

Trade Science Inc.

October 2006

Volume 2 Issues 2-4

Macromolecules

An Indian Journal

Full Paper

MMAIJ, 2(2-4), 2006 [57-62]

Effect Of Some Organic Compounds And Metal Compounds On The Thermal Stability And Degradation Of Polyvinyl Chloride



Corresponding Author

Abbas Mehrdad
Physical Chemistry Department,
Chemistry Faculty, Tabriz University,
Tabriz, (IRAN)
Fax: +98 411 3340191
E-mail: a.mehrdad@tabrizu.ac.ir

Received: 20th June, 2006

Accepted: 2nd August, 2006

Web Publication Date : 12th October, 2006



Co- Author

Mohammad Taghi Taghizadeh
Physical Chemistry Department, Chemistry Faculty, Tabriz University,
Tabriz, (IRAN)

ABSTRACT

In this study, we examined the effect of p-chlorophenol, acetyl acetone, vanadium pentoxide and vanadium (IV) oxide acetyl acetonate on the thermal stability and degradation of polyvinyl chloride at 165, 170, 175, 180 and 185°C in inert atmosphere. The result reveals that the higher stabilizing efficiency was obtained for p-chlorophenol and acetylacetone, respectively. The vanadium oxide was indicated a little stabilizing efficiency and vanadium (IV) oxide acetyl acetonate was accelerated the degradation of polyvinyl chloride. The activation energies of the degradation of the PVC in the presence of p-chlorophenol, acetylacetone, vanadium oxide and none stabilizer were obtained 116.6, 112.5, 106.9 and 100.2 kJ mol⁻¹, respectively. © 2006 Trade Science Inc. - INDIA

KEYWORDS

Polyvinyl chloride;
Thermal stability;
Degradation.

INTRODUCTION

Polyvinyl chloride (PVC) is an important technical polymer. One of the problems associated with the processing and use of PVC is its low thermal stability. It is an unstable polymer when exposed to high temperatures during its moulding and applications. Thermal degradation of PVC occurs by an

autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds [1-4]. This results in an unacceptable discoloration of the polymer and a change in the physical and mechanical properties together with a decrease or an increase in molecular weight as a result of chain scission or crosslinking of the polymer molecules, respectively [5-7].

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The mechanisms of the two basic steps involved in the degradation, namely initiation through labile structures and propagation or the build up to polyenes, have been given particular attention. Most authors agree that initiation is due to the presence of a few abnormal structures such as allylic chlorine^[8], tertiary hydrogen and chlorine atoms^[9], terminal end groups such as double bonds^[10], oxygen containing groups^[11], or peroxide residues^[12], head-to-head structures^[13], and steric order of the monomer units in the polymeric chain (tacticity)^[14]. This instability requires stabilization of the polymer for practically all technical applications. A wide variety of stabilizers are used industrially to improve the thermal stability of the polymer. Several workers have reported on the degradation and stabilization of PVC^[14-25]. Additives finding practical application as thermal stabilizer for PVC include metal salts of organic acids, organometallic compounds, esters or mercaptides of dialkyl tin^[26-29], inhibitors of radical chain reactions^[12], zinc and barium carboxylate^[30] which can react with the evolved hydrogen chloride gas, thus retarding the deleterious catalytic action of the eliminated hydrogen chloride^[25]. More recently, interests have been shown in the use of epoxides and mercaptans in the thermal stabilization^[24].

Metal chlorides are considered as strong catalysis for the subsequent dehydrochlorination process^[26, 27]. For this reason, stabilizers for an organic nature have been used recently for the thermal stabilization of PVC^[28,31,32]. In this study, we examined the effect of *p*-chlorophenol, acetyl acetone, vanadium pentoxide and vanadium (IV) oxide acetyl acetate on the thermal stability and degradation of polyvinyl chloride at 165, 170, 175, 180 and 185°C in inert atmosphere.

EXPERIMENTAL

Materials

Polyvinyl chloride with molecular weight 108000 (Fluka) was purified by solution in THF/acetone mixture and precipitated, with constant stirring, in a large excess of methanol. The precipitated polymer was filtered off after 24 hr, washed with methanol

and air-dried^[29]. *p*-Chlorophenol, acetyl acetone, vanadium pentoxide and vanadium (IV) oxide acetyl acetate (Merck) used without further purifications.

Preparation of PVC samples

Samples of PVC for thermal degradation were prepared by thoroughly mixing 0.5 g of PVC powder and different amount of the additive in a mortar for each experiment and 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 controlled^[17,18].

Evaluation of stabilizing efficiency

The amount of HCl evolved was established after various periods of time by conductometry. The extent of dehydrochlorination (% conversion) was calculated from the ratio of HCl evolved to the amount available in the polymer^[29].

RESULT AND DISCUSSION

Effect of the stabilizer concentration on the stabilization

Thermal degradation of PVC was carried out in different concentration of stabilizer. The plots of percent of conversion versus time of degradation in presence various amount of *p*-chlorophenol (PCP) at 175 °C is shown in figure 1. The rate of degradation can be estimated from the slope of plots in this figure. The result indicates that PCP can be stabilized PVC and the rate of degradation decrease with the increasing of ratio [PCP]/[PVC] and then has been constant. The optimum stabilizing efficiency of this stabilizer is 8 g per 100 g PVC. The plots of percent of conversion versus time of degradation in presence various amount of acetylacetone (AA) at 175 °C is shown in figure 2. The result indicates that AA can be stabilized PVC and the rate of degradation are constant with variation of ratio [AA]/[PVC]. Therefore presence of AA stabilized PVC but amount of AA is not effective in stabilizing PVC. The plots of percent of conversion versus time of degradation in presence various amount of vanadium

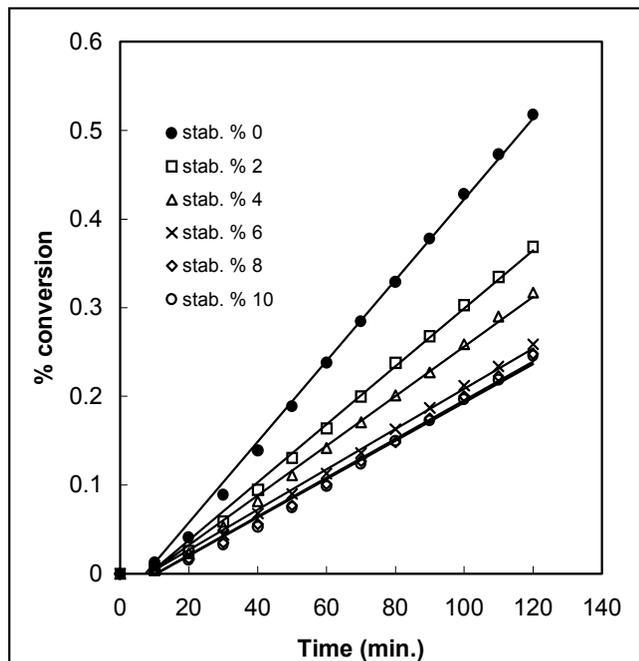


Figure 1: Plot of % conversion versus time in various concentrations PCP at 175°C

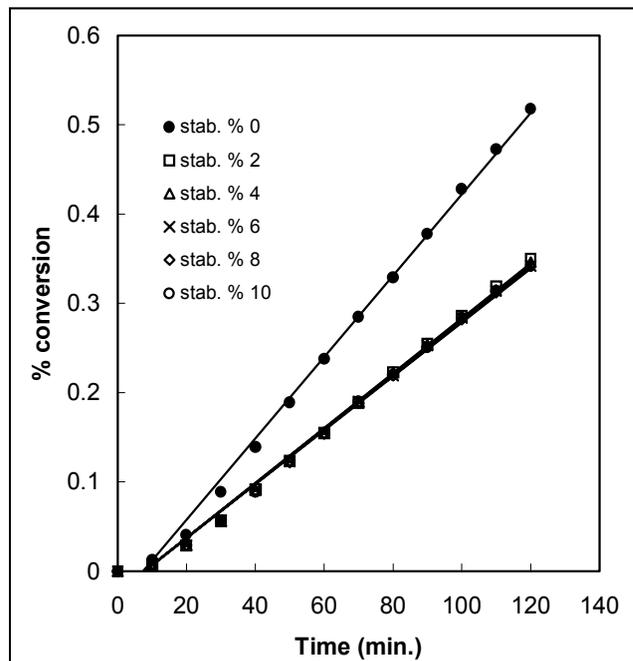


Figure 2: Plot of % conversion versus time in various concentrations AA at 175°C

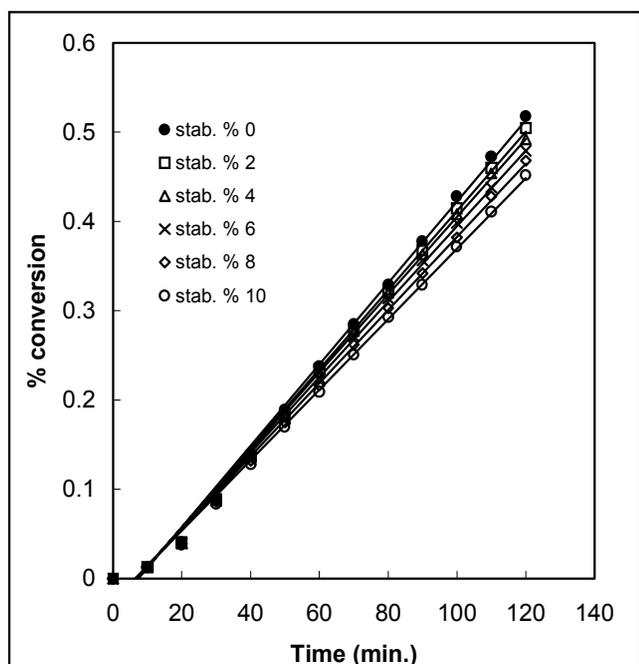


Figure 3: Plot of % conversion versus time in various concentrations VPO at 175 °C

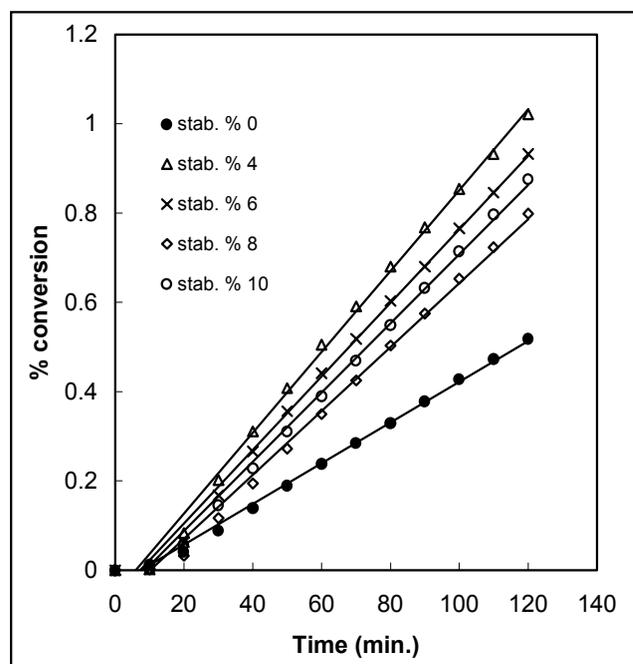


Figure 4: Plot of % conversion versus time in various concentrations VOAA at 175 °C

pentoxide (VPO) at 175°C is shown in figure 3. The vanadium oxide was indicated a little stabilizing efficiency and the rate of degradation decrease slowly with the increasing of ratio $[VPO]/[PVC]$. The plots of percent of conversion versus time of degrada-

tion in presence various amount of vanadium (IV) oxide acetylacetonate (VOAA) at 175°C is shown in figure 4. The result indicates that VOAA not only can not be stabilized PVC but also accelerated the degradation of PVC. The obtained degradation rates

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TABLE 1: The obtained degradation rates with various stabilizers and concentrations at 175°C

% w Stabilizer	$r \times 10^{-5}$ (conversion/min)			
	PCP	AA	VPO	VOAA
0	4.71	4.71	4.71	4.71
2	3.40	3.19	4.57	-
4	2.91	3.16	4.48	9.30
6	2.35	3.14	4.36	8.51
8	2.28	3.12	4.22	7.48
10	2.27	3.12	4.06	8.06

with various stabilizers and concentrations at 175 °C are listed in TABLE 1. The stabilizing efficiency of the used compounds defined as follows:

$$R = 1 - \frac{r}{r_0}$$

Where r and r_0 are the rate of degradation in presence and absence of stabilizer, respectively. The stabilizing efficiency of the used compounds are shown in figure 5. The result of figure 5 indicated that order of stabilizing efficiency as follows:

$$PCP > AA > VPO > \text{None} > VOAA$$

Kinetics of degradation of PVC

The rate of degradation depends on the concentration of stabilizer and polymer as follows:

$$r = \left(\frac{d\alpha}{dt} \right) = k[\text{PVC}]^{n1} [\text{S}]^{n2}$$

Where α is the percentage of conversion and $n1$ and $n2$ are the reaction order with respect of PVC

and stabilizer, respectively. By considering that concentration PVC nearly constant rate equation as follows:

$$r = k'[\text{S}]^{n2}$$

The plot of $\text{Ln}(r)$ versus $\text{Ln}[\text{S}]$ is plotted in figure 6. The slopes of the line are -0.28, -0.016, -0.1 for PCP, AA and VPO, respectively. Which suggests that the order of the reaction with respect of PCP, AA and VPO are -0.28, -0.015, -0.1, respectively.

Calculation of activation energy

The degradation of PVC was carried out at different temperatures (165, 170, 175, 180 and 185°C) in constant concentration of stabilizer (%2 w). The plots of percent of conversion versus time of degradation with various stabilizers and temperatures are shown in figures 7-10. It was observed that the degradation of PVC increases with increasing temperature. The degradation rates were determined from

TABLE 2: The obtained degradation rates with various stabilizers and temperatures in %2 w stabilizer

Temperature (°C)	$r \times 10^{-5}$ (conversion/min)			
	None	PCP	AA	VPO
165	2.56	1.72	1.63	2.35
170	3.48	2.47	2.29	3.33
175	4.71	3.40	3.19	4.57
180	6.34	4.96	4.52	6.28
185	8.50	6.96	6.26	8.48

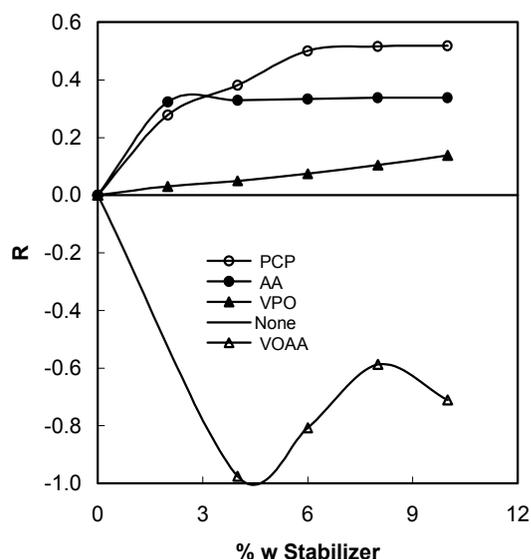


Figure 5: The stabilizing efficiency of the compounds versus %w stabilizer

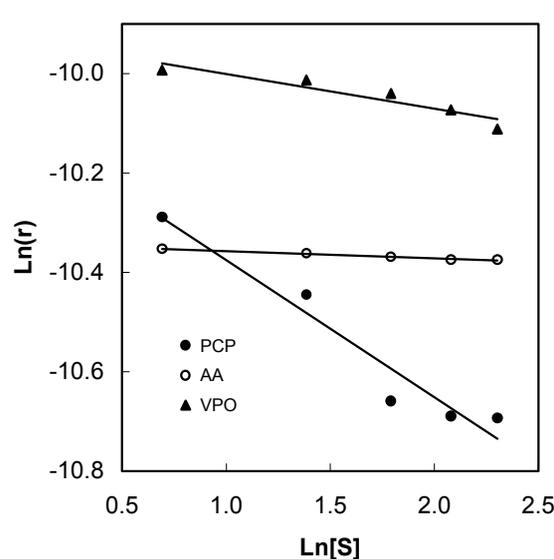
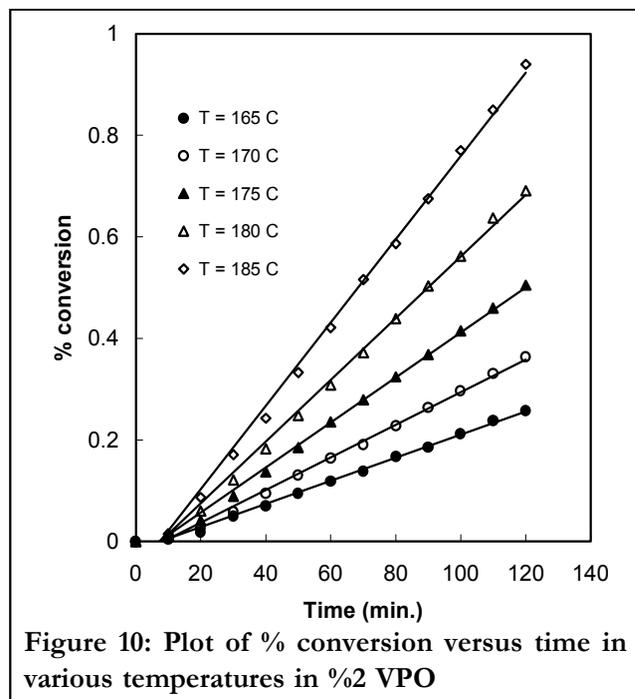
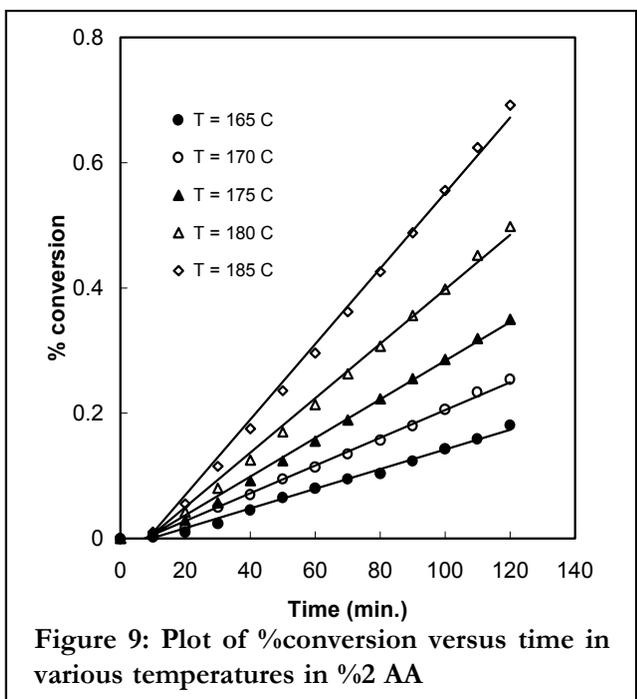
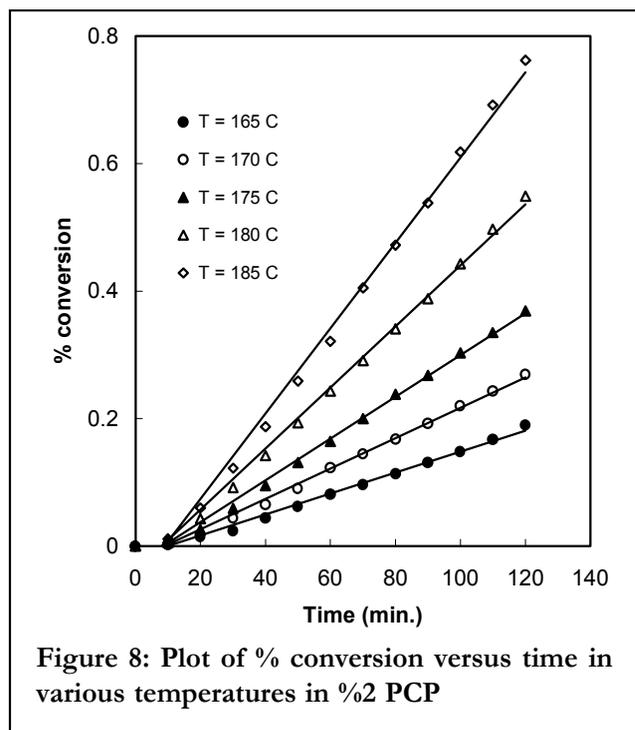
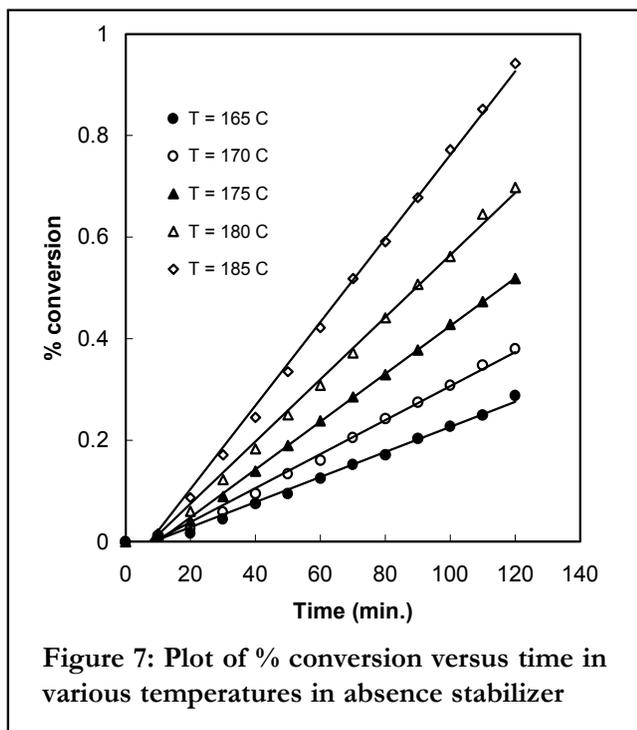


Figure 6: Plot of $\text{Ln}(r)$ versus $\text{Ln}[\text{S}]$ for stabilizers at 175°C



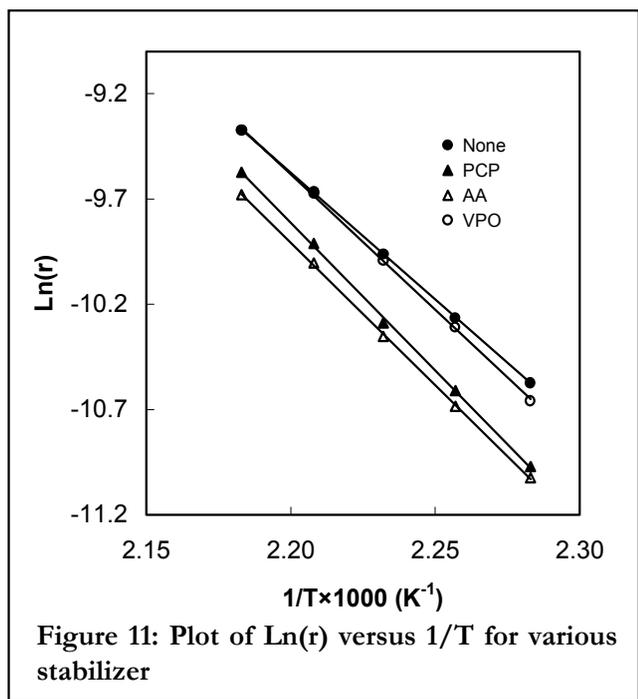
the slopes of these plots. The obtained degradation rates with various stabilizers and temperatures are listed in TABLE 2. According to the Arrhenius equation $\ln(r)$ versus $1/T$ yields a straight line which the activation energy determined from the slope of theirs. The plots of $\ln(r)$ versus $1/T$ are shown in figure 11. The activation energies of the degradation of

the PVC in the presence of PCP, AA, VPO and none stabilizer were obtained 116.6, 112.5, 106.9 and 100.2 kJ mol^{-1} , respectively.

CONCLUSION

In this work, degradation and stability of PVC

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were studied in absence and presence of different stabilizers at various temperatures. The result indicated that order of stabilizing efficiency as follows:



The activation energies of the degradation of the PVC in the presence of PCP, AA, VPO and none stabilizer were obtained 116.6, 112.5, 106.9 and 100.2 kJ mol⁻¹, respectively.

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