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Thermochimica Acta 333 (1999) 147–153

thermochimica acta

Polymorphism and polymorphic transformation of photographic coupler

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Received 18 November 1998; accepted 20 May 1999

Abstract

The polymorphism and the solid-state transformation between two polymorphic forms of a photographic coupler were studied using differential scanning calorimetry. The two polymorphic forms, namely polymorph I (T_m=168°C) and polymorph II (T_m=181°C), were confirmed on melting. The polymorphic transformation of a metastable form into the stable form (I→II) occurred upon a temperature annealing and was found to be monotropical. The isothermal transition appeared to follow a distinct rate relationship. The effects of heating rate on polymorphism and polymorphic transformation were also investigated. It is shown that the polymorphism depended upon the history of heat treatment. The kinetics parameters including rate coefficient, activation energy, and half-time for the transformation indicate that the polymorphic transformation I→II followed a first-order reaction. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polymorphism; Polymorphic transformation; Differential scanning calorimetry; Photographic coupler; Kinetics

1. Introduction

Polymorphism is defined as the ability to exist in different unit cell structures in the crystalline form, originating from a variety of molecular conformations and molecular packings. Since the different modifications have the same chemical composition, they have similar chemical properties; but their physical properties such as density, specific heat, melting temperature etc., which are dependent on the arrangement of molecules in the crystal structure, may be widely different [1].

The phenomenon of polymorphism is commonly encountered in the production of speciality chemicals such as dyestuffs, pharmaceuticals and pesticides. Compounds that can exist in two or more solid-phases (e.g., polymorphs) often offer some distinct advantages in the end use of the product. For example, a metastable solid may be preferred for a pharmaceutical drug, where such a phase can dissolve rapidly in the body [2]. The metastable form of certain photographic chemicals is also preferred for use in film manufacture, because of increased solubility over the more stable phase. However, in other cases the formulation of a product as a metastable phase may be unacceptable because of phase transformation and crystal growth, which could occur during storage and cause product degradation [3].

Couplers are the dye forming materials on photographic film, which are dissolved in an organic solvent and emulsified in the photosensitive formulation. The coupler compounds contain large and complex molecules, which can reveal polymorphism in

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PII: S0040-6031(99)00136-7

photographic processes. They may undergo a crystalline transformation on heating, and then form more stable crystals, or polymorphs. The appearance of polymorphs in the final product can diminish photographic performance [2].

Differential scanning calorimetry (DSC) can measure the energy changes of phases as materials are either cooled or heated. For many years, DSC has been used in the study of fats and fatty acids [4–15]. It is demonstrated that DSC is not only an auxiliary tool for identifying the different polymorphs, but also a powerful technique for investigating the kinetics of transition and crystallisation.

In this paper we describe the confirmation of polymorphs and polymorphic transformation of a photographic coupler by means of calorimetric measurements. The detailed kinetics of the transformation is also discussed.

2. Experimental

2.1. Sample

The photographic chemical coupler was supplied by Kodak (Australasia). The chemical name of the coupler is 5-[2-(2,4-di-*tert*-amylphenoxy)hexanamide]-2-(*p*-cyanophenylureido)phenol. It has a formula $C_{36}H_{46}N_4O_4$ with molar mass of 598.86 g mol^{-1}.

2.2. Differential scanning calorimetry

The thermal measurements were performed on a Perkin-Elmer DSC7, which was calibrated with indium to ensure the accuracy of the calorimetric data. The weighed sample (3–5 mg) was sealed in an aluminium pan, and a similar empty pan was used as a reference.

In this study, two types of thermograms were recorded: (i) the samples were heated to 200°C at heating rates of 2–20°C min^{-1}, (ii) the samples were kept at a suitable temperature for different times, and then heated to 200°C. The scanning rate was 10°C min^{-1} in the second instance. In the first instance, the peak temperatures were obtained from DSC heating curves and were used for determination of possible crystalline phases and the polymorphic transformation. In the second instance, the changes of two peaks with time were used to study the transformation kinetics with temperature.

The endothermic changes appear above the baseline. The peak area is a direct calorimetric measure of the heat absorbed when a particular polymorph melts. Both endothermic and exothermic changes are represented in the endothermic peak when a partial melting of a polymorph accompanied by a conversion or transition to a higher polymorph takes place.

3. Results and discussion

3.1. Effect of heating rate

The heating rate is a decisive parameter, which can determine the polymorph observed and the rate of polymorphic transformation [9]. The DSC curves at different heating rates between 2°C min^{-1} and 20°C min^{-1} are shown in Fig. 1. It is clear that peak I is the main peak at the tested heating rates, while peak II only appears at lower heating rates (2°C min^{-1} and 5°C min^{-1}). The two endothermic peaks (peak I and II) indicate the existence of two possible crystalline phases. The phase with low melting temperature (T_m=167.62°C), corresponds to the melting of polymorph I, and the phase with high melting temperature (T_m=180.76°C) is attributed to the melting of polymorph II. Slow heating prefers the appearance of the

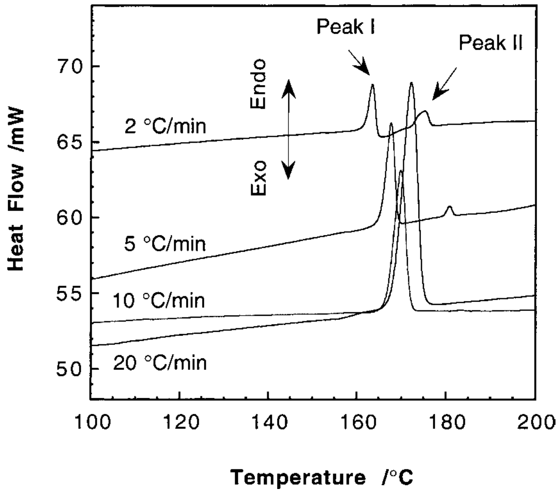


Fig. 1. DSC thermograms of heating at different heating rates.

more stable form (polymorph II). Fast heating produces only melting of the less stable form (polymorph I). The melting temperatures of two peaks increased as increasing heating rates due to thermal lag in the samples.

The existence of endothermic and exothermic peaks depend on the heating rate. Clearly the lower heating rate enables the polymorphic transformation to occur. As seen from the thermogram at a heating rate of 2°C min^{-1} (Fig. 1), the two endothermic peaks corresponded to the melting of polymorphs I and II. The exothermic peak corresponded to the crystallisation from the metastable polymorph I into the stable polymorph II. Polymorph I melted before transforming into polymorph II during heating. The enthalpies of the two polymorphs can be used as quantitative estimates of the amount of polymorphs I and II that undergo melting. Assume that polymorph I is associated with the mechanism of transformation, while polymorph II indicates the extent of transformation for polymorph I→II [9]. A large enthalpy in polymorph I means that a high portion of polymorph I melts before transforming into polymorph II. On the contrary, a small enthalpy means the melting of a small portion. The mechanism of the polymorphic transitions depends on the different modes, either through solid–melt–solid transformation or through solid–solid transformation. It seems that polymorph I may undergo a solid–melt–solid transformation into polymorph II at relatively low heating rates.

3.2. *Effect of annealing temperature and time*

It is obvious that the temperature of annealing plays a dominant role in polymorphic behaviour, the sharp transition temperatures appear to play a minor role [16]. The polymorphic transformation with time and temperature was studied by annealing samples at a temperature range between 145°C and 155°C. The corresponding DSC thermograms, which show the similar effects of time on the two peaks, are displayed in Fig. 2(a)–(d). Initially, polymorph I was predominant. After holding for some time polymorph I decreased, while polymorph II began to increase. Finally polymorph I disappeared, and polymorph II became predominant. It is indicated that the less stable polymorph I undergoes a transformation into the more stable polymorph II under the isothermal conditions below the melting temperature of polymorph I. The growth of polymorph II is at the expense of the melt and recrystallisation of polymorph I.

The time required to complete the transformation decreased with increasing isothermal annealing temperature. The complete transformation occurred after 45 and 95 min holding at 155°C and 150°C, respectively. The effect of time on the melting temperature of polymorph I (Fig. 3) shows that the melting temperatures decreased slightly at the beginning, and significantly decreased at the end. The higher annealing temperature causes the more complete transformation of polymorphs I to II.

The rate of transformation in a crystalline-state from polymorphs I to II is defined as the change in fractional concentration in the powders. The relationship between concentration of polymorph II and time (Fig. 4) shows that the two time regimes are involved in the transformation polymorph I→II, the induction time and the transformation time. The induction time is for the formation of stable nuclei. The transformation time allows the growth of stable nuclei. The ratio of concentrations of two polymorphs versus time, presented in Fig. 5, gives a direct observation of the transformation. The plot of $C(\mathrm{I})/C(\mathrm{II})$ is separated into the two parts by the half-time and each part seems to be remarkably linear. The slope of the plot is steeper before the half-time; while it is moderate after the half-time. The transformation rate is variable and depends on the temperature and time. The relationship of the half-time ($t_{1/2}$ min) with annealing temperature (T°C) is given by Eq. (1). According to Eq. (1), the half-times are concluded to be 154.9, 61.6, 35.5 and 24.6 min, corresponding to 145°C, 150°C, 153°C and 155°C.

$$\log t_{1/2} = -0.08T + 13.79. \tag{1}$$

Two separate rate coefficients involved in the transformation (as seen from Fig. 5) may mean that the transformation is controlled by the faster rate in initial state, and finally it is controlled by the slower rate. The former process seemed to be a activated-control process, while the latter process was a concentration-dependent process. A transformation pathway of polymorphs I to II on heating is summarised in Scheme 1. The solid lines represent the irreversible transitions. The transformation occurring only in one direction

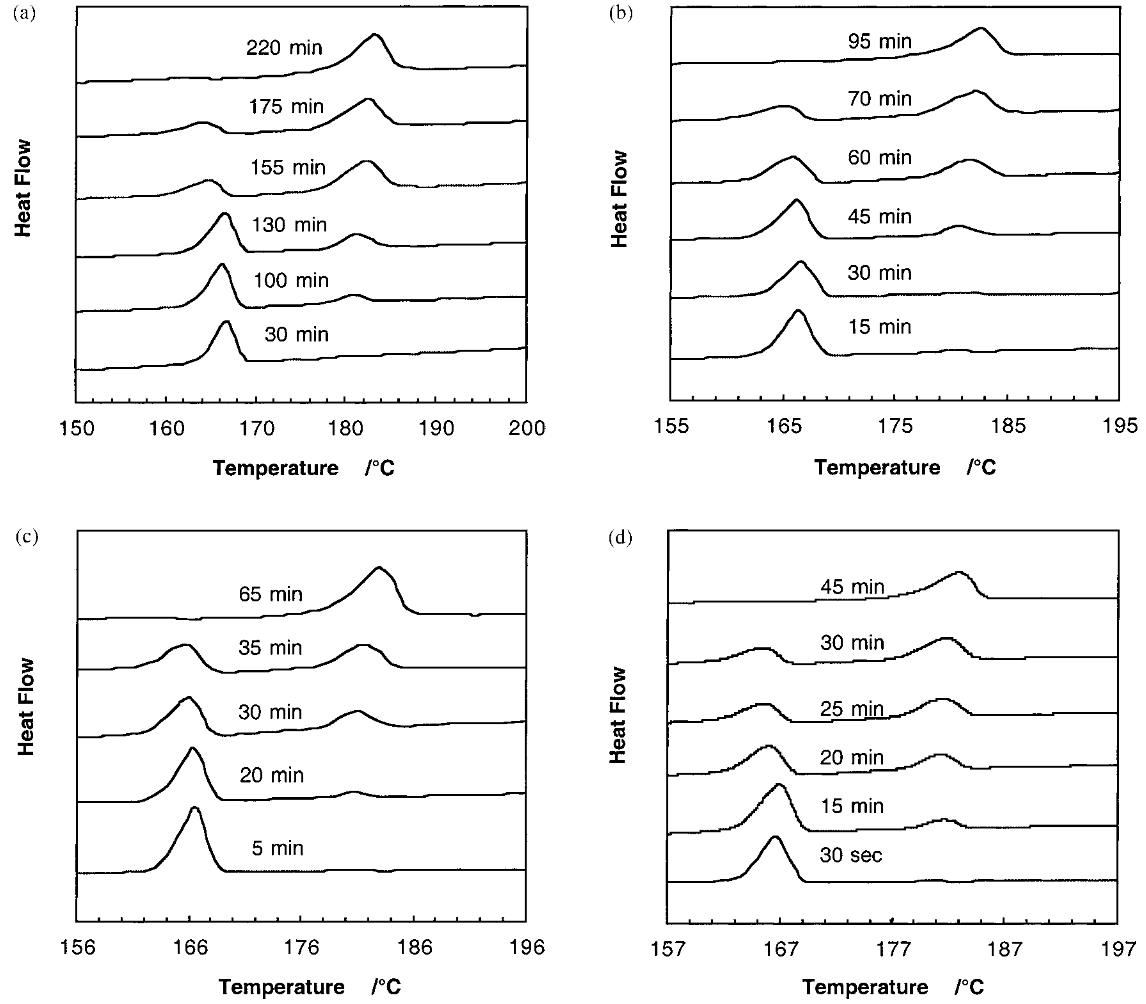
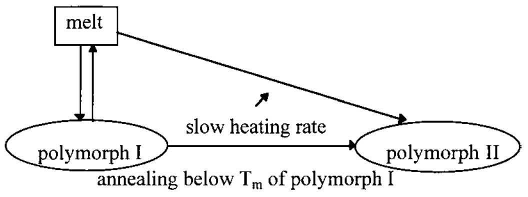


Fig. 2. The transformation DSC thermograms of annealing: (a) 145°C, (b) 150°C, (c) 153°C, and (d) 155°C.

(polymorph I→II) means that polymorph II is thermodynamically stable throughout the range of its existence, i.e., polymorphism is monotropic.



Scheme 1. A transformation path for polymorph I to II

3.3. The overall transformation kinetics

The isothermal phase transformation is represented by plotting the fraction transformation (X) as a function of time and temperature, i.e., temperature(T)–time(t)–transformation(T) TTT diagram, a point on the diagram represents a certain value of transformed fraction $X(t,T)$. The TTT diagram is commonly used for describing solid–solid phase transformation in metallurgical industries, especially for the purpose of heating treatment [17]. Fig. 6(a) presents the percentage of polymorph II as a function of time at various temperatures. X is just the mass fraction of

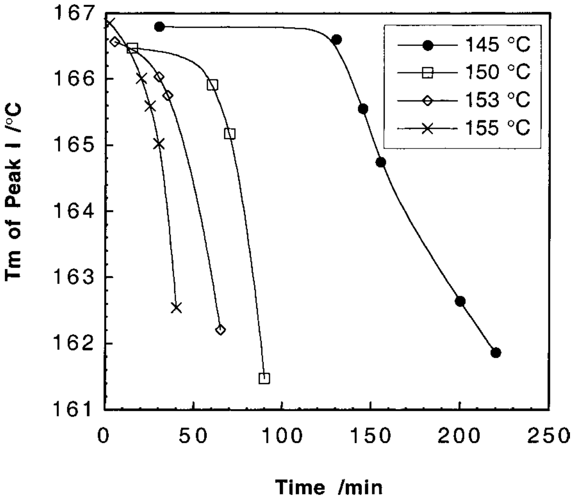


Fig. 3. The relationship between the melting temperature of polymorph I with time.

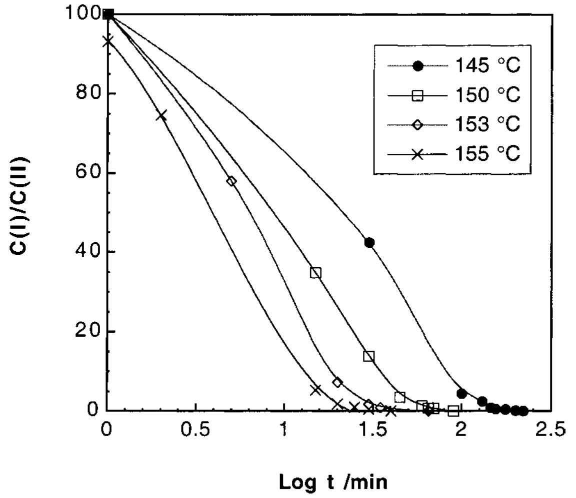


Fig. 5. The plot of $C(\mathrm{I})/C(\mathrm{II})$ as a function of time at various temperatures.

polymorph II at any time, which varies 0–1 from the beginning to the end of the transformation. The TTT diagram for the phase transformation, obtained from Fig. 6(a), is displayed in Fig. 6(b). Usually 1% of polymorph II corresponds to the start of the transformation. The end of the transformation is taken as the time to transform 99% of the polymorph I→II. The area to the first left curve (1%) corresponds to polymorph I. Any point to the far right (99%) of these curves represents polymorph II. Between the two curves is a region of polymorphs I and II with the relative ratios of these two constituents.

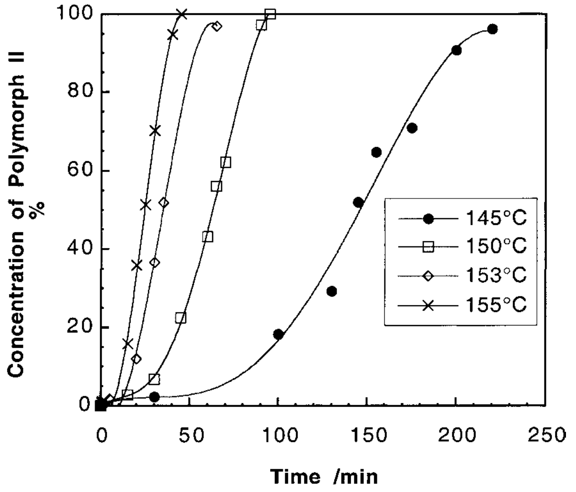


Fig. 4. The concentration of polymorph II at various temperatures during transformation I→II.

The enthalpies of two polymorphs, as measured from the DSC curves at 155°C, were plotted versus time (Fig. 7). It is clear that the enthalpy values in peak I decreased with increasing time, while the enthalpy values in peak II increased. The measurements at 145°C, 150°C and 153°C, not shown in here, give the similar dependencies of the enthalpies on time. The crossing point of the enthalpies of the two polymorphs corresponds to the half-time for the transformation. The half-times for the polymorphic transformation I→II are found to be 146.11 min for 145°C, 62.76 min for 150°C, 34.40 min for 153°C and 24.06 min for 155°C. These results are in agreement with those from Eq. (1). The lower the temperature, the longer the half-time for the transformation.

The kinetics parameters, including the rate coefficients (k), are shown in Table 1 for their variation with

Table 1
Kinetic parameters of transformation polymorph I→II

Temperature, T (°C)	Half-time, $t_{1/2}$ (min)	Rate coefficient, $k\times10^4$ (s^{-1})
145	146.11	0.79
150	67.76	1.84
153	34.40	3.36
155	24.06	4.80

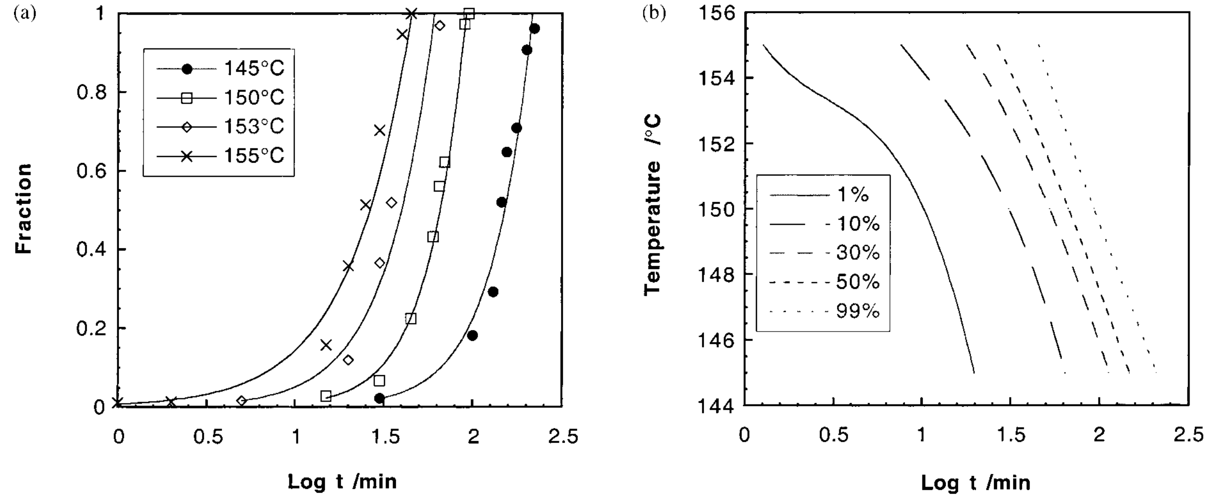


Fig. 6. (a) The percentage transformation versus time at various temperatures. (b) The TTT diagram for the polymorphic transformation I→II.

temperature. The rate coefficients increase upon increasing annealing temperature, i.e., a rapid transformation is associated with large value of k.

$$k = A \exp(E_a/RT). \qquad (2)$$

Eq. (2) describes the effective activation energy E_a varying with temperature for a transformation. In the equation, R represents the Boltzmann constant and T is temperature in K. In general, this activation energy is a combination of the activation energies for nucleation and growth, and is determined by the particular kinetic process involved. An Arrhenius plot of the logarithm of the rate coefficient versus the reciprocal of the absolute temperature (K^{-1}) is shown in Fig. 8. A straight line indicates that the polymorphic transformation between two polymorphs follows the law of the first-order reaction, which the activation energy is 269.56 kJ mol^{-1}.

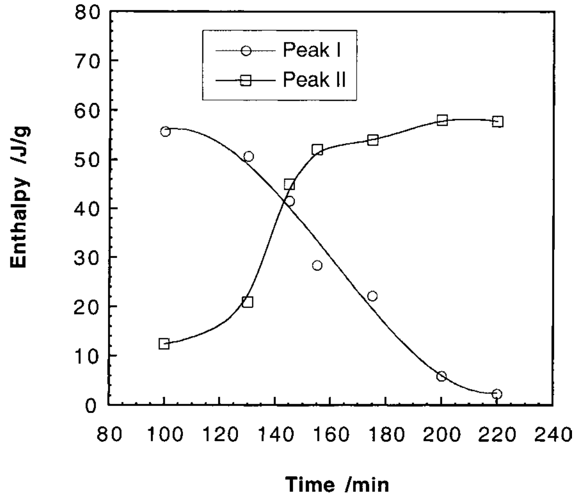


Fig. 7. The enthalpy values of two polymorphs as a function of time at 155°C.

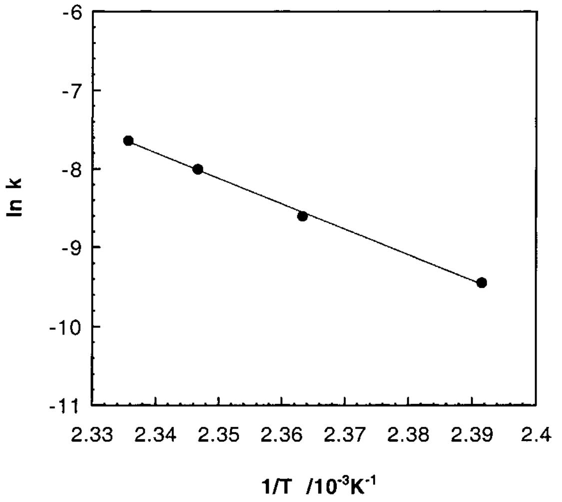


Fig. 8. The Arrhenius plot for the polymorphic transformation.

Acknowledgements

This work is supported by a scholarship supplied by Kodak (Australasia). We would like to acknowledge Kodak (Australasia) for permission of publication of this paper.

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