derivatives of jatropha seed oil on the thermal degradation of in poly (vinyl chloride). *Eur. Polym. J.* **12**: 1457–1462.
- Onozuka M., Asahina M. 1969: Dehydrochlorination and stabilization of poly (vinyl chloride): *J. Macromol. Sci. Rev. Macromol. Chem.* **C3**: 235–280.
- Panek M.G., Villacorta G.M., Starnes W.H. Jr., and PLTZ I.M. 1985: Thermolysis rates and products of the putative ketochloroallyl groups in poly (vinyl chloride), as inferred from the behavior of analogous model compounds: *Macromolecules.* **18**: 1040–1041.
- Patel K., Velazquez A., Calderon H.S., Brown G.R. 1992: Studies of the solid – state thermal degradation of PVC. I. Auto catalysis by hydrogen chloride: *J. Appl. Polym. Sci.* **45**: 179–187.
- Ping Xu. DAFEI ZHOU. DEREN ZHAO. 1989: Studies of the thermal stability of poly (vinyl chloride)—II. Influence of molecular weight on the thermal stability of PVC. *Eur. Polym. J.* **25**: 581–583.
- Shindo Y., Murakami M., Nishida T. 1972: On the solution properties of chemically dehydrochlorinated poly (vinyl chloride). *J. Polym. Sci.* **81**: 555–560.
- Simon P. 1990: Kinetics of polymer degradation involving the splitting off of small molecules: Part 1—Basic concepts: *Polym. Degrad. Stab.* **29**: 155–163.
- Simon P. 1992: Kinetics of polymer degradation involving the splitting off of small molecules: Part 7—Thermooxidative dehydrochlorination of PVC: *Polym. Degrad. Stab.* **36**: 85–89.
- Talamini G., Pezzin G. 1960: Kinitic study on the reaction of poly vinyl chloride thermal dehydro chlorination: *Makromol. Chem.* **39**: 26–38.
- Zegelman V.I., Titova V. A., Bort D. N., Popov V.A., Pakhomova I. K., Kankhin Yu. A., Lisitskii V.V., Minsker K.S. 1980: Effect of conversion on the formation of chain defects and the heat of poly (vinyl chloride): *plast. Massy.* **8**: 8–12.