
**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# A Kinetic Investigation of Thermal Shrinkage of Aromatic Polymers by Thermomechanical Analysis

Hirotaro Kambe[a]; Teiji Kato[a]; Masakatsu Kochi[a]
[a] Institute of Space & Aeronautical Science University of Tokyo, Tokyo, Japan

**To cite this Article** Kambe, Hirotaro , Kato, Teiji and Kochi, Masakatsu(1974) 'A Kinetic Investigation of Thermal Shrinkage of Aromatic Polymers by Thermomechanical Analysis', Journal of Macromolecular Science, Part A, 8: 1, 157 — 164
**To link to this Article: DOI:** 10.1080/00222337408065821
**URL:** http://dx.doi.org/10.1080/00222337408065821

J. MACROMOL. SCI.—CHEM., A8(1), pp. 157-164 (1974)

# A Kinetic Investigation of Thermal Shrinkage of Aromatic Polymers by Thermomechanical Analysis

HIROTARO KAMBE, TEIJI KATO, and MASAKATSU KOCHI

Institute of Space & Aeronautical Science
University of Tokyo
Komaba, Meguro-ku, Tokyo, Japan



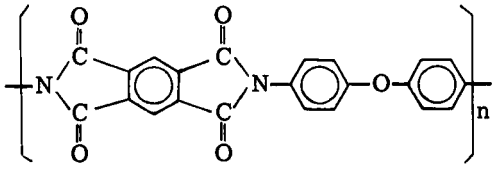
## ABSTRACT

The kinetics of thermal shrinkage of the stretched polypyromellitimide (PI) films, Du Pont Kapton H, were investigated by thermomechanical analysis (TMA) at a constant rate of heating. The two-stage model of extended polymers has been applied to analyze the TMA data. The activation energy of the contraction reaction could be obtained from TMA curves at various heating rates. The one-step shrinkage of the 12.5% stretched PI film gives an activation energy of 10 kcal/mole for the first shrinking. From the 30% stretched sample, the second activation of contraction is 25 kcal/mole, and from 40% sample the third one is 33 kcal/mole. These three contraction reactions are observed successively for the TMA curves for highly stretched samples, and correspond to the various kinds of molecular motion of this special rigid polymer structure, which are also observed in the dynamic mechanical and dielectric properties of the same polymer.

Polypyromellitimide (PI) is a typical thermally stable polymer due to the rigid aromatic and heterocyclic ring structures in its backbone chain. This polymer is able to be cold-drawn in the glassy state, and it shrinks markedly on heating. The thermal shrinkage was investigated thermoanalytically by thermomechanical analysis (TMA) at a uniform heating rate. The activation energies of thermal shrinkage in three stages are estimated by this method.

## EXPERIMENTAL

The sample is the commercial polypyromellitimide film, Du Pont Kapton H, with the basic structure



The specimen was stretched up to 50% under tension with a constant rate of stretching at room temperature. The TMA apparatus, as shown in Fig. 1, was a modified linear expansion apparatus of Rigaku Denki Co. with a balance-type loading and detection units. The TMA specimen was cut from an extended film sample to a thin strip. The change in length of the specimen was recorded continuously in vacuum at the various heating rates under a tensile load of 10 g. The creep of the film was negligible for this load.

## THERMAL SHRINKAGE

The TMA curves at 10°C/min, obtained for cold-drawn samples with different degrees of stretching, are shown in Fig. 2. The ultimate degree of shrinkage increases and the temperature range in which the sample shrinks is broadened with the degree of stretching. Figure 3 shows the temperature derivative curves of the same data. The thermal shrinkage of the 12.5% stretched sample constitutes a one-step reaction with a maximum rate at 90°C. In the 20 and 25% samples, another reaction was observed at 200°C, and more stretched samples show a distinct contraction at 350°C. Therefore, in highly stretched samples, three contraction reactions occur successively.

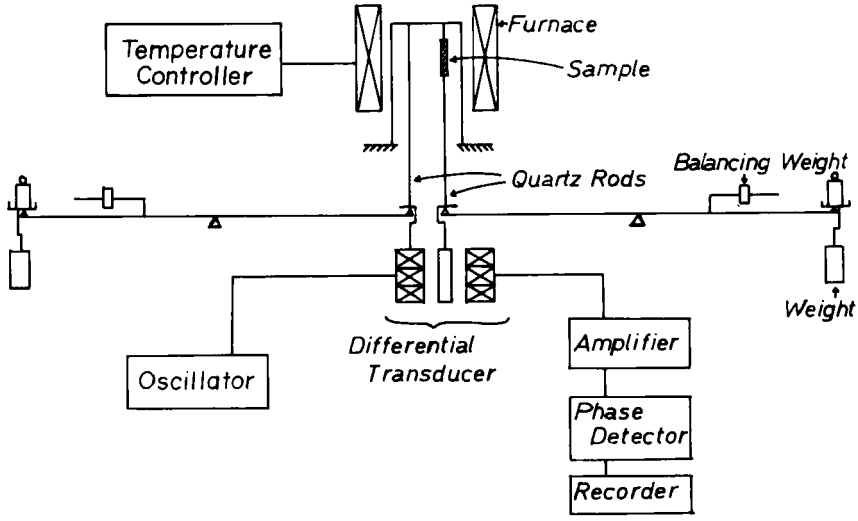



FIG. 1. Schematic diagram of TMA apparatus.

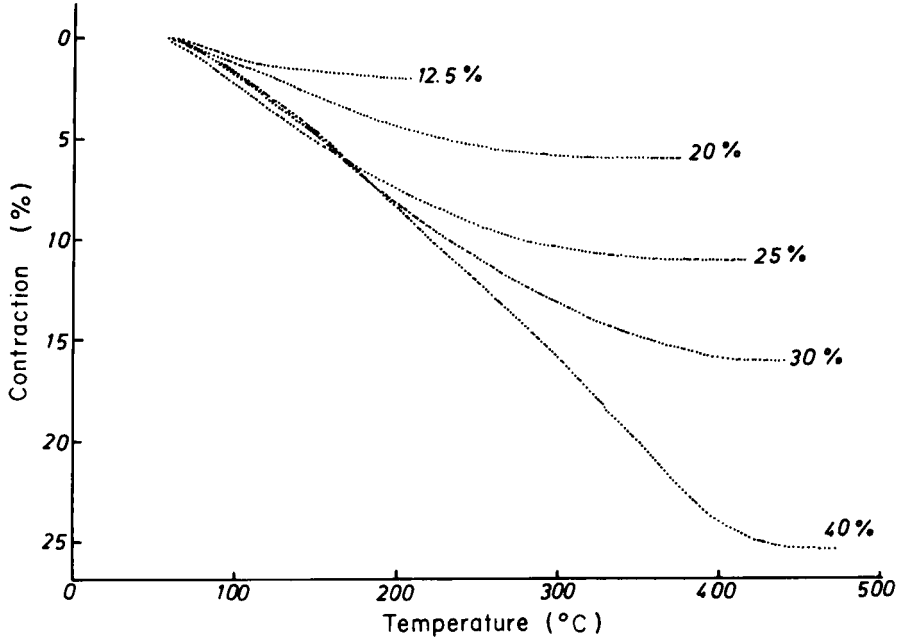



FIG. 2. Thermal contraction of extended PI films with various degrees of stretching.

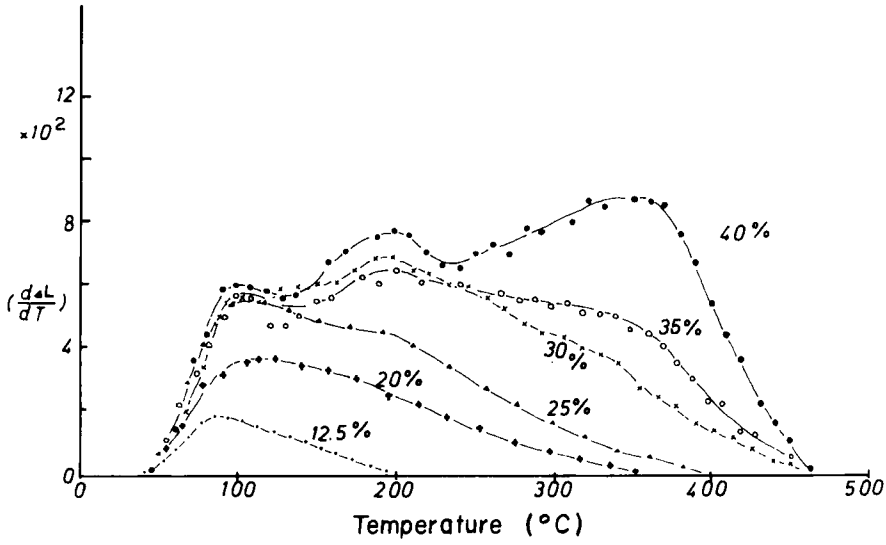



FIG. 3. Temperature derivative curves of thermal contraction.

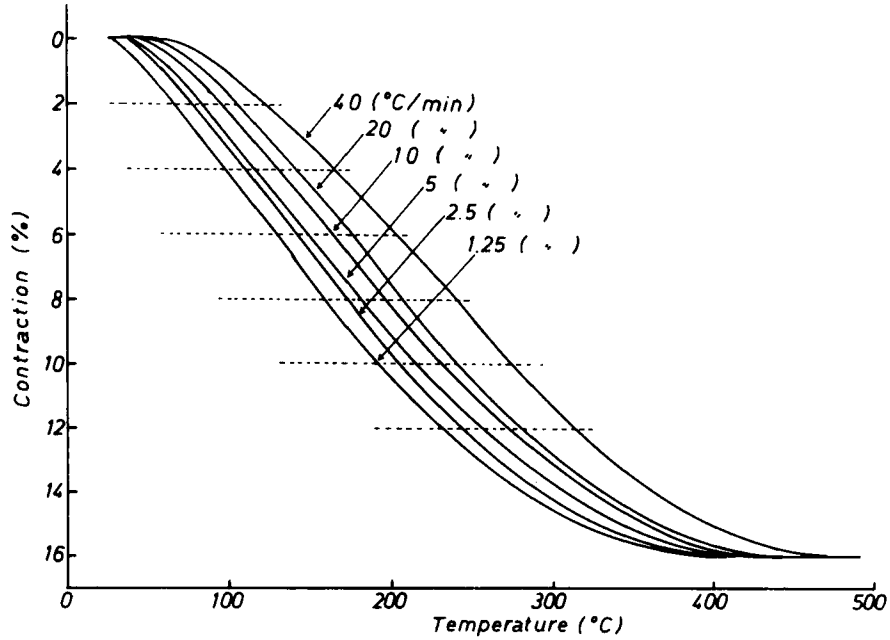



FIG. 4. TMA curves of PI films stretched by 30%.

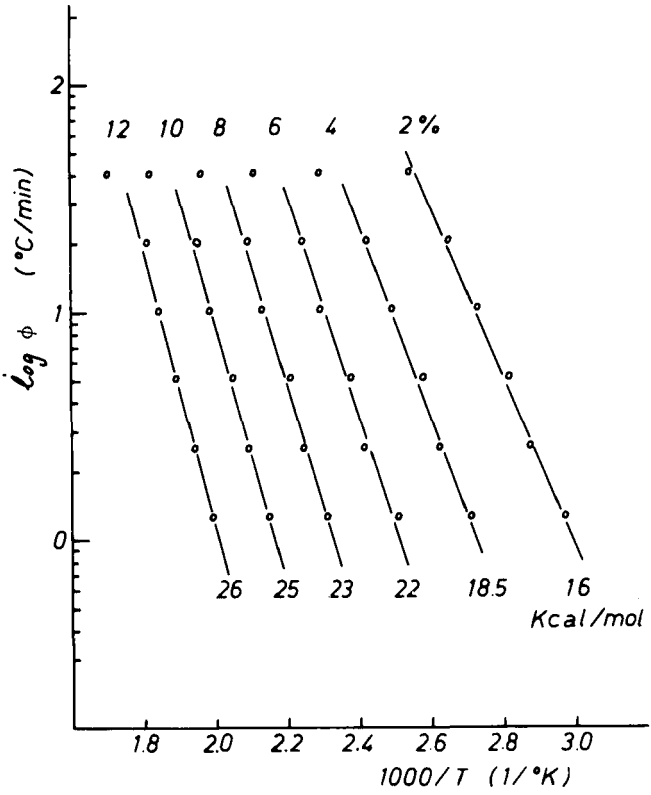



FIG. 5. Kinetic plots for 30% stretched sample.

## THEORETICAL ANALYSIS OF TMA CURVE

A two-state model of the extended molecule is assumed for the analysis of TMA curves. This analysis is to be published elsewhere [1], but a brief summary is given here. We consider the lower $\alpha$ and the upper $\beta$ states to correspond to the normal and extended states of segments. At time t in thermal shrinkage, the number of segment fractions changed from $\beta$ to $\alpha$ is taken as x. The rate of shrinking is expressed by a simplified form with the Arrhenius equation:

$$\frac{dx}{dt} = A \exp\left(-\frac{\Delta E}{RT}\right) g(x) \qquad (1)$$

By integrating, with a uniform heating rate $\phi$ of TMA,

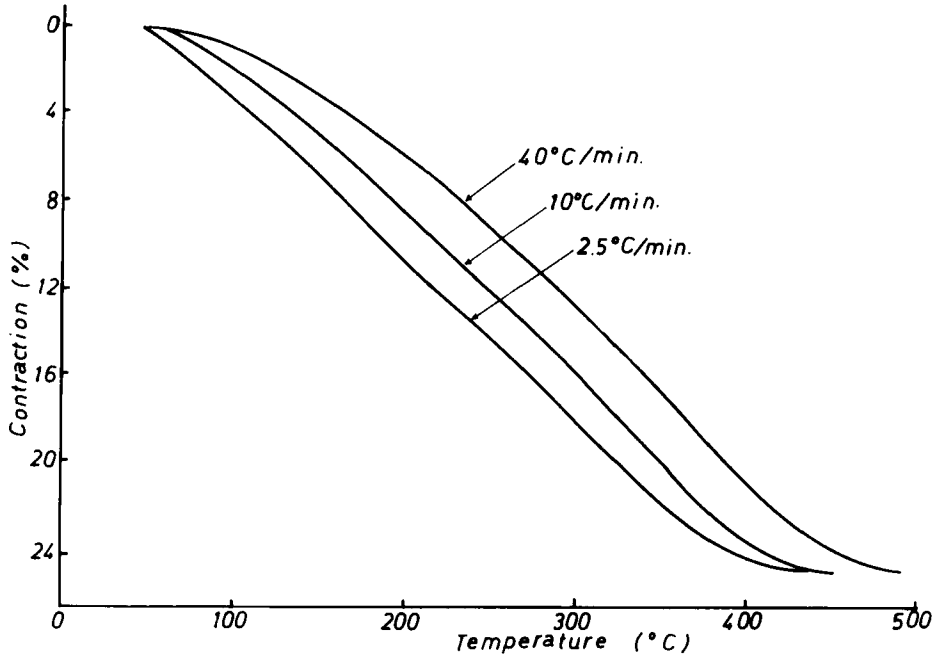



FIG. 6. TMA curves of PI films stretched by 40%.

$$G(x) = \int_0^x \frac{dx}{g(x)} = A\theta \tag{2}$$

where

$$\theta = \frac{1}{\phi} \int_0^x \exp(-\frac{\Delta E}{RT})\, dT \tag{3}$$

Let y be $\Delta E/RT$, and integrating by parts

$$\theta = \frac{\Delta E}{\phi R} [\frac{\exp(-y)}{y} + Ei(-y)] = \frac{\Delta E}{\phi R} P(y) \tag{4}$$

where

$$Ei(-y) = - \int_y^\infty \frac{\exp(-y)}{y}\, dy \tag{5}$$

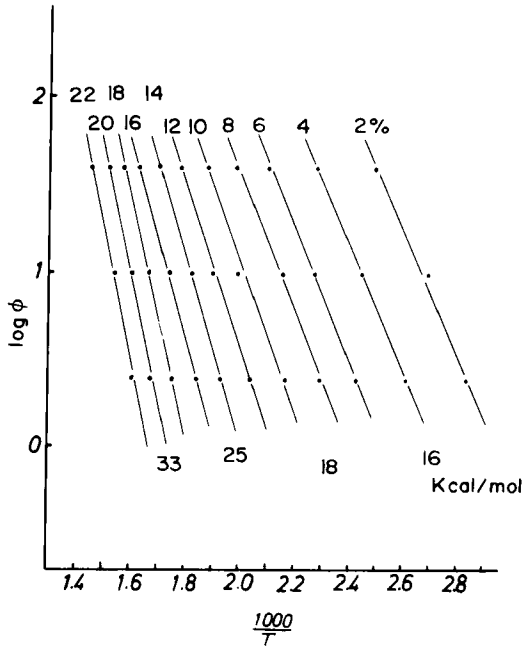



FIG. 7. Kinetic plots for 40% stretched sample.



Equation (4) is very familiar in the kinetic analysis of thermogravimetry. By using Doyle's approximation [2], we obtain

$$\log \phi_1 + 0.4567 \frac{\Delta E}{RT_1} = \log \phi_2 + 0.4567 \frac{\Delta E}{RT_2} = \ldots$$

where $T_1$, $T_2$, etc. are obtained at a degree of contraction from TMA curves for various heating rates $\phi_1$, $\phi_2$, etc. Therefore, if log $\phi$ is plotted against 1/T, we obtain the activation energy of the contraction reaction by the slope of the straight line.

## RESULTS AND DISCUSSION

The kinetic analysis of the TMA curve for one-step shrinkage of 12.5% stretched film gives an activation energy of 10 kcal/mole for this reaction. Figure 4 shows the TMA curves at various heating rates

for a 30% stretched sample. From them, we obtain straight lines for the log $\phi$ vs 1/T curves at various contraction levels, as seen in Fig. 5, which give an activation energy of 25 kcal/mole for the second contraction reaction. The values from lower contraction levels are somewhat lower because of the effect of the first reaction. From Figs. 6 and 7 for a 40% stretched sample, the activation energy is estimated as 33 kcal/mole for the third contraction. These three contraction reactions correspond to the loss maxima in the dynamic mechanical and dielectric measurements [3], and they suggest the existence of different mechanisms of contraction of the rigid polyimide chains.

## REFERENCES

[1] H. Kambe and T. Kato, Appl. Polym. Symp., 20, 365 (1973).
[2] C. D. Doyle, J. Appl. Polym. Sci., 6, 639 (1962).
[3] H. Kambe and T. Kato, Presented at the IUPAC Symposium on Macromolecular Chemistry, Aberdeen, Scotland, September, 1973.