Thermochimica Acta 510 (2010) 122–125

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

# A kinetic investigation and X-ray analysis of thermal shrinkage of diphenyl carbazide

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ARTICLE INFO

*Article history:*
Received 22 May 2010
Received in revised form 30 June 2010
Accepted 2 July 2010
Available online 13 August 2010

*Keywords:*
Thermal shrinkage
Dilatometry
Phase transition

ABSTRACT

The kinetics of thermal shrinkage of diphenyl carbazide (DPC) is investigated above and below room temperature by thermo-mechanical analysis (TMA) at various constant rates of heating. The contraction measurements include two temperature regions. The first lies above 0 °C up to ≈53 °C. The second lies below 0 °C and extended down to −165 °C using liquid nitrogen. Two-stage model is applied here to analyze the TMA data. The activation energy of contraction reaction could be obtained from the TMA curves at different heating rates and found to be 30 Kcal/mol for high temperature thermal shrinkage and 2.7 Kcal/mol for low temperature one. The study reveals the presence of two different characteristic shrinkage anomalies above and below zero temperature for amorphous DPC. This contraction behaviour is attributed to the various kinds of molecular motion of this rigid organic structure. X-ray analysis showed that the shrinkage in amorphous DPC samples ceases behind 50 °C where the amorphous state change to monoclinic crystal structure with $a = 15.037$ Å, $b = 8.242$ Å, $c = 12.760$ Å and $\alpha = \gamma = 90^\circ$ and $\beta = 99.25^\circ$ with a space group P21/A. Also, X-ray analysis showed that the low temperature shrinkage is not due to a crystal structure change but can be attributed to a molecular rearrangement process of DPC molecules.

## 1. Introduction

Development of efficient methods for studying polymorphism in pharmaceutical materials is very important in medical fields and drug applications. The thermal stability of such compounds is very essential [1]. In addition, these compounds have potential for use in manufacturing different electronic components [2]. Diphenyl carbazide $C_{13}H_{14}N_4O$ is one of these compounds. It is also used in analytical chemistry and in the field of differential regulation as photon activated sites on the electron transfer chain [3].

Our previous work on reheated diphenyl carbazide (DPC) showed the polymorphic character of this compound [4,5]. DPC has two phenyl hydrazide groups lying on either side of a crystallographic symmetry plane passing along the bond direction of the carbonyl group. At room temperature, DPC has orthorhombic crystal structure, which melts at ≈162 °C and on subsequent cooling transforms to an amorphous structure. According to De Ranter et al. [6], DPC has an orthorhombic structure with space group pbnm with $a = 5.7171$ Å, $b = 8.4121$ Å and $c = 25.6982$ Å. Crystallization of amorphous substance can obtained by changing various parameters, e.g. temperature, optical radiation, electric field, pressure, impurities. . . etc. [7–10].

Thermo-mechanical analysis (TMA) is a useful and successful technique for studying the kinetics and thermodynamics of change between crystallization and amorphous state. The present work is an extension for our previous work and deals with some shrinkage measurements for DPC above and below 0 °C. The present study aims to reveal what happened in DPC sample during its shrinkage process when subjected to thermal heating action. In addition, the nature of such contraction in DPC samples will study by X-ray analysis.

## 2. Experimental

Amorphous DPC samples are prepared by melting crystalline DPC at 162 °C and then cooled to room temperature. The obtained powder compressed in the form of solid disc 6 mm diameter and 2 mm thickness. The TMA apparatus (dilatometer) is shown in Fig. 1, type Heraus TA 500 manufactured by Germany. The probe resolution of the TMA instrument is 0.1 μm. The TMA instrument is provided by well-controlled electric furnace with temperature regulator such that various heating rates can be used. These heating rates are 0.1, 1, 5, 10. . . 200 °C/min.

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doi:10.1016/j.tca.2010.07.005

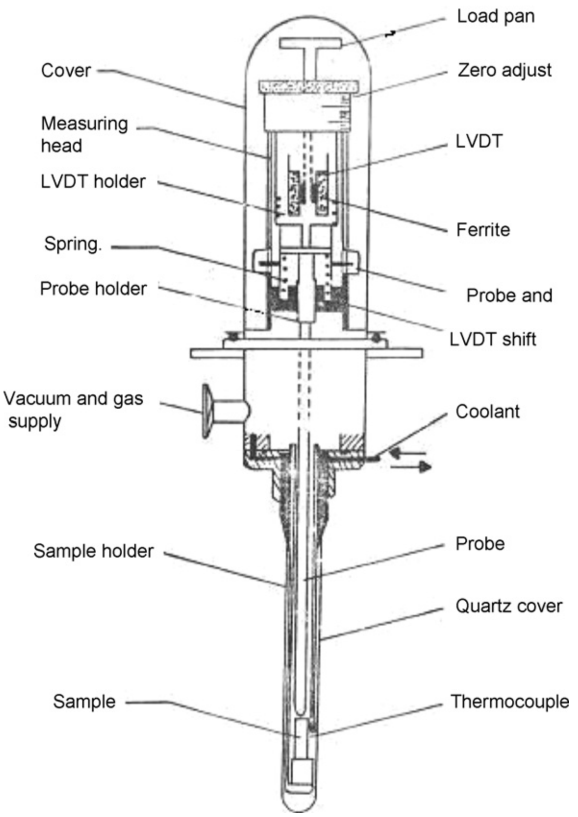

**Fig. 1.** Schematic section of dilatometric unit.

X-ray diffraction analysis is carried out by X-ray diffraction unit (XRD, type Bruker axs $D_8$, Germany) with Cu-$K_\alpha$ ($\lambda = 1.540$ Å) radiation and secondary monochromator in the $2\theta$ range from 20° to 70°. The program which is used in the present study is crysfire 2002 interactive powder indexing support system. Crysfire program assists users to find possible solutions to the powder indexing problems, in the form of complete or partial unit cells.

## 3. Results and discussion

Fig. 2 shows a set of TMA curves obtained for amorphous DPC samples using different heating rates 5, 10... 200 °C/min. A clear shrinkage can be observed. This thermal shrinkage of amorphous DPC constitutes a one-step distinct contraction of DPC during heating. The shrinkage seems to be slow for high heating rates.

In addition, TMA set of curves; Fig. 3 are recorded for amorphous DPC samples below 0 °C and down to −160 °C using liquid nitrogen in the dilatometer unit. Here the shrinkage seems to be relatively slow and extended over a wide temperature range. The effect of different heating rates on the sample shrinkage below 0 °C is shown in Fig. 3. However, here, one can see that fast heating cause slow sample shrinkage.

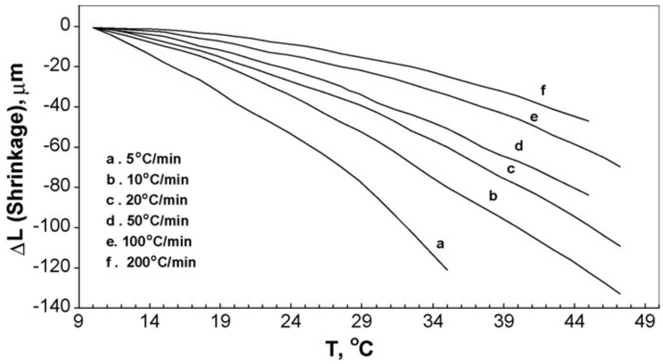

**Fig. 2.** Effect of different heating rates on the characteristic shrinkage of amorphous DPC samples.

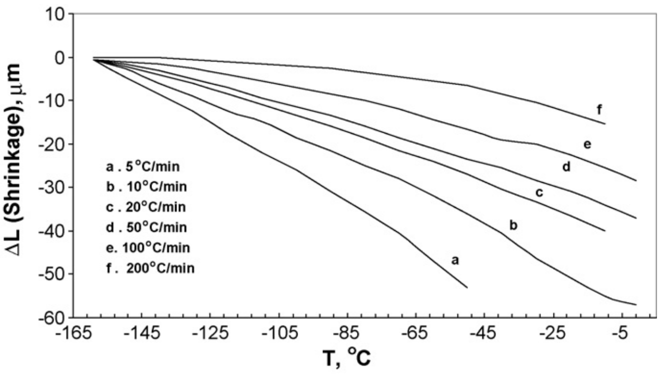

**Fig. 3.** Effect of different heating rates on the low temperature shrinkage of amorphous DPC samples.

### 3.1. Theoretical approach to TMA curve

Consider a two-state model of the DPC molecule for analysis of the TMA curve [11]. Consider the first state is the normal state to be (I) and the second state (II) is that during which shrinkage process takes place. These two states correspond to the normal (I) and shrinkage (II) conditions of amorphous DPC.

At time ($t$) in thermal shrinkage, the number of molecules changed from state (I) to state (II) is taken as ($x$). The rate of shrinkage can be expressed by a simplified form using Arrhenius equation:

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

Let $\alpha$ to be a uniform heating rate of the TMA system, where:

$$\alpha = \frac{dT}{dt} = \text{const.}$$

$$dt = \frac{dT}{\alpha}$$

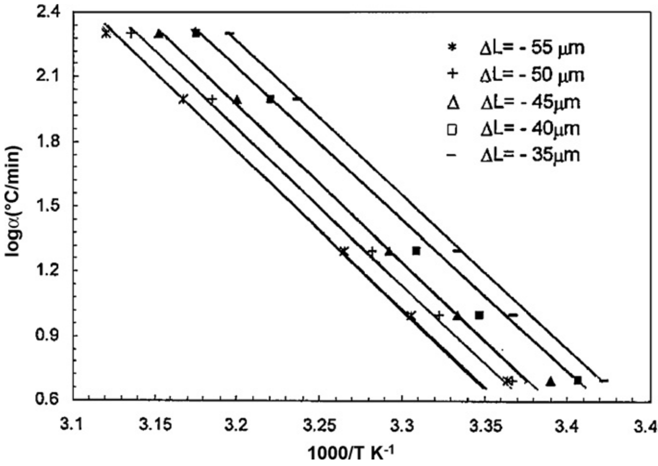

**Fig. 4.** Kinetic plots for the logarithm of rate of heating above zero runs against the reciprocal of temperature.

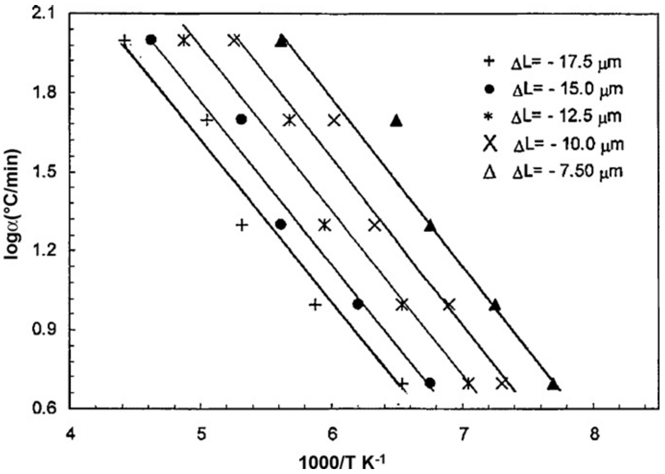

**Fig. 5.** Kinetic plots for the logarithm of rate of heating below zero runs against the reciprocal of temperature.

Let $Y = \Delta E/RT$ and integrating Eq. (1), therefore

$$\int_0^x \frac{dx}{f(x)} = \int_0^x A\exp(-Y)dt = A\beta$$

where

$$\beta = \frac{1}{\alpha}\int_0^x \exp(-Y)dT \tag{2}$$

Integrating by parts, one obtains:

$$\begin{aligned}\beta &= \frac{\Delta E}{\alpha R}\left[\frac{\exp(-Y)}{Y} + E_i(-Y)\right]\\ &= \frac{\Delta E}{\alpha R}P(Y)\end{aligned} \tag{3}$$

where

$$E_i(-Y) = -\int_Y^\infty \frac{\exp(-Y)}{Y}dY$$

By using Dole's approximation [12] in Eq. (3), one obtains:

$$\mathrm{Log}\,\alpha_1 + 0.4567\frac{\Delta E}{RT_1} = \mathrm{Log}\,\alpha_2 + 0.4567\,\frac{\Delta E}{RT_2} = \ldots\ldots$$

or

$$\mathrm{Log}\,\alpha + 0.4567\frac{\Delta E}{RT_1} = \mathrm{const.} \tag{4}$$

Eq. (4) represents a straight line with negative slope ($S$) where

$$S = 0.4567\frac{\Delta E}{R} \tag{5}$$

Therefore, by drawing the relation between log $\alpha$ and $1/T$, one can deduce the activation energy $\Delta E$ required for the shrinkage process of amorphous DPC sample.

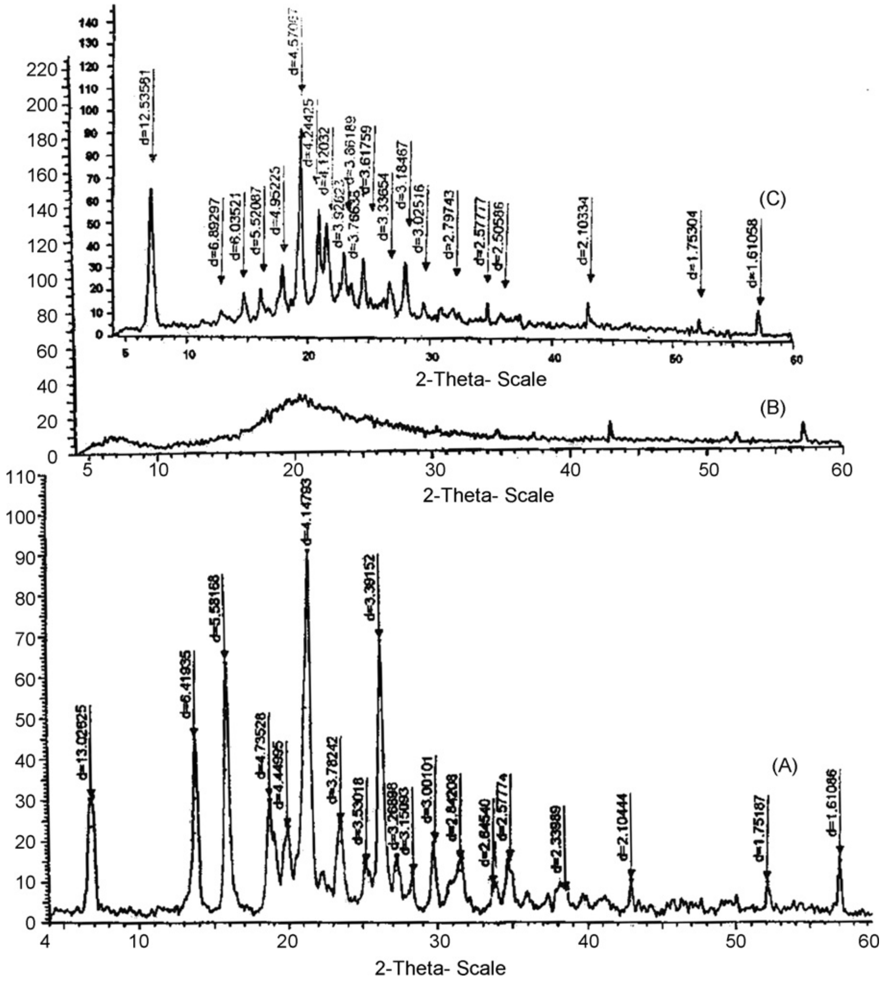

**Fig. 6.** X-ray diffraction analysis in orthorhombic state (A), amorphous state (B) and monodinic state (C).

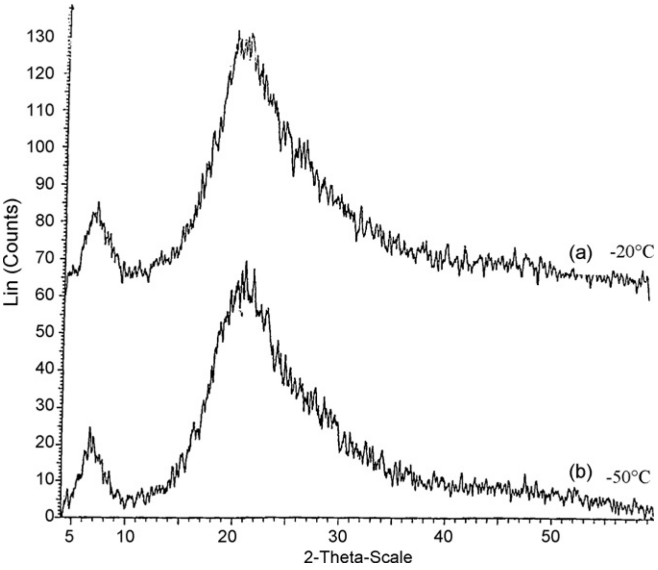

**Fig. 7.** X-ray diffraction patterns of DPC at −20 °C and −50 °C.

Now, in the following steps we will apply all the above to the shrinkage curves obtained. To carry out the kinetic analysis of the TMA curve for one-step shrinkage, a set of the TMA curves utilized to get the relation between log $\alpha$ and $1/T$ at different regions of the shrinkage curve (i.e. at different contraction levels). From these, we obtain a set of straight lines as seen in Figs. 4 and 5. According to this analysis, the activation energies are found to be 30 Kcal/mol for the DPC shrinkage above zero temperature and 2.7 Kcal/mol for that below zero temperature. One can see that the activation energy of shrinkage above zero temperature is more than 10 times of that of below zero temperature. This result suggests the existence of two different mechanisms of contraction of the rigid aromatic DPC structure.

According to our present X-ray analysis Fig. 6A, fresh DPC has orthorhombic crystalline structure at room temperature with $a = 22.698$ Å, $b = 12.862$ Å, $c = 5.097$ Å and $\alpha = \gamma = \beta = 90^\circ$ and space group PMNA. After melting DPC at ≈162 °C and cooled to room temperature, it transforms to amorphous or glassy state structure, Fig. 6B. Reheating of amorphous sample of DPC showed clear shrinkage above 10 °C whatever the heating rate. X-ray structure analysis indicates the presence of another crystal structure, Fig. 6C as the sample temperature exceeds 50 °C. This new crystal structure system is monoclinic with space group P21/A and crystal parameters $a = 15.037$ Å, $b = 8.242$ Å, $c = 12.760$ Å and $\alpha = \gamma = 90^\circ$ and $\beta = 99.25^\circ$. This means that the shrinkage start in the amorphous state of DPC ceases as the sample transforms to the monoclinic structure. In such case rearrangement of DPC molecules takes place and so shrinkage behaviour observed. The thermal activation energy required to achieve this condition is found to be 30 Kcal/mol.

Below zero temperature, using liquid nitrogen, the DPC sample shrinkage, Fig. 3, showed relatively slow rate of shrinkage extended over a wide temperature range. It starts at −160 °C and ceases near 0 °C. The X-ray crystal structure analysis, Fig. 7(a) and (b), at two different temperature regions −20 °C and −50 °C showed no more than clear amorphous structure of DPC sample. This means that the low temperature DPC shrinkage obtained here is not due to molecular crystal structure change but just due to molecular rearrangement. A relatively small thermal energy is required (2.7 Kcal/mol) to perform this condition.

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