

Thermoanalytical study of the cure characteristics of a main-chain liquid crystalline oligoester Model-free approach to kinetic analysis of non-isothermal data

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Abstract

The curing behavior of a liquid crystalline oligoester (LCO), based on 4,4'-diacetoxybiphenyl and sebacic acid in presence of a mixture 75:25 of diglycidyl terephthalate and triglycidyl trimellitic acid ester (D&TGE), as a curing agent, was studied by non-isothermal differential scanning calorimetry (DSC). The analysis of non-isothermal data was carried out using the model-free isoconversional method. Activation energy as a function of extent of conversion, α , have been calculated by the Friedman technique. It shows a constant value of 95.5 ± 2.5 kJ/mol, in the $0.27 < \alpha < 0.68$ range. The activation energy, out of the above-mentioned interval, is strongly dependent on the degree of extent of the curing reaction.

The $y(\alpha)$ and $z(\alpha)$ plots, which were obtained through transformation of DSC data, are not completely identical at a variety of heating rates. It indicates that the kinetic process does not follow a single-step curing reaction model and a multi-step process controls it during curing. To approve the non-isothermal analysis result, we carried out further, depolarizing transmittance measurements and optical microscopy observations on the stoichiometric mixture of LCO/D&TGE during curing, at various heating rates. The results of these experiments exhibit that the kinetic process of the investigated system is strongly influenced by altering the mesomorphism features of the sample.

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1. Introduction

Liquid crystalline thermosets (LCTs) have been investigated by several groups since the early 1970s [1–39]. These materials have desirable properties because of the combination of a polymer network and a liquid crystal [17–25]. LCTs suggest many potential advantages over liquid crystalline thermoplastics and conventional isotropic networks, for example, they can improve the mechanical properties in transverse direction to the chain orientation [12,19,26,30,32,35]. LCTs are required to have both mesogenic structure and cur-

able functional groups. These reactive groups, by which the LC molecules are generally functionalized, consist of diglycidyl ether [13,19–28,35], triazine [14], maleimide [8,9], nadimide [8,9], cyanate [18], isocyanate [37] and vinyl [5–7,10,11,15]. The molecular orientational order of polymers is preserved through thermal or photo cross-linking of these functional groups. In general, stilbene, benzoate and biphenyl groups were employed for the cores of the mesogenic moieties of LCTs. To diminish the melting points of LCTs, flexible spacer may be used between two mesogenic groups or between mesogenic group and a functionalized reactive site.

On the other hand, semiflexible homopolyesters having rigid and flexible segments in the repeating unit are attractive because the transition temperatures can be controlled

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by varying the number of methylene unites in the flexible segments [40,41]. Among the semiflexible homopolyesters, the polyesters based on 4,4'-dihydroxybiphenyl and aliphatic acids is well known and its liquid crystalline behavior was extensively studied [42–47]. Much of the research activity involving this polyester till now has focused on development of high strength, high-temperature resistant fibers and thermoplastics. To the best of our knowledge, the potential of using the low fractions of these polyesters as LCTs has not been considered so far. On the contrary of these types of polymers, LC diepoxides are considered more than others. It is because of the high reactivity of the epoxy group which may offer ready processing at readily controlled cross-linking rates. The synthesis and the curing of LC diepoxides with a variety of mesogenic [28] and non-mesogenic [16,19,20–26] cross-linking agents have been studied by many authors. Up to now, the use of non-mesogenic epoxy compounds as curing agent for LCTs has not been reported. With introducing the curing agents containing epoxy groups, it may be possible to use LCTs which are functionalized with carboxyl groups.

The process of curing reaction of the mixture of a thermotropic oligoester and a non-mesogenic curing agent, accompanied by liquid crystalline domain formation could be of great importance from the properties and economical point of view. As is known, there is a close relationship between network structure and chemo-physico-mechanical properties of a cross-linked material. It has been reported that the overall curing reaction kinetics is strongly affected by the presence of a liquid crystalline phase [16,27,33,39]. In fact, there is a competition between chemical and physical network formation. In this regard, the ending properties of the cured LCTs rely on this competition. In spite of the fact that liquid crystalline thermosets have gained increasing interest as advanced materials, until recently the possible utility of these materials as binder in powder coating technology appears to have been neglected [48]. To have a suitable liquid crystalline thermoset as a component in binder system in powder coatings, one needs to evaluate the influence of cure reaction and mesophase formation on each other. In this paper we studied the curing behavior of a LCT based on 4,4'-dihydroxybiphenyl and sebacic acid, in the presence of a mixture of di- and trifunctional diglycidyl ester as the curing agent. The reaction between the epoxy and acid functional groups is the most important curing reaction used in practice for cross-linking of thermosetting powder coatings [49]. The cure kinetics of the studied system was elucidated by non-isothermal differential scanning calorimetry (DSC) at different heating rates. The experimental results have been studied using isoconversional method. Recently, the model-free kinetics of epoxy cure has been considered as an interested subject by Vyazovkin et al. [50–53]. It is disappointing that DSC exotherms, seemingly caused by cross-linking reactions, interfered with the recognition of liquid crystalline phase transitions during curing. Therefore, we employed a novel technique to follow the variation of mesomorphic be-

havior of the system with cure progression. It was made on a depolarizing transmittance apparatus.

2. Experimental

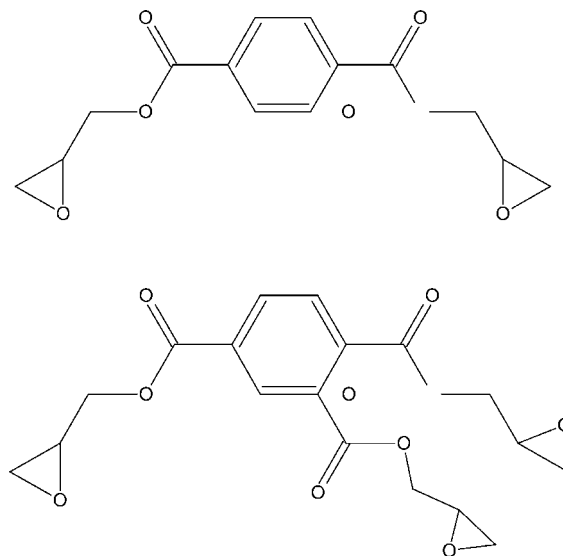
2.1. Materials

4,4-Dihydroxybiphenyl mp 275–280 °C, as the rigid monomer was from Merck-Germany and recrystallized from methanol before use. Sebacic acid mp 135–137 °C, as the flexible monomer purchased and other chemical reagents were purchased also from Merck-Germany and used as received. The curing agent was a mixture of di- and trifunctional glycidyl ester, diglycidyl terephthalate and triglycidyl trimellitic acid ester, in the ratio of 75:25 giving a functionality of 2.3, with epoxy equivalent weight of 141–154 g/eq. and mp 90–102 supplied by Vantico-Switzerland. The chemical structure of curing agent is given in Scheme 1.

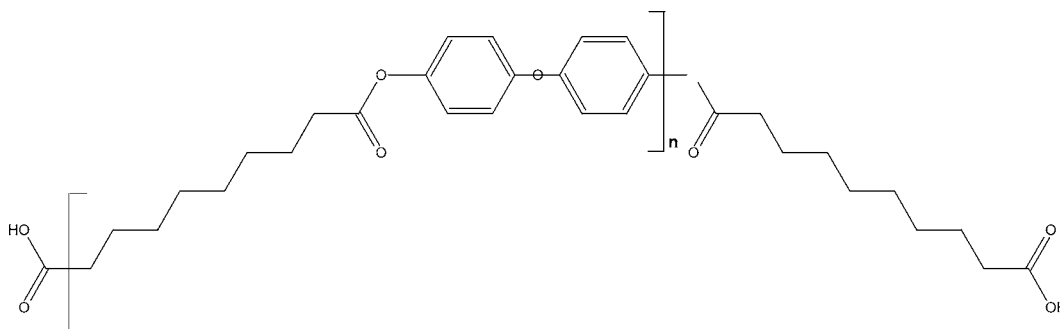
2.2. Polymer and curing condition

Poly(4,4'-biphenyl sebacate) was prepared by melt-transesterification using non-equimolar amounts of 4,4'-diacetoxybiphenyl and sebacic acid (molar ratio of 1:2, respectively) according to the method which was adapted from Asrar et al. [42] procedure for making main-chain liquid crystalline high polymers. A two-fold excess of sebacic acid was used to suppress molar mass and obtain a carboxylated linear oligoester. The synthesized oligoester was well purified and dried. The chemical structure of that is given in Scheme 2.

The acid value of the sample was measured using modified standard techniques [54] and it was 123.32 mg KOH/g_{oligoester}. The inherent viscosity of the sample was 0.1012 dL/g, determined by an ubbelohde viscometer



Scheme 1. Chemical structure of curing agent.



Scheme 2. Chemical structure of liquid crystalline oligoester.

at 25 °C by using 0.5 g/dL solution in a 60/40 (w/w) mixture of phenol and tetrachloroethane. The transition temperatures of the sample were measured by differential scanning calorimetry in a temperature range 25–250 °C by using a DSC (TA Instrument 2010 model) purged with nitrogen. Indium was used as thermal standard for temperature and enthalpy calibration. In order to enhance the thermal contact between the samples and the heat source and omit the thermal history effects, the samples in the form of a powder were firstly melted to take up the shape of the aluminum sample pan, then cooled at 10 °C/min and after that heated again with a rate of 10 °C/min. Optical microscopic studies were performed with a Leica DMR polarizing microscope equipped with a hot stage (linkam LTS 350). The variations of the depolarizing transmittance of the polyester with temperature were obtained through the measurements of the exposure time using a Leica MPS 60 automatic exposure time measuring unit attached to the microscope. Reciprocal of this time was anticipated to be proportional to the intensity of light transmitted through the sample. The block diagram of the system which was used for this mean is shown in Fig. 1.

Depolarizing transmittance method has already been used to investigate the kinetics of phase transitions for main-chain liquid crystalline polyesters [55]. This technique is based on the equation which was proposed by Mckie and Mckie [56]. They considered a monodomain sample viewed between crossed polars in monochromatic light. The formula for transmitted intensity was derived as follows:

$$\frac{I}{I_0} = \text{Sin}^2[2\theta] \text{Sin}^2 \left[\left(\frac{nd}{\lambda} \right) (n_2 - n_1) \right] \quad (1)$$

where, I is the depolarized light intensity which is transmitted through sample and I_0 is the polarized light intensity which is incident on the sample, its value can be considered constant according to the adjustments of the apparatus. λ is the wavelength of light, d is the thickness of specimen, $\Delta n = (n_2 - n_1)$ is the birefringence and θ is the angle between the vibration direction in specimen and the vibration direction of transmitted light. However the liquid crystalline oligoester (LCO) which was prepared in this work is not aligned and it is polydomain, so we consider the intensity of the transmitted depolarized light through the sample in the form of summa-

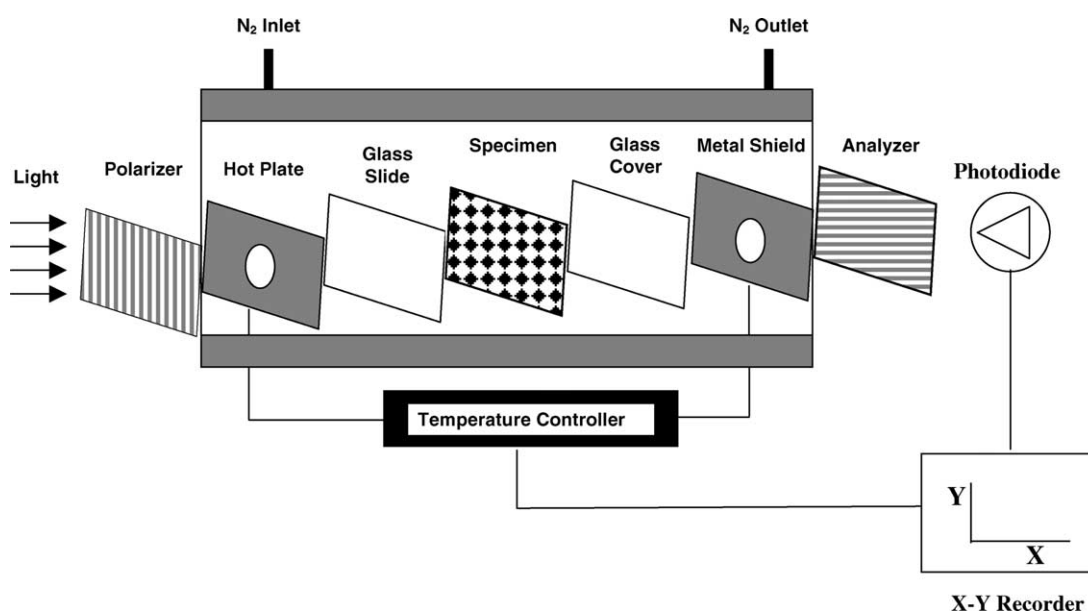


Fig. 1. The schematic diagram of experimental apparatus for the measurement of temperature dependence of depolarizing transmittance of the specimens.

tion of the depolarized light flux which transmitted through each domain.

$$\begin{aligned} \left(\frac{I}{I_0}\right)_{\text{total}} &= \sum \left(\frac{I}{I_0}\right)_i \\ &= \sum \left\{ \sin^2[2\theta_i] \sin^2 \left[\left(\frac{nd}{\lambda}\right) (n_2 - n_1)_i \right] \right\} \quad (2) \end{aligned}$$

In this way, $(I/I_0)_{\text{total}}$ could be considered as a criterion for the birefringence and consequently as a measure for liquid crystallinity of the samples.

The curing thermal behavior was studied by means of above-mentioned model differential scanning calorimeter on 5 mg sample encapsulated in standard pans in a nitrogen atmosphere. Experiments were performed under non-isothermal conditions at four heating rates of 1, 2, 4 and 6 °C/min. The reactants were accurately weighted and mixed together in stoichiometric portion prior to the measurements.

3. Kinetic approach

The heat flow measured in DSC is proportional to both overall heat release and the rate of the kinetic process [57,58]:

$$\frac{d\alpha}{dt} = \frac{\varphi}{\Delta H} \quad (3)$$

where ΔH is the enthalpy of the curing reaction and φ is the heat flow.

The kinetics of consecutive and competing chemical reactions are usually expressed by:

$$\frac{d\alpha}{dt} = \sum_{P=1}^{P=q} f_P(\alpha) k_P(T) \quad (4)$$

We will make a primarily assumption in the kinetic treatment of our curing process. This assumption is given as following:

The rate of the kinetic process, for non-isothermal conditions, once the temperature varies with time with a constant heating rate $\beta = dT/dt$, is described as a result of temperature dependent rate constant $k(T)$. Additionally, from the concept of the variable apparent activation energy with conversion proposed by Vyazokin [59,60], the mechanism can be predicted to be complex and multi-step. To verify this, it is possible to show that the system does not obey a single-step overall model function. According to the later model we can write:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \times f(\alpha) \times k(T) \quad (5)$$

where $k(T)$ is the rate constant, $f(\alpha)$ is the overall reaction model and α is the extent of reaction. The rate constant in Eq. (5) follows Arrhenius form:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature.

It seems reasonable that to evaluate the above consideration, one must determine the model independent value of the activation energy. An appropriate method is the use of the isoconversional analysis. To determine the activation energy of the curing process, we use the Friedman isoconversional method [61]. Under non-isothermal conditions, Eqs. (5) and (6) may be combined and rewritten in its logarithmic form to obtain Eq. (7). E_a is calculated from the slope of $\ln(d\alpha/dt)$ versus $1/T$ plot from the same value of α (Eq. (8)):

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln[A_\alpha \times f(\alpha)] - \frac{E_a}{RT} \quad (7)$$

$$\left[\frac{d \ln(d\alpha/dt)}{d(1/T)}\right]_\alpha = -\frac{E_a}{R} \quad (8)$$

This procedure can be repeated for various values of α for both isothermal and non-isothermal data.

Budrugaec et al. [62] have presented some problems concerning the evaluation of the activation energy from non-isothermal data for reactions with activation parameters dependent on the degree of conversion. They have found out that if activation energy depends on conversion, Friedman method, which uses directly the equation of the reaction rate, can be used as a recommended procedure. However, this method known to be noise sensitive.

The isoconversional methods can be applied without knowledge of true $f(\alpha)$ function. But this function must be invariant for all isothermal temperature and heating rates. If this basic assumption is not fulfilled, an apparent E_a value would be calculated, which differs from the actual value. The invariance can be examined by the method which is offered by Málek [57,58]. He has suggested that $f(\alpha)$ is proportional to the $y(\alpha)$ and $z(\alpha)$ functions that can simply be obtained by a simple transformation of DSC data. In non-isothermal conditions these functions are defined as:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) \times e^{E_a/RT} \quad (9)$$

$$z(\alpha) = \psi\left(\frac{E_a}{RT}\right) \times \left(\frac{d\alpha}{dt}\right) \times \frac{T}{\beta} \quad (10)$$

where $\psi(E_a/RT)$ is the expression of the temperature integral. It was suggested that $\psi(E_a/RT)$ may be accurately estimated by means of the fourth rational expression of Senum and Yang [63,64].

$$\psi(x) = \frac{(x^3 + 18x^2 + 88x + 96)}{(x^4 + 20x^3 + 120x^2 + 240x + 120)} \quad (11)$$

where x is reduced activation energy (E_a/RT). For practical reasons the $y(\alpha)$ and $z(\alpha)$ functions are normalized within the (0,1) ranges.

If there are considerable differences in the shape of the $y(\alpha)$ and $z(\alpha)$ functions then, we can conclude that the assumption

in which the reaction model was considered to be a single-step model has not fulfilled.

4. Results and discussion

A stoichiometric mixture of the carboxylated polyester with mesogenic segments and diglycidyl terephthalate and triglycidyl trimellitic acid ester (mixture of 75:25) was cured under non-isothermal conditions at various heating rates (1, 2, 4 and 6 °C/min). Thermal and mesomorphic properties of the oligoester were examined using DSC as well as a polarized microscope at heating rate 10 °C/min. DSC thermograms of the oligoester are displayed in Fig. 2. The heating curve shows multi endothermic peaks. The cooling curve illustrates two exothermic peaks: one at lower temperature is due to freezing ($T_f = 69.73$ °C) and the other at higher temperature to anisotropization ($T_i = 196.69$ °C). The complicated behavior of the DSC scan of the sample during heating and the existence of two exotherms during cooling of that, has already been observed for some segmented-chain crystalline polymers with low molecular weight by Sung et al. [65]. To clarify more precisely the transition temperatures and reveal the behavior of liquid crystallinity of the sample during heating, we carried out depolarizing transmittance measurement and optical microscopic observation for it with a rate of heating of 10 °C/min. The results of these experiments are shown in Figs. 3 and 4, respectively. As can be seen in Fig. 3, the sample presented a crystalline state up to 95 °C, then the transmittance starts to increase at around the DSC peak temperature of 100–105 °C and the oligoester began to transform to liq-

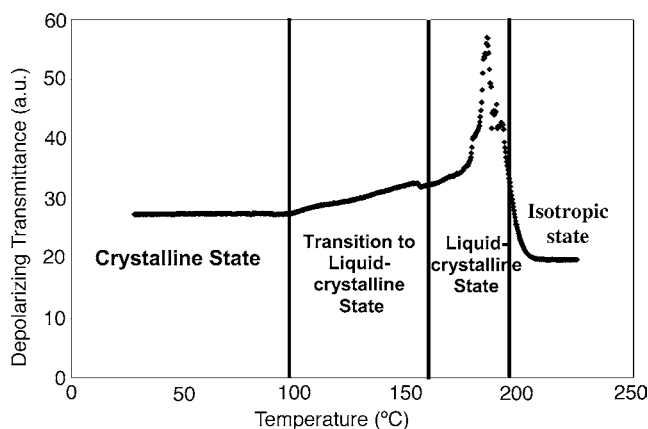


Fig. 3. Temperature dependence of the depolarizing transmittance curve of the liquid crystalline oligoester (LCO) taken at 10 °C/min.

uid crystalline state. This transformation has been completed around 160 °C, while above 180 °C (c.f. DSC peak) the transmittance reaches to a maximum and then decreases rapidly and at about 205 °C the liquid crystalline state completely disappears. The corresponding phase transitions during heating from crystalline state to mesomorphic phase and also from mesophase to isotropic state were presented in Fig. 4. As illustrated for the uncured liquid crystalline oligoester in Fig. 4, the birefringent texture is apparent. Elongated particles, reminiscent of the batonnets seen in conventional smectics, are observed for the liquid crystalline oligoester by polarized light microscope.

The value of thermodynamic quantities relating to the non-isothermal curing DSC curves of the stoichiometric mixture

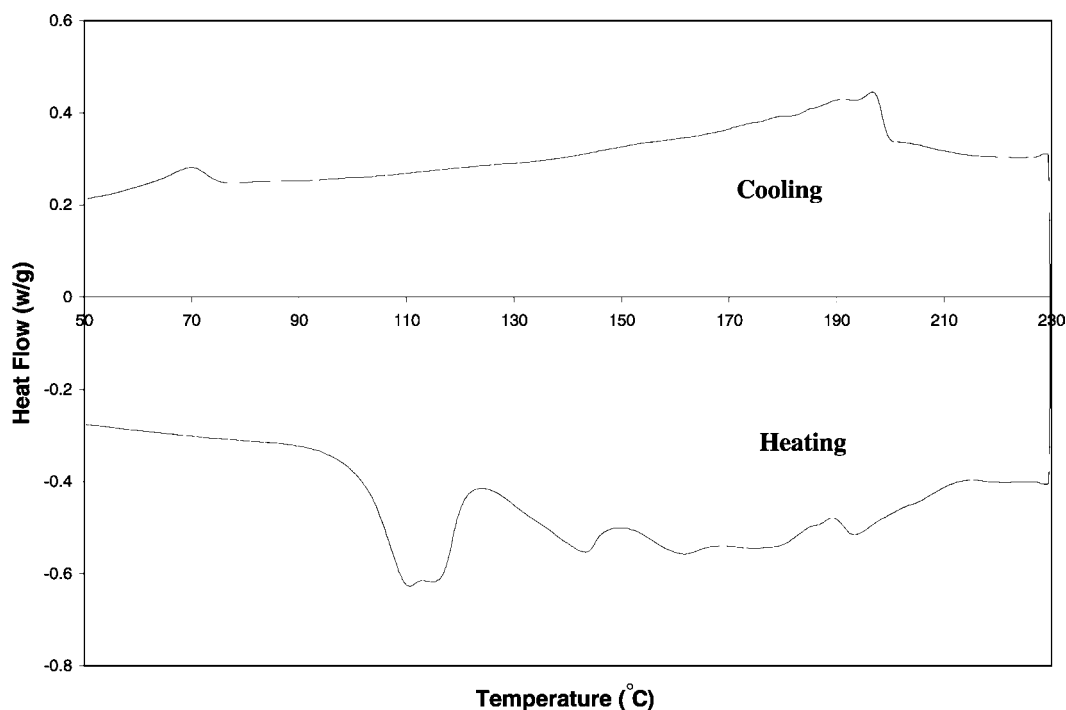


Fig. 2. DSC heating and cooling traces of the liquid crystalline oligoester (LCO) taken at 10 °C/min.

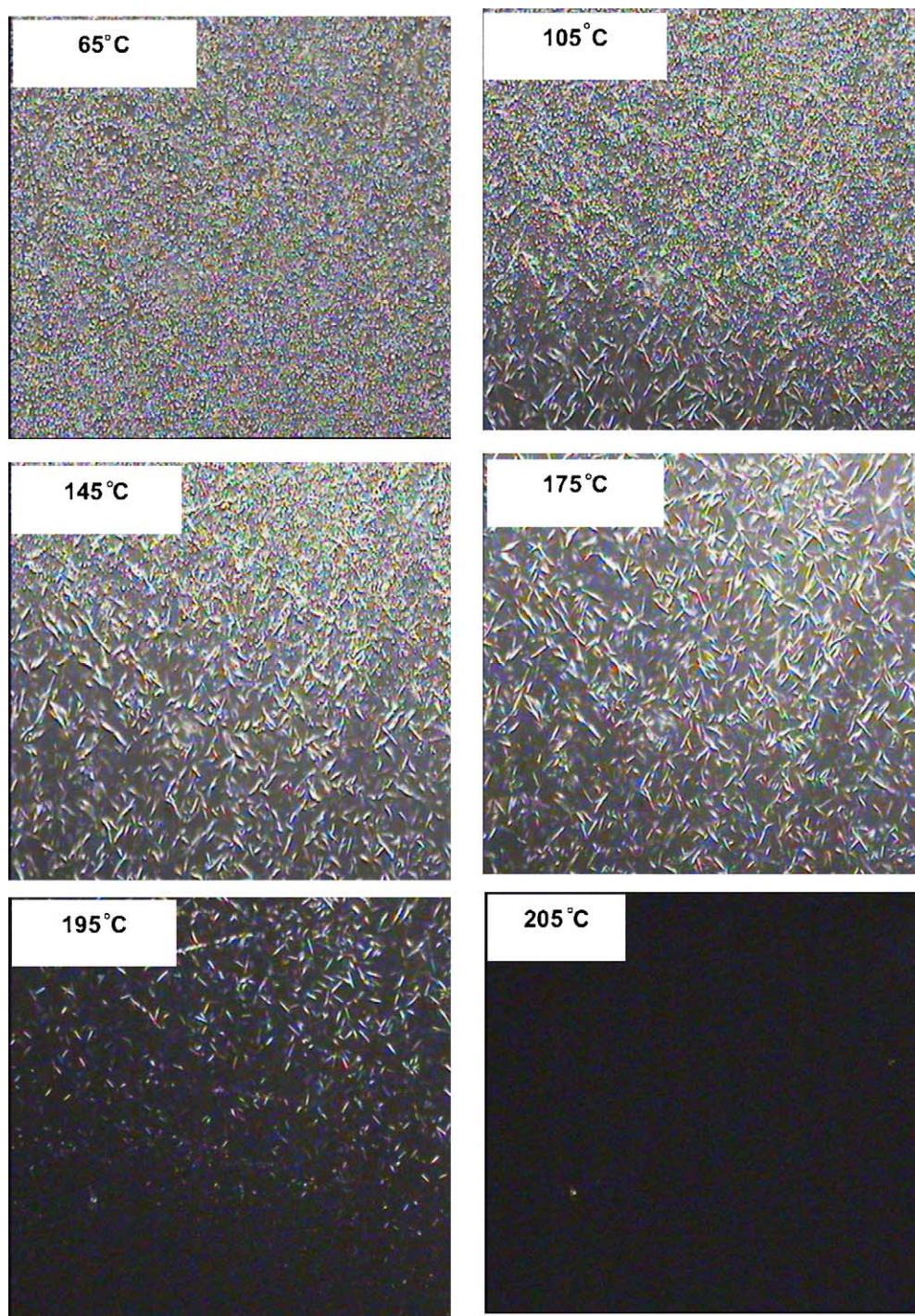


Fig. 4. Polarized photomicrograph of the liquid crystalline oligoester (LCO)3 during heating at 10 °C/min, (65 °C: crystalline phase; 105, 145 °C: transition from crystalline to smectic phase; 175 °C: smectic phase; 195 °C: from smectic to isotropic phase; 205 °C: isotropic phase), magnification 100×.

of the liquid crystalline oligoester and di- and trifunctional glycidyl ester (D&TGE) reported in Table 1. The information about the curing reaction was obtained as follows: the start, onset, maximum and end of the curing reaction exotherm (T_s , T_o , T_m , and T_e , respectively) of the studied system. Also shown in Table 1 the enthalpy of the curing reaction (ΔH). The existence of difference between the reaction enthalpies,

at the various heating rates, may be attributed to error in baseline approximation.

The exotherms obtained by DSC for the mixture of LCO and D&TGE at a variety of non-isothermal conditions with heating rates of 1, 2, 4 and 6 °C/min are illustrated in Fig. 5. The diagram of reaction rate as a function of curing temperature can therefore be obtained with the assumption that the

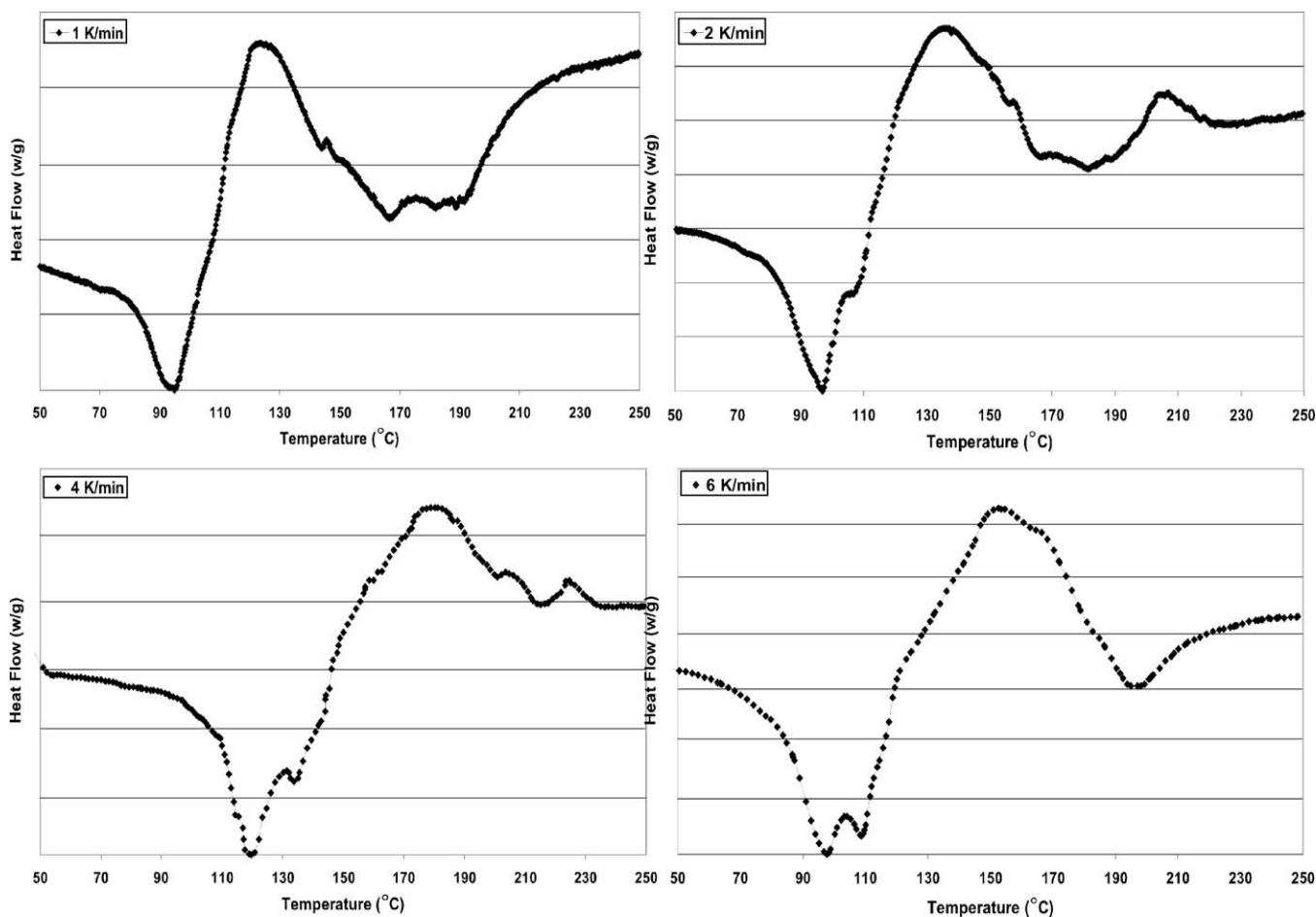


Fig. 5. The heat flow vs. temperature during non-isothermal curing reaction of the mixture of the liquid crystalline oligoester (LCO) and D&TGE at the different heating rates (1, 2, 4 and 6 °C/min).

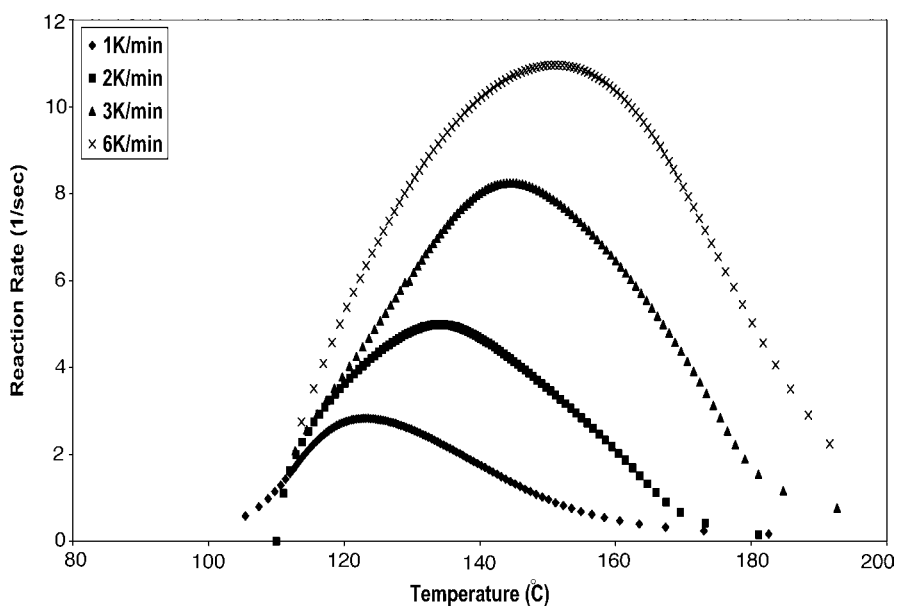


Fig. 6. The rate of reactions of the liquid crystalline oligoester (LCO) and D&TGE at the various heating rates (1, 2, 4 and 6 °C/min).

Table 1
The value of thermodynamic quantities relating to the non-isothermal curing of the LCO/D&TGE system for the different heating rates

Heating rate (°C/min)	T_s (°C)	T_o (°C)	T_m (°C)	T_e (°C)	ΔH (J/g)
1	101.82	106.54	122.06	181.36	92.47
2	106.36	109.17	133.76	182.27	95.12
4	108.67	109.75	148.39	194.02	111.9
6	109.04	109.64	150.92	194.02	117.2

heat generated during cure is directly proportional to the rate of reaction. Fig. 6 shows the rate of reaction as a function of temperature for LCO and D&TGE at above-mentioned heating rates. The variation of the fractional conversion as a function of temperature for the sample at the different temperatures is indicated in Fig. 7.

According to the Friedman method, linear relationships of $\ln(d\alpha/dt)$ versus were established (Fig. 8). It describes well data from non-isothermal DSC measurements in the α range 0.05–0.95. The values of activation energy were calculated by means of this method and the obtained results are pointed out in Fig. 8. It can be observed that the activation energy for the LCO/D&TGE system is practically constant in the $0.27 < \alpha < 0.68$ range and its values was found to be $E_a = 95.5 \pm 2.5$ kJ/mol. The activation energy, out of the above-mentioned interval, is strongly dependent on the degree of extent of the curing reaction. Alternatively, $\ln[Af(\alpha)] - \alpha$ plot

demonstrates an identical manners (Fig. 9), which it may suggest that the activation energy (E_a) and the pre-exponential factor (A) both depend on the extension of curing reaction.

The variations of values of correlation coefficients of linear fits for each conversion presented in Fig. 10. It must be expressed that the goodness of fit of the linear relationship $\ln(d\alpha/dt)$ versus $1/T$ follow a poor manner in the conversion values of lower than 27% and higher than 68%, which may lead to some errors in activation energy computation. But in the important range of around 30–70% the fitness is very good and the activation energy can be computed with good confidence.

Furthermore, the variation of $y(\alpha)$ and $z(\alpha)$ functions with conversion are indicated in Figs. 11 and 12, calculated using Eqs. (9) and (10), respectively. We normalized the values of both $y(\alpha)$ and $z(\alpha)$ within (0,1) interval using the different non-isothermal conditions for the curing reaction of LCO/D&TGE. The conversions, in which the $y(\alpha)$, $z(\alpha)$ and DSC peaks exhibit the maximum values (α_M , α_P^∞ and α_p , respectively) for the different heating rates, are listed in Table 2. The shapes of the $z(\alpha)$ plots, and slightly $y(\alpha)$ plots, are practically variant with respect to heating rate. As was noted, the data in Table 2 which has been extracted from Figs. 10 and 11, show that α_M , α_P^∞ and α_p values depend on the heating rate. The maxima of $y(\alpha)$ and $z(\alpha)$ plots fall into range of $0.5 \leq \alpha_M \leq 0.53$ and $0.4 \leq \alpha_P^\infty \leq 0.55$, respectively. These variances are corresponded to the variances in the calculated values of the activation energies. Indeed, it can be concluded that

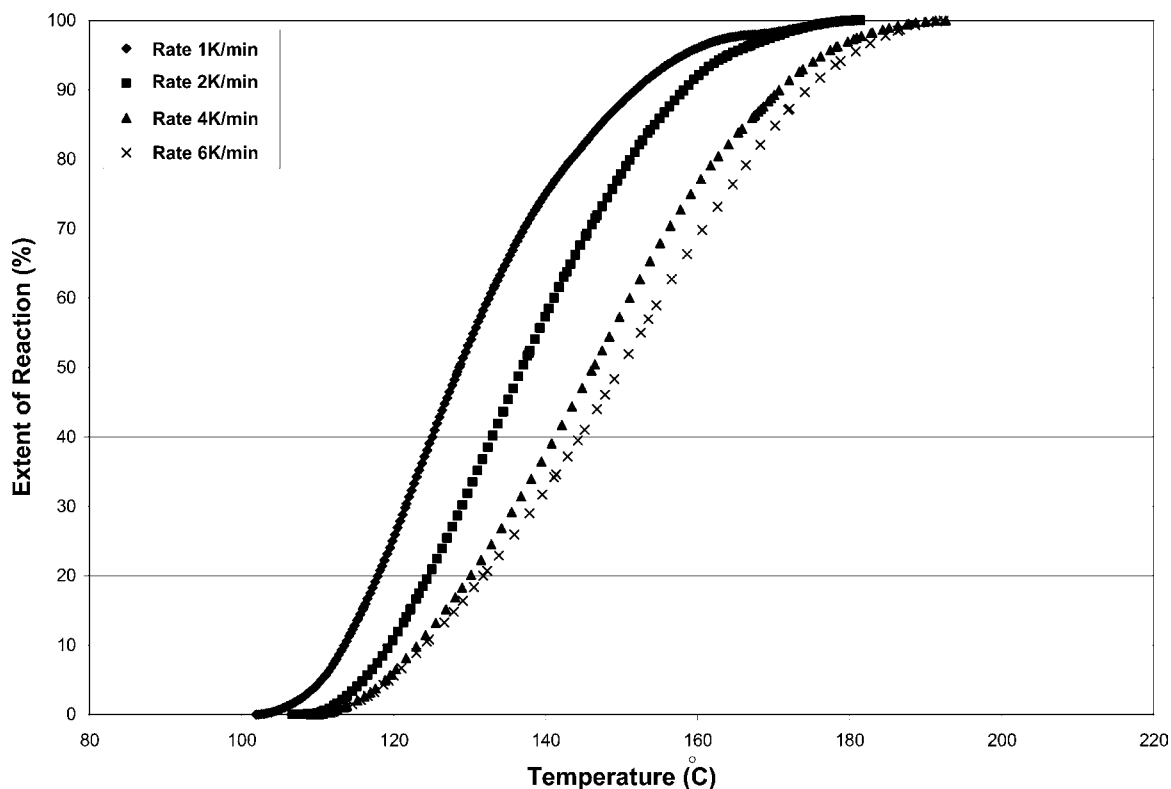


Fig. 7. The extent of reaction vs. temperature data for non-isothermal curing reaction of the mixture of the liquid crystalline oligoester (LCO) and D&TGE at the different heating rates (1, 2, 4 and 6 °C/min).

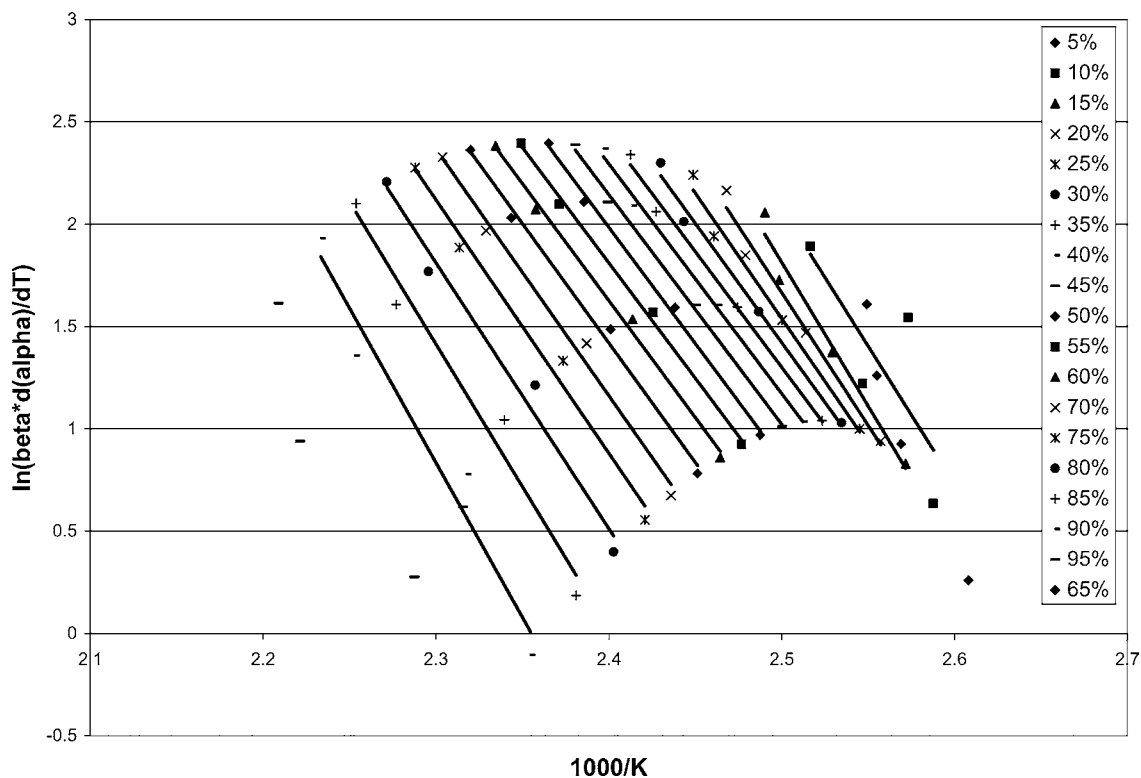


Fig. 8. Friedman plots of $\ln(d\alpha/dt)$ vs. $1/T$ the points for non-isothermal curing reaction of the mixture of the liquid crystalline oligoester (LCO) and D&TGE.

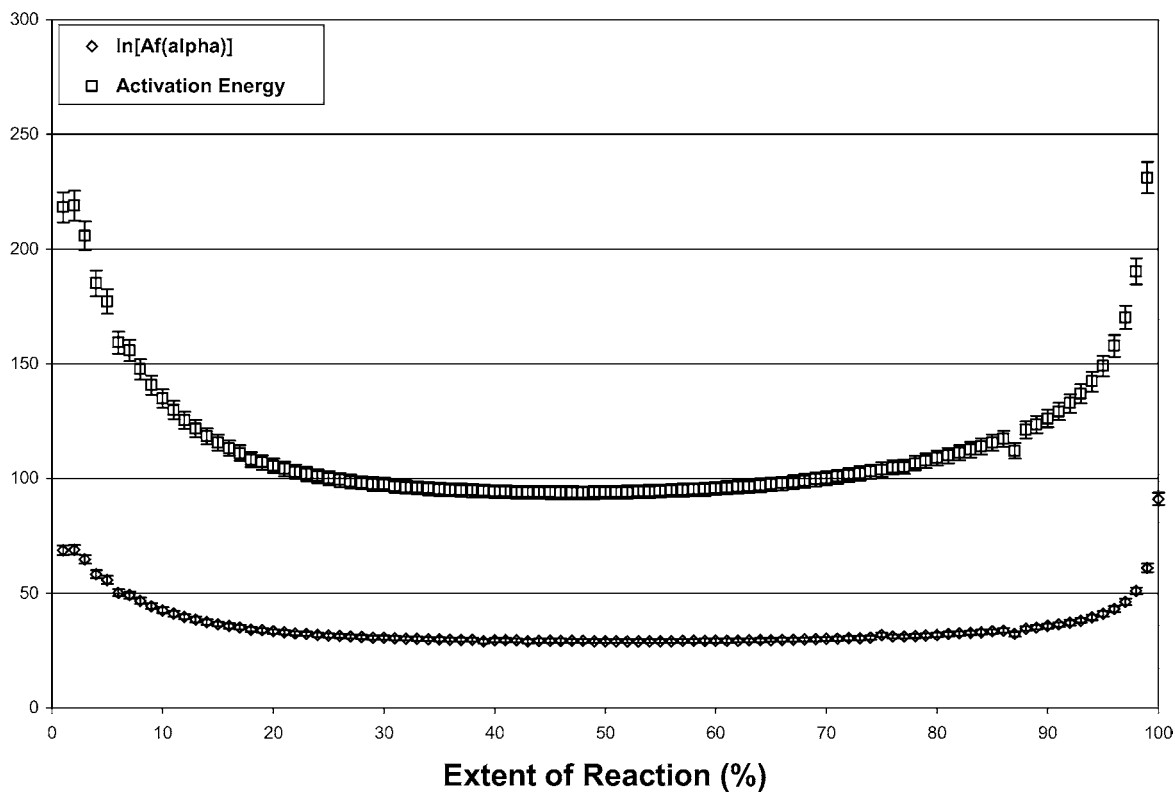


Fig. 9. The apparent activation the $\ln[Af(\alpha)]$ as functions of fractional conversion calculated from DSC data for non-isothermal curing reaction of the mixture of the liquid crystalline oligoester (LCO) and D & TGE according to Friedman isoconversional method.

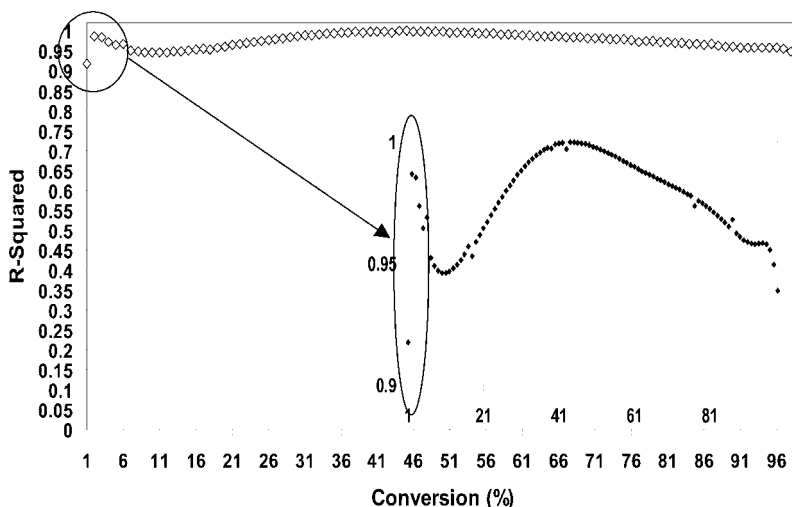


Fig. 10. The variation of values of correlation coefficients of Friedman plots of $\ln(d\alpha/dt)$ vs. $1/T$ the points for non-isothermal curing reaction of the mixture of the liquid crystalline oligoester (LCO) and D&TGE for each conversion. Inset shows the same curve with an expanded scale.

the kinetic process dose not follow a single-step curing reaction model and the calculated values of activation energy are apparent values and differ from the actual values.

According to Vyazovkin and Sbirrazzuoli [51] a generalized linear relationship can be established between pre-exponential factor and activation energy as:

$$\ln A_{\xi} \cong aE_{\xi} + b \tag{12}$$

This relationship has been known as the compensation effect. The compensation effect can be used to find out whether the variations of activation energy with different factors (ξ), which produce a change in the Arrhenius parameters, has a physical back ground or they are caused by variations of process conditions or calculation manipulation. According to Eq. (7), the constant $\ln[Af(\alpha)]$ can be determined from the intercept of each conversion line. The plots of $\ln[Af(\alpha)]$

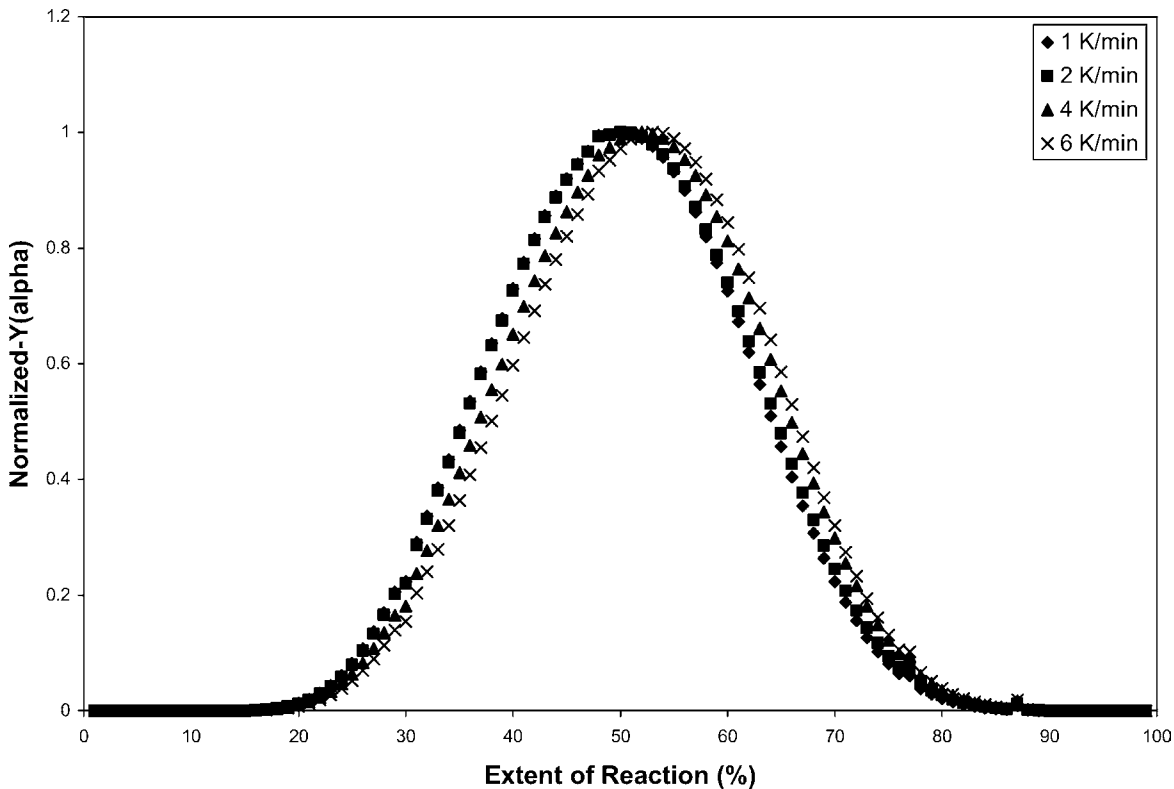


Fig. 11. Normalized $y(\alpha)$ function obtained by transformation of DSC data from Fig. 5 by using Eq. (9) for LCO/D&TGE system cured at the different heating rates(1, 2, 4 and 6 °C/min).

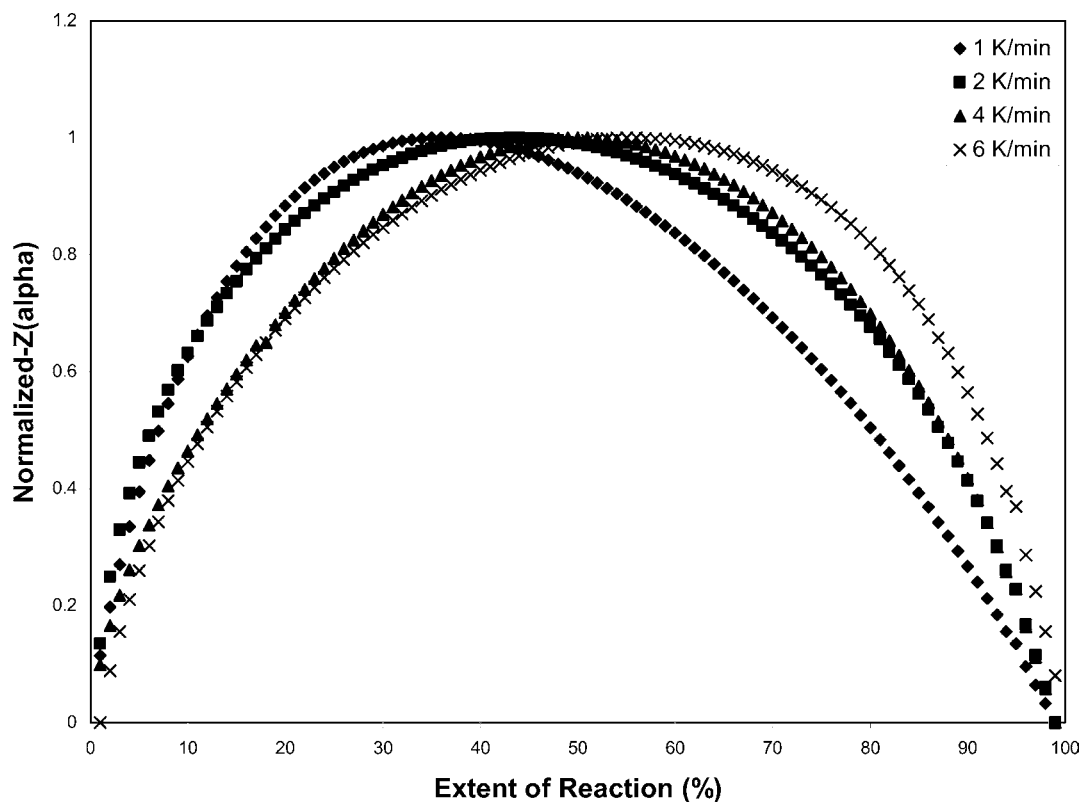


Fig. 12. Normalized $Z(\alpha)$ function obtained by transformation of DSC data from Fig. 5 by using Eq. (10) for LCO/D&TGE system cured at the different heating rates (1, 2, 4 and 6 °C/min).

versus E_a for the system is shown in Fig. 13. It presents two very different processes at the start and at the last part of the reaction (the two branches) and a middle process linking them. It can be deduced that the process of curing divided into three distinctive areas in term of the extent of reaction. At the middle area, the conversion values of 0.27–0.68, the amounts of $\ln[Af(\alpha)]$ and activation energy could be considered nearly constant. In Fig. 13, the trendlines marked with * and (\diamond) are related to the conversions of lower 0.27 and conversion values of higher than 0.68, respectively. The values of slope (a), intercept (b) and r -squared (r^2) related to these linear curves are listed in Table 3. The existence of difference between the values of a and b for these lines implies that the curing process at lower and upper values of conversion follows different routes. In fact, the Fig. 13 and the results which were listed in Table 3, suggest two very different processes at the beginning

and at the end of the reaction and an intermediate process linking them.

Although the reaction of carboxylated polyester with this curing agent in our work does not present a complex reactive process, the overall curing reaction kinetics is powerfully affected by the presence of liquid crystalline phase and it will make difficult the prediction of the general chemical and physical behavior of the system. To identify the mesomorphic behavior of the LCO/D&TGE during curing, we carried out further, the microscopic observation at different heating rates (1, 2, 4 and 6 °C/min). As observed in Fig. 14, we found out that the optical texture of the sample varies during curing. A stir-opalescent texture developed finally after curing at the various heating rates.

The reaction mechanism between the carboxylic acid and epoxy groups has been studied by many authors [66–71]. Four possible reactions may be considered in the curing of

Table 2

The conversions, in which the $y(\alpha)$, $z(\alpha)$ and DSC peaks exhibit the maximum values (α_M , α_{P^∞} and α_p , respectively) for the different heating rates

Heating rate(°C/min)	α_M (%)	α_{P^∞} (%)	α_p (%)
1	50	40	31.35
2	50	46	41.91
4	52	51	54.42
6	53	55	51.95

Table 3

The values of slope (a), intercept (b) and r -squared (r^2) of the trendlines related to the branch 1 (the conversion values of lower than 0.27) and branch 2 (the conversion values of higher than 0.68)

Branch	a	b	r^2
1	0.3153	−0.0204	0.9999
2	0.2277	7.3868	0.9966

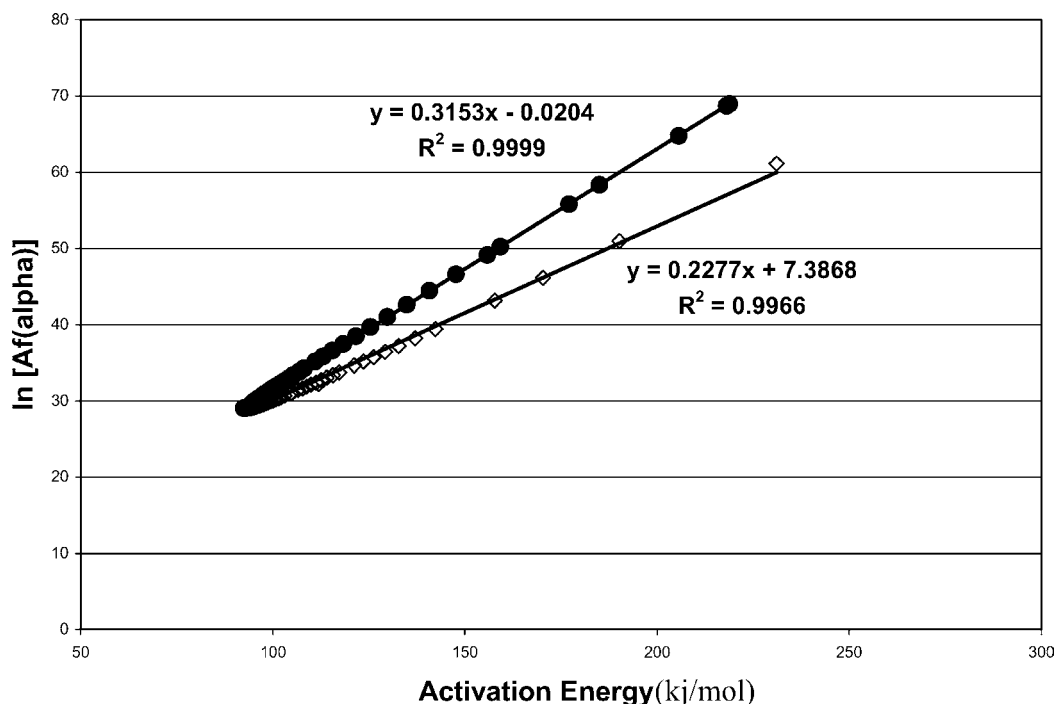
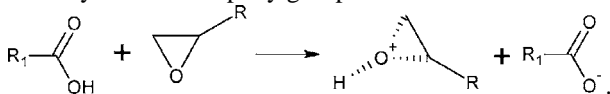


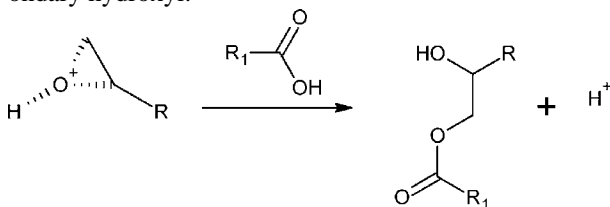
Fig. 13. The plots of $\ln[Af(\alpha)]$ vs. activation energy (E_a) at different degree of conversion for the for non-isothermal curing reaction of the mixture of LCO and D&TGE.

carboxylated polyesters with the curing agents containing epoxy group:

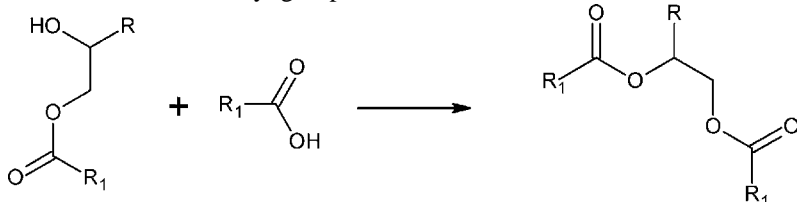
1. formation of an oxonium ion by ring opening attack of carboxylic acids to epoxy group:



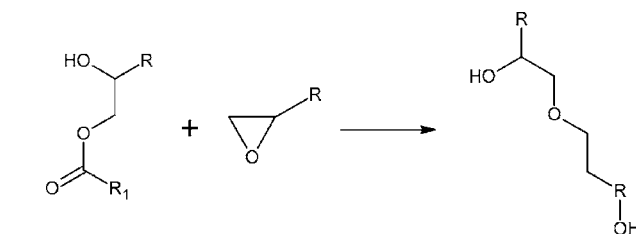
The resultant oxonium ion may react with a carboxyl moiety. It leads to the formation of the corresponding secondary hydroxyl:



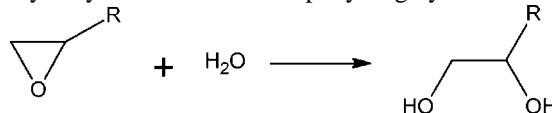
2. The hydroxyl group formed in the before reactions esterifies with a carboxyl group:



3. Condensation reaction between the hydroxyl group formed in the step 1 and an epoxy group and ring opening of the epoxy group. It leads to form an ether alcohol:



4. Hydrolysis reaction of the epoxy ring by water:



The occurrence of the above reaction depends on the catalyst used. In the absence of catalyst, when the reaction takes place under stoichiometric conditions for the reactive groups (our system), the first three reactions proceed at the same rate to a comparable extent. It has been reported that when the curing occurs in above-mentioned conditions the ratio between

the reaction products according to the steps 1–3 lies between 2:1:1 and 1:2:2, respectively [66]. The chemical reactivities of diglycidyl ester and triglycidyl ester components in the

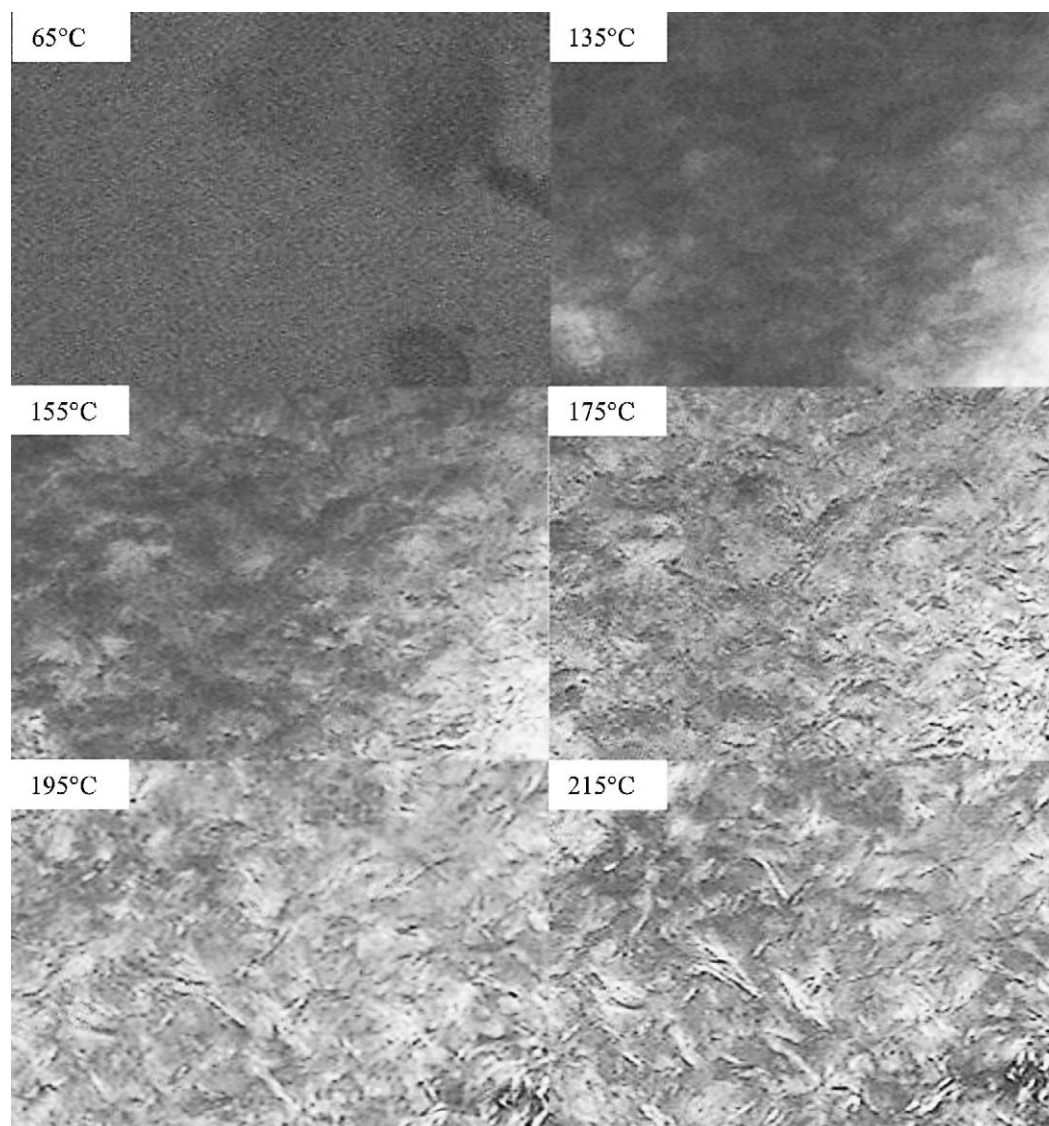


Fig. 14. The variations of optical texture of the LCO/D&TGE system during dynamic curing at the heating rate 6 °C/min. (magnification 100×).

curing agent are comparable [72]. Therefore, it would be reasonable that the linearly extension of the polymer chains occurs simultaneously with the cross-linking reaction. But due to the molar ratio 75:25 of diglycidyl ester to triglycidyl ester in the curing agent, respectively, the first process would be prevailing and thus the conformation of the polymer chains changes. It will ensue to develop a new liquid crystalline state before to reach to gel point. It may be a reason for the observed difference in the $y(\alpha)$ and $z(\alpha)$ plot with extent of reaction at the different heating rates.

The temperature dependence of the depolarizing transmittance for the mixture of LCO and D&TGE at a variety of non-isothermal conditions with heating rates of 2, 4 and 6 °C/min are illustrated in Fig. 15. It seems that the temperature dependence of depolarizing transmittance of the curing system, and consequently its mesomorphic behavior, varies with heating rates. So it could be reasonable to say that the

kinetic process was influenced by changes in the mesomorphism features of the liquid crystalline oligoester, e.g. size of liquid crystalline domains and/or its temperature transitions, during heating at the various rates.

The variation of the activation energy at the beginning of the reaction could be attributed to two different phenomena. On one hand, since the sample was a powdery mixture of the liquid crystalline oligoester and the curing agent, some variations may be caused by the transformation from a powdery solid state to a melt state (Fig. 14). On the other hand, it could be observed that the intensity of depolarized light, which transmitted through the curing system, began to increase at the temperatures which were corresponded to the extent of reaction around 27% at the different heating rates (Fig. 15). Since the depolarizing transmittance of LCO in absence of D&TGE started to increase at lower temperature (about 100 °C), so we attributed some of the variations of

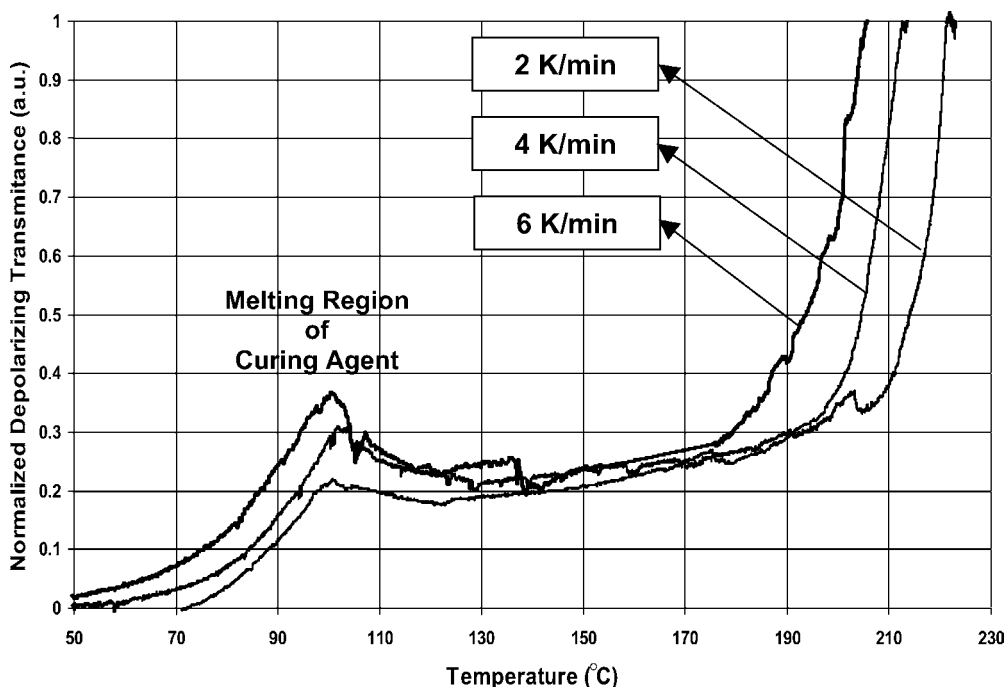


Fig. 15. Temperature dependence of the depolarizing transmittance curves of the LCO/D&TGE system during dynamic curing at the different heating rates (2, 4 and 6 °C/min).

activation energy at the beginning of the reaction to changes in mesomorphism features including transition temperatures and liquid crystalline domain size. According to our microscopic observation it is hard to attribute the alteration of the

mesomorphic features to changes in the order of liquid crystalline phase.

Fig. 16 shows the liquid crystalline phase time–temperature–transformation (TTT) diagram for the LCO/D&TGE

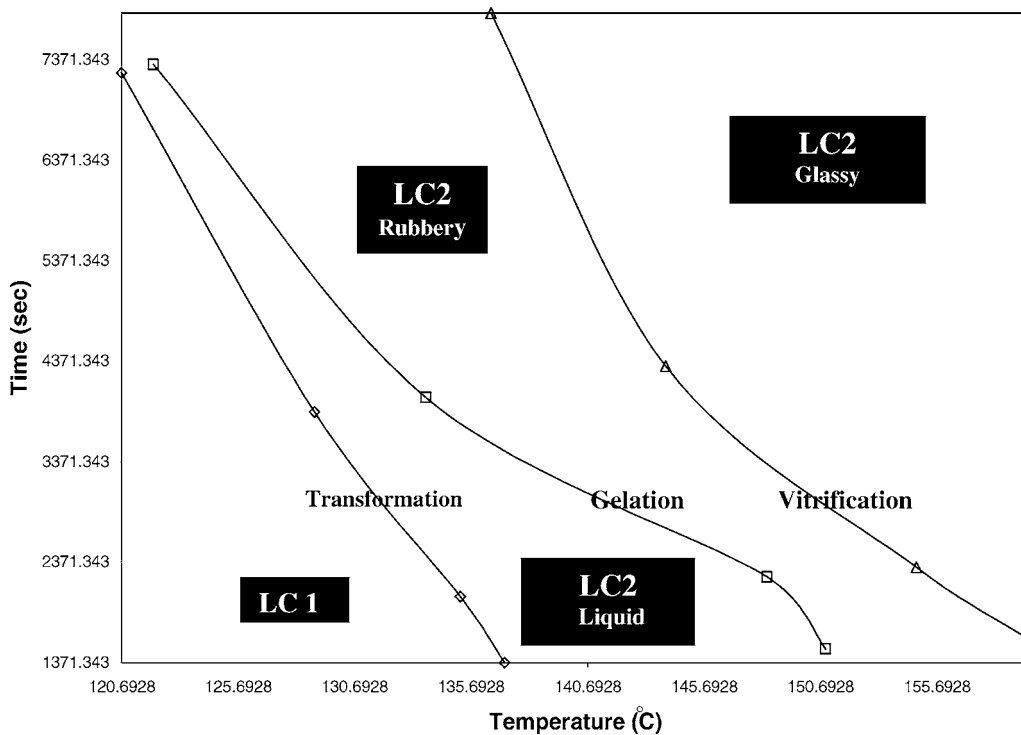


Fig. 16. The liquid crystalline phase time temperature transformation (LCTTT) diagram for of the LCO/D&TGE system during dynamic curing at the heating rates: (◇) completion of transformation of primary mesomorphism features to secondary mesomorphism features; (□) gelation; (△) vitrification.

system. This diagram shows the transition from primary mesomorphic features (LC 1) to secondary mesomorphic features (LC 2) during cure for the system. The conversion at the gel point varied with the heating rates. It shows that the isoconversion theory of gelation does not hold for the LCO/D&TGE system and gelation is dependent to liquid crystalline phase as well as cure temperature. The network with lower cross-link density (low conversion, < 27%) exhibits a change in texture when making from 0 to around 27% conversion. In the last states of curing (high conversions) the system shows a stir-opalescent texture.

Due to the complexity of potentially mesogenic reacting systems, other authors have carried out analysis of kinetic process of their curing reaction by fitting of separate parts of the DSC curves [16,27,33,39]. It seems that our system is very complicated and the existence of liquid crystalline phase in the beginning of the curing reaction, in contrast to the potentially mesogenic reacting systems, causes an ambiguity in extracting the kinetic parameter values.

It can be concluded that the kinetic process of the investigated system is robustly influenced by altering the liquid crystalline state of the sample. It is essential to consider the curing reaction as an intricate system. In fact, the reaction is affected not only by the presence of the liquid crystalline phase but also by the variation of the mesomorphism features, for instance, magnitude of liquid crystalline domains, transition temperatures and anisotropic temperature range.

5. Conclusion

Model independent values of the activation energy were calculated for the curing reaction of the liquid crystalline oligoester based on 4,4'-diacetoxybiphenyl and dodecanedioic acid in presence of a mixture 75:25 of diglycidyl terephthalate and triglycidyl trimellitic acid ester (D&TGE), as a curing agent using the isoconversional method which has been suggested by Friedman. It was found that the calculated activation energy depends on the extent of reaction, α , and it shows a constant value 95.5 ± 2.5 in the range of degree of conversion 27–68%. To identify that whether the true model reaction is invariant for different non-isothermal curing conditions, or is not, the $y(\alpha)$ and $z(\alpha)$ functions were obtained through transformation of DSC data. The $y(\alpha)$ and $z(\alpha)$ functions exhibit maxima at α_M , and α_P^∞ , respectively. The maxima fall into range of $0.5 \leq \alpha_M \leq 0.53$ and $0.4 \leq \alpha_P^\infty \leq 0.55$. These variances illustrate that the calculated values of activation energy are apparent values and differ from the actual values. The depolarizing transmittance measurement and microscopic observations during curing, at different heating rates of 2, 4 and 6 °C/min show that the mesomorphic properties of the system during curing changes and as a consequence the kinetic process of that is strongly influenced by these alterations.

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