

# **SUPERFAST THERMAL DECOMPOSITION REACTIONS OF POLYMERS AND CRYSTALLOHYDRATES**

*O. F. Shlensky*

Mendeleev Institute of Chemical Technology, Miusskaja pl. 9, 125190 Moscow, Russia

(Received August 30, 1994)

## **Abstract**

Evidence of the existence of a high-limit degradation temperature for polymers is reported. At this high-limit temperature, the rate of polymer thermolysis exceeds the reaction rate predicted by the Arrhenius law by many orders of magnitude. An explanation is proposed for the observed behaviour, based on the disappearance of intermolecular interactions. For the study of degradation reactions under high-limit temperature conditions, new methods of fast (pulsed) thermal analysis are presented. The investigated samples, as very thin films, are brought into tight contact with a hot moving metal surface. Under these conditions, the heating rate exceeds  $10^4$  deg/s, allowing estimation of accompanying decomposition rates for heating times of the order of 0.01 s.

**Keywords:** crystallohydrates, polymers, superfast thermal decomposition reactions

## **Introduction**

It is well known that both physical and chemical bonds are affected by thermal energy. Because the energies of chemical bonds are usually much higher than those of physical bonds, the evaporation of low-molecular compounds is generally not accompanied by their destruction. On the other hand, due to the increased probability of formation of physical bonds by interaction (intermolecular association), the scission of macromolecules becomes energetically more favourable than their evaporation. Indeed, the heat of evaporation of polymers increases with the number of groups associated by interaction, finally exceeding the energy of chemical bond scission. This explains why, instead of evaporation, polymers undergo thermodestruction and/or other chemical processes during moderate heating.

The rate of equilibration between associated and free interacting groups in polymers is usually much higher than the rate of chemical reactions. Thus, it can be expected that for a very fast energy supply (fast heating or strong compression followed by sudden pressure release) intermolecular interaction bonds

are released before chain scission becomes possible. Because of the low rate of reequilibration, under such conditions the macromolecules appear isolated from each other, as if a 'polymeric gas' has been formed. The life-time of this 'polymeric gas', however, is very short, the system being thermodynamically unstable.

Up to a critical temperature (the temperature of 'polymeric gas' formation),  $T_{lim}$ , the relative number of intermolecular bonds is governed by Van't Hoff's law. Since the association of macromolecules implies at least the cooperation of a certain minimum number of intermolecular bonds [1], polymers of high molecular mass cannot be separated from each other or from a given surface without decomposition, because the involved energy supply exceeds the chemical bond energy.

Both routes of attainment of isolated macromolecules, a sudden temperature rise or compression followed by pressure release, have been accomplished in our laboratories [2-5]. The observed rate of polymer degradation proved to be several orders of magnitude higher than the usual rates of thermolysis for associated macromolecules. Such high rates of polymer thermolysis in the bulk, however, have not been achieved before.

For linear polymers such as poly(styrene) or poly(methylmethacrylate), the energy  $D$  of intermolecular bond association is about 1.6 kcal/mol, the related  $T_{lim}$  value therefore being of the order of 800 K. Under such temperature conditions, the probability of persistence of any chemical bond is very low, because the supplied thermal energy exceeds the bond energy,  $D$ :

$$R T_{lim} \geq D$$

Attempts to approach temperatures close to  $T_{lim}$  by slow heating are always accompanied by chemical reactions of the polymers, contributing to various changes in structure and composition. That is, they occur without the desired result. It is therefore necessary to ensure a short heating time, such that a well-defined amount of the polymer has time to react. This time can be estimated in a knowledge of the overall reaction rate constants and their temperature dependences.

Assuming an overall first-order degradation reaction (typical for chain scission), the mass loss at a given temperature obeys the well-known exponential law:

$$M = M_0 \exp(-kt)$$

where  $M_0$  is the initial mass of the polymer and  $k$  is the overall degradation rate constant. Thus, the necessary heating time,  $t$ , for a given amount of still unreacted compound  $M$  can be estimated if  $k$  is known. Supposing, for instance,

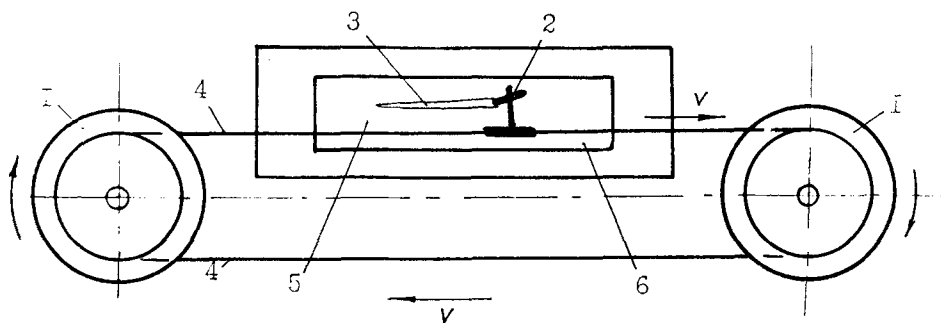
$M/M_0=0.5$ , the heating time needed to reach a given temperature is  $t = (-\ln 0.5/k)$ .

Consequently, for most linear polymers the heating time up to 800 K must be below 1 s. For a more accurate calculation of the heating time, it is necessary to account not only for the rate of temperature increase, but also for the temperature dependence of the rate constant, supposing the validity of the Arrhenius law.

Standard instruments for thermal analysis are generally not adapted for the study of such fast thermolysis processes because of the large thermal lag of the system. Not only are the characteristic heating times of these instruments longer than 1 s, but additionally the recording systems are mostly not able to reproduce reactions occurring with high reaction rates.

## Experimental

To investigate fast thermolysis processes, we have developed new techniques and procedures for high-speed thermal analysis. High heating rates were realized by applying very thin polymer films on metal plates preheated to the desired reaction temperature. To obtain these thin polymer films, the sample was pressed against the hot metal surface and drawn along at a given velocity [5-7]. The working principle of the high-speed thermal analyzer is shown in Fig. 1. In some experiments, the polymer sample was maintained immobile and the hot metal plate was drawn along the sample. The thickness of the film (5-7  $\mu\text{m}$  or even less) is dependent on the drawing velocity used.



**Fig. 1** Working principle of the high-speed thermal analyzer; 1 - roller, 2 - sample holder, 3 - polymer film, 4 - band rope, 5 - heated metallic support-plate, 6 - heater; life time  $t=l/v$ ;  $l$  - length of the polymer film,  $v$  - speed of the band rope

The polymer film is firmly retained on the metal surface by adhesive forces and, despite an intensive gas evolution, no gaps appeared between the film and the metal. The preservation of the tight contact is explained by the free diffusion

of the gaseous thermolysis products through the thin polymer film. However, for films thicker than 7  $\mu\text{m}$  blisters appeared.

In response to the high temperature, the polymer decomposes and the polymer film visibly disappears from the hot metal surface. The life-time of the polymer film on the metal surface was recorded at each temperature used by shooting the infrared image of the film with a videoanalysis system consisting of the digital videomemory of a videoprofile device, a synchron pulse generator and the CF-200 TV monitor of Thermocam SOFRETEC.

## Results and discussion

The best images of the molten film were obtained in the infrared, since not reflection, but self-radiation of the film was recorded. One of the obtained images is shown in Fig. 2B. The white spot represents the trail of the sample, which disappears like the 'tail of a comet'. The life-time of the film can be de-

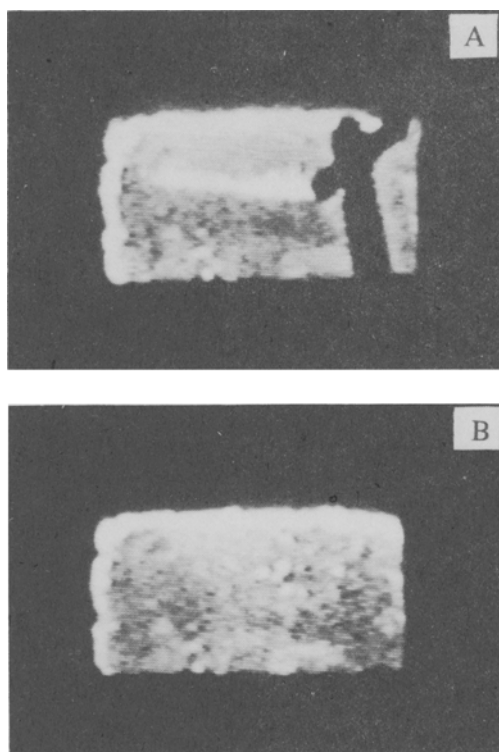
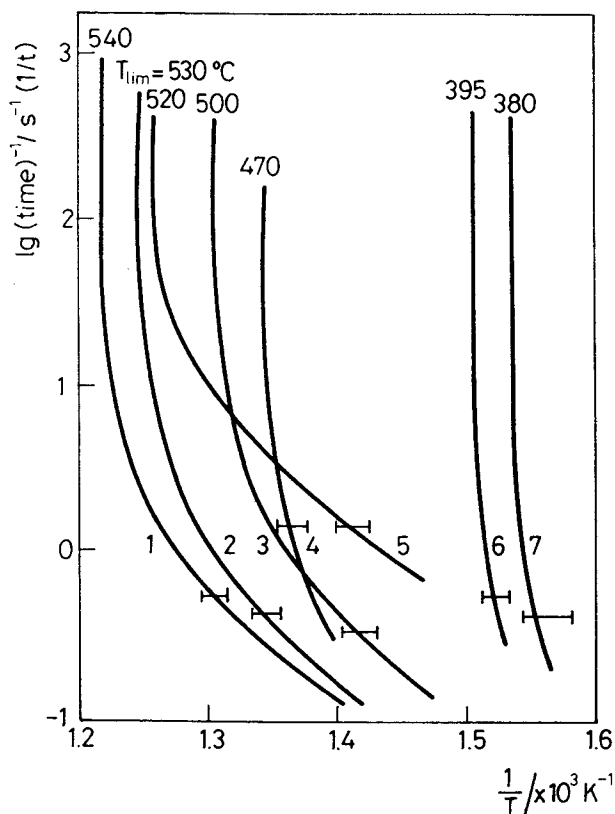


Fig. 2 Infrared image of the molten polymer film (B), initial view (A)

terminated with high accuracy via the length of this 'tail'. For a drawing rate of  $V=3$  m/s and a 'tail' length of  $l=15$  mm, a life-time of  $t=l/V=5\cdot 10^{-3}$  s results. On the other hand, for a plate temperature of 800 K and a time of 0.01 s for the polymer film to be heated up to that temperature, an average heating rate of  $5\cdot 10^4$  deg/s results.

The elaborated thermovision equipment allows determination of the heating time of the polymer film up to a given final temperature. This was achieved by observing the variation in the radiation intensity of the film from frame to frame of the video-images on the recorder screen. For a film thickness of 20  $\mu\text{m}$ , this time did not exceed 40 ms. Numerical calculations have shown that the heating time decreases in proportion to the square of the film thickness [4]. The sensitivity depends on the resolution of the lenses used.



**Fig. 3** Characteristic temperatures of the thermal decomposition and decomposition rates of linear polymers; 1 - high-impact poly(styrene), 2 - poly(styrene), 3 - high-density poly(ethylene), 4 - poly(vinyl chloride), 5 - poly(ethylene terephthalate), 6 - low-density poly(ethylene), 7 - poly(methylmethacrylate), 8 - mineral colemanite, 9 - borax

Some typical results obtained with the proposed method for different compounds are presented in Fig. 3 [3–5] in a  $\log(1/t)$  vs.  $1/T$  plot.

For lower temperatures (up to 400–480°C), the  $1/t$  vs.  $1/T$  dependence is almost linear, suggesting the validity of the Arrhenius law. At high temperatures, however, the decomposition rate increases substantially, approaching infinity asymptotically for  $1/T_{lim}$ . This means that polymers cannot be overheated above this critical temperature,  $T_{lim}$ . It has been observed that polymers with different chemical structures, but with similar intermolecular interactions, generally exhibit close  $T_{lim}$  values. This is indicative of the substantial contributions of the intermolecular interactions to the thermal degradation of polymers. For  $T = T_{lim}$ , the polymers are volatilized ('gasified') in an avalanche-like manner.

For poly(styrene) ( $M_n = 600.000$ ), besides the video-images of film removal from the hot metal surface, the reaction products obtained at  $T = T_{lim}$  (about 550°C) were analysed by gel permeation analysis. Both the gaseous reaction products and those condensed on the cold walls of the glass vessels were collected. The residual polymer film was washed off with toluene. All products were analysed on a Waters gel chromatograph. The chromatogram showed the presence of a whole spectrum of products, with molecular weights ranging from that of the monomer up to 3.000–4.000.

This means that the release of intermolecular interactions as  $T_{lim}$  is approached changes the reaction mechanism of poly(styrene) degradation. It is well known that at moderate temperatures the thermal degradation of poly(styrene) yields prevailing monomer and, at most, dimers due to an 'unzip' depolymerization reaction [6], whereas at temperatures close to  $T_{lim}$  random scission contributes not only to an additional increase in the reaction rate (the polymer 'volatilization' rate far exceeding the rate increase predicted by the Arrhenius law), but also to substantial changes in the composition of the reaction products.

Moreover, as it occurs in the 'gaseous' phase, i.e. in the absence of 'cage effects' (by interaction) and/or hindrance (by diffusion) to the elimination of the reaction products, the thermolysis reaction is accompanied by an unexpected increase in the volatilization ('gasification') rate. The main contributions to the increased thermolysis rate are of an entropic nature. In the absence of association, the macromolecules are in an apparently 'overexcited - isolated' state. The conformational states characteristic of isolated macromolecules are realized, however. Therefore, the molecules have an excess of free energy, which explains the observed occurrence of an avalanche-like process of chain scission with a maximum first-order chemical reaction rate of about  $10^{10} \text{ s}^{-1}$ .

The second way to diminish the intermolecular interaction includes strong compression followed by a sudden pressure release to low pressure. Estimations show that the usual physical bonds in polymers are broken at pressures as low as 1 GPa [7]. Experimentally, the polymer was first compressed in a cylinder with a piston to pressures higher than 2 GPa, and the pressure was then released

through a small opening-valve [2]. As a result of the pressure release, tensile stresses developed and were uniformly distributed within the polymer as in a suddenly straightened compressed spring. These stresses reduce the intermolecular interaction. During these experiments, not only the emerging pressure jet from the valve was observed, but also thermolysis of the polymer at room temperature. This phenomenon has been called a 'rheological explosion'. In contrast with a thermal explosion, a rheological explosion is accompanied not by the evolution, but by the absorption of heat. Similarly as under fast thermal heating conditions, polymer degradation occurs at rates much higher than predicted by the Arrhenius law. However, in contrast with the 'superfast' chemical reactions initiated by short energy impulses, the processes discussed above are essentially of an entropic nature. This is explained both by the chain structure of the polymers and by the initiation of the reaction due to the diminution of intermolecular interactions.

Identification of the peculiarities of polymer thermolysis at high temperatures therefore permits an elucidation of the different processes associated with the treatment and use of polymers, and in particular those accompanying the combustion processes in polymers, woods and natural coals [8].

Fast thermolysis reactions observed by means of rapid heating are also characteristic of some crystallohydrates [9]. Thermal explosion-like decomposition was observed, for instance, during the rapid heating of the mineral colemanite, showing a polymeric structure, and of deca- and octahydrate boraxes  $\text{Na}_2\text{B}_4\text{O}_7 \cdot n\text{H}_2\text{O}$  for samples placed as powders between metal plates heated to  $T = 320^\circ\text{C}$  (the heating rate was about 550 deg/S).

## Conclusion

It has been shown that it is possible to achieve the thermal degradation of polymers under conditions of vanishing interactions. Due to the absence of interactions, the degradation occurs at very high reaction rates, far exceeding the rates predicted by the Arrhenius law. Substantial changes in reaction mechanism are observed at the high-temperature limit of degradation, expressed by an unexpected increase in the volatilization rate. Due to the absence of interactions, the main contributions to the increased thermolysis rate are of an entropic nature.

\* \* \*

Suggestion of Dr. H. A. Schneider of the Institute of Macromolecular Chemistry of the University Freiburg during the elaboration of the MS are acknowledged.

## References

- 1 E. F. Vainshtein, Ph. D. Thesis, Mendeleev Institute of Chemical Technology, Moscow, 1981.
- 2 A. S. Kechekyan, *Vysokomol. Soedin.*, 26B (1984) 884.
- 3 O. F. Shlensky, A. A. Matyukhin and E. F. Vainshtein, *J. Thermal Anal.*, 31 (1986) 107.
- 4 O. F. Shlensky, E. F. Vainshtein and A. A. Matyukhin, *J. Thermal Anal.*, 34 (1988) 645.
- 5 O. F. Shlensky et al., *Teplofiz. Vysok Temperature*, 5 (1987) 269 (in Russ.).
- 6 C. N. Cascaval, C. Vasile and I. A. Schneider, *Makromol. Chem.*, 131 (1970) 55.
- 7 O. F. Shlensky, E. F. Vainshtein and N. N. Lyasnikova, *Inzh. Fiz. Zhurn.*, 53 (1987) 774 (in Russ.)
- 8 O. F. Shlensky, A. G. Shashkov and L. N. Aksenov, *Thermal Decomposition of Materials*, Elsevier, 1991.
- 9 A. N. Bondar, *Izv. AN Latv. SSR.*, 1981, p.580.

**Zusammenfassung** — Bei Polymeren wird über den Beweis der Existenz einer Hochgrenz-Zersetzungstemperatur berichtet. Bei dieser Hochgrenztemperatur übersteigt die Geschwindigkeit der Polymerthermolyse die durch das Gesetz von Arrhenius vorausgesagte Reaktionsgeschwindigkeit um mehrere Größenordnungen. Für das beobachtete Verhalten wurde eine Erklärung, basierend auf dem Wegfall von intermolekularen Wechselwirkungen vorgeschlagen. Zur Untersuchung der Zersetzungsreaktionen unter Hochgrenztemperatur-Bedingungen wurden neue Methoden schneller (gepulster) Thermoanalyse vorgestellt. Die untersuchten Proben werden als sehr dünne Filme in engen Kontakt mit der heißen beweglichen Metalloberfläche gebracht. Unter diesen Bedingungen übersteigt die Aufheizgeschwindigkeit  $10^4$  deg/s, was eine Schätzung der entsprechenden Zersetzungsgeschwindigkeit für Aufheizzeiten in der Größenordnung von 0,01 s ermöglicht.