Curing of the Diethylene Glycol Bis(Allyl Carbonate) Determination of the Kinetic Triplet *A, Ea,app, f*(α) Using the Isoconversional Method and Compensation Effect

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Lenses (made of allyl monomers like DADC) of different shapes and sizes are produced via free-radical bulk polymerization in a casting process. Preparation of large number products of different sizes can represent a problem because of the heat released during polymerization, which can consequently lead to distortion of the structure. An investigation of the polymerization, using DSC, was performed in order to determine apparent kinetic parameters of the system. Isoconversional multiple heating rate method (MHR) according to Friedman, residual heat analysis of isothermally precured samples and single heat method (SHR), was applied to determine the kinetic parameters. ROn single step reaction model was used to approximate the complex and multi step process. With the application of the "compensation effect" in the form of linear equation *lnA* = a*Ea,app* + b the possibility to unify the kinetic parameters, from the different methods to common one, was established. Kinetic triplet from the common point *Ea,app = 128.23 kJ/mol*, *lnA = 37.133* ($1.34 \cdot 10^{16}$ s^{-1}) and $f(\alpha) = (1\text{-}\alpha)^{1.33}$ can be successfully used for the simulations of nonisothermal and isothermal curing processes of DADC initiated with 5 % of CHPC. On a basis of the proposed method it can be concluded that all applied kinetic analysis methods give almost the same equivalent kinetic results.

Keywords:
DSC, curing kinetics, compensation effect

Introduction

Allyl monomers form high transparent high abrasion and impact resistance thermally stable polymers. Among them diethylene glycol bis(allyl carbonate) (DADC) is one of the most used monomers for the producing of the high performance ophthalmic lenses. High heat evolution (approx. 390 J/g) and unpleasant geometry (lens shape) are the reasons for most of the problems during its polymerization process. A well-controlled, slow polymerization is needed to prevent optical defects in the resulting polymer. To assure such requirements correct and accurate kinetic data must be used for the developing of an application cure cycle. Our finding gives the possibility to unify *Ea,app* data from single heating rate – SHR and multiple heating rate – MHR method to single or common kinetic triplet (*Ea,app*, *A*, *f*(α)). Such data can be applied for the prediction of isothermal and dynamic or nonisothermal kinetic mode from which any application curing cycle consists of. Study is based on differential scanning calorimetry (DSC) experiments performed in nonisothermal or dynamic and isothermal mode.

Allyl polymerization expresses no microgelation and no Trommsdorff effect[1] and this is the main reason that the heat evolved during isothermal curing process is very low and cannot be detected by common DSC. Alternatives are to perform indirect isothermal curing method[2] where isothermally precured samples are scanned for residual heat and nonisothermal or dynamic curing mode. To establish the kinetic parameters of the curing system from DSC data, some assumptions should be accepted: reaction extent is associated with conversion (α), the conversion rate ($d\alpha/dt$) is proportional to the measured heat flow (dQ/dt), and the temperature dependence of the rate constant $k(T)$ is described by the Arrhenius equation. Basic differential equations can be described as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}Q}{\mathrm{d}t} \cdot \frac{1}{Q_{\mathrm{tot}}} = k(T) \cdot f(\alpha) = A \cdot \exp\left(\frac{-Ea,app}{R \cdot T}\right) \cdot f(\alpha) \quad (1)$$

and its logarithmic form is

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha} = \ln\left[A_{\alpha} \cdot f(\alpha)\right] - \frac{(Ea,app)_{\alpha}}{R} \cdot \frac{1}{T} \quad (2)$$

Total heat flow (Q_{tot}) was obtained with the integration of the total peak area of the measured heat flow (dQ/dt) in mW normalized to a sample mass.

Isoconversional kinetic analysis (MHR-method) was performed using differential equations proposed by Friedman[3] (Eq. 2), which allows “model-free” calculation of apparent activation energy from the slopes of the lines when $ln(d\alpha/dt)$ is plotted against $1/T$ at different α.

To calculate the Arrhenius preexponential factor A from the Eq. 2 the reaction model $f(\alpha)$ should be determined. Reaction model was selected among basic models[2] for thermosets. Reaction is not autocatalyzed so the general one-step reaction model of *ROn* type was applied:

$$f(\alpha)=(1-\alpha)^n. \qquad (3)$$

The logarithmic form of the combination of the Eq. 1 and 3 can be used for the multilinear regression calculation method of the kinetic parameters (SHR-method):

$$\ln\left(\frac{d\alpha}{dt}\right)=\ln A-\frac{Ea,app}{R}\cdot\frac{1}{T}+n\cdot\ln(1-\alpha) \qquad (4)$$

Eq. 2 and 4 give the possibility to calculate the kinetic triplet (Ea, A, $f(\alpha)$) at whole range of conversions from nonisothermal experiments.

Such results from MHR or SHR method vary with the reaction extent, heating rate and the calculation method used. The problem of this variation is that no chemical or physical evidence for the variation can be identified. The main reason for this situation comes from the concept of the reaction kinetics definition. They introduce the concept of homogeneous reaction system into the solid (and/or transition)-state kinetics and many reaction models were developed.[4] The mechanistic interpretation of solid-state kinetics is based on the concept of single-step reaction mechanism:

$$\frac{d\alpha}{dt}=k(T)\cdot f(\alpha)\cong k_1(T)\cdot f_1(\alpha)\cong k_m(T)\cdot f_m(\alpha) \qquad (5)$$

The kinetic rate constant $k(T)$ is temperature dependent part and $f(\alpha)$ represents the reactant concentration dependent part. And from this point, still controversial[5,6,7] views start to occur.

Basic intention is to separate measured reaction rates data ($d\alpha/dt$) mathematically into temperature and concentration dependent part. Both parts are interdependent and with the selection of reaction model $f(\alpha)$ other part $k(T)$ is defined, such dependence is defined as a “compensation effect”[8] or isokinetic relationship (IKR). There exist two “compensation effects” in Eq. 5, first one exists among $k(T)$ and $f(\alpha)$ and second one inside $k(T)$. Temperature dependence of reaction rate constant is described by Arrhenius equation (Eq.1) that consists of preexponential factor Ao and activation energy Ea and compensation effect appears among them. This last compensating behaviour is defined as a “compensation effect”[8,9] which is of the main concern in this article. The problem begins with the definition of “true” or “real” reaction model what is practically impossible. Reaction model is often supposed as possible one and according to this selection reaction rate constant $k(T)$ is defined. Vyazovkin[10] proposed “independent” and “model-free” (without predefined reaction model) definition of calculation of the apparent activation energy (Ea,app) from which, in second step, reaction rate constant can be calculated (and also related A, Eq. 2).

As for most of the reaction models, the variation in $f(\alpha)$ with α is practically negligible as compared to the variation of the $k(T)$ with T,[8] one can derive from the logarithmic form of Eq. 5 the following approximate equality:

$$\ln k_0\cong\ln A_i-\frac{1}{R\cdot T_0}\cdot E_i \qquad (6)$$

And the Eq. 6 suggests a linear correlation between the values of E_i and lnA_i[8]:

$$\ln A_j\cong\ln k_0+(R\cdot T)^{-1}\cdot E_j\Rightarrow\ln A_\xi=b+a\cdot E_\xi \qquad (7)$$

Finally, it is obvious that linear relation can compensate (give the same $k(T)$) between A and Ea, practically for any of defined Ea. This means that the correct or “real” definition of the Ea becomes a crucial point of this procedure.

Another problem is the application of the isothermal and nonisothermal kinetic results because they often disagree among each other.[8] There are two major reasons for this disagreement: (i) the prevalent use of kinetic method that involves force fitting of nonisothermal data to hypothetical reaction model and (ii) the experiments are conducted inside significantly different temperature regions. Arrhenius parameters are determined by separating the contributions of $k(T)$ and $f(\alpha)$ to the rate of given process. Usually this is done by “best fit” procedure of some reaction models to experimental kinetic curve. This procedure is correct only for isothermal kinetics where $f(\alpha)$ and $k(T)$ are experimentally separated ($k(T)$ = const.) what is not the case in nonisothermal experimental data. However, most of commonly accepted computation methods use such an assumption for nonisothermal calculations8 and this means that practically any reaction model $f(\alpha)$ can be compensated with $k(T)$ to “best-fit” experimental data.

The use of model-free analysis according to Friedman,[3] Ozawa-Flynn-Wall[18] or Vyazovkin[19] is simple enough and avoids errors connected with the choice of reaction model but there are some necessary conditions required for its application.[6] The DSC signal should not be composed of opposite signs (like endothermic and exothermic), process should not consist of branched reaction paths and it should not be under diffusion control, there should be no back reactions and distinct variation of the reaction stoichiometries.[6] However, these restrictions are not valid for kinetic analysis using non-linear regression and model-fit method. Some disadvantages of this procedure can be eliminated with the use of model-free analysis data as starting values.

From our previous work[11] it is possible to apply the procedure where only one kinetic triplet (Ea,app, A, $f(\alpha)$) can be find out to fit accurate enough, both, isothermal and nonisothermal experimental data. Anyway, it is obvious that constant activation energy can only be expected for single-step reactions and such an *Ea* can only be apparent quantity based on quasi single reaction step.

In many polymerization systems main problem is heat balance in the system and the detail mechanism of polymerization is not of the main concern. In such cases overall kinetics can help to predict accurately heat generation and temperature profile during polymerization in different shapes and sizes. DSC as simple and accurate method, beside its bad sides, give enough possibility for technologists to use them as a valuable instrument for studying the necessary background needed to manage the polymerization processes successfully. From this point of view the aim of this work is to represent a method for determining the consistent and reliable kinetic triplet independently of process conditions and method of calculation.

Experimental

Monomer, diethylene glycol bis(allyl carbonate) (DADC) technically pure (AKZO NOBEL, Netherlands) was applied for the preparing of the polymerization mixture with dicyclohexyl peroxy dicarbonate (CHPC) (Laporte, Germany). Clear, homogeneous particle free solution was prepared at room temperature under nitrogen atmosphere. Curing experiments were conducted with 5 % solution of CHPC in DADC. Polymerization was performed in differential scanning calorimeter (DSC) Mettler Toledo 821c at constant atmospheric pressure in nitrogen atmosphere. Nonisothermal experiments were performed at heating rates (β) from 2 to 20 K/min, respectively, in a temperature range of approx. 40–160 °C with N_2 flow of 100 ml/min. DSC samples were placed in 40 μL aluminium crucibles with a perforated lid. Samples have been weighted accurately in a range of 3–12 mg. The sample mass was selected according to recommendation from ASTM 698,[12] that peak of heat flow at given geometry and mass (40 μL Al crucible) should not exceed 8 mW to avoid auto acceleration.

Isothermally precured samples to different reaction extent (α) were prepared in DSC under N_2 atmosphere. The samples were scanned for residual heat immediately after isothermal curing without removing the sample inside the same temperature program.

Thermal decomposition of the CHPC is a highly exothermic process. Because of that the heat of the decomposition was subtracted from the heat of the polymerization. The reason is to eliminate the reaction of the initiator decomposition from the polymerization process. Reaction of the thermal decomposition of the CHPC was evaluated in the DSC at the same conditions and concentration as a studied sample. Dibutyl phthalate (DBP) was used as a neutral solvent to simulate thermal decomposition of CHPC without polymerization.

Results and discussion

Nonisothermal method

Isoconversional kinetic analysis was performed using differential equation according to Friedman[3] (Eq. 2). Calculation is based on experiments performed at different heating rates. We select consistent reaction rates in three ranges: LOW heating range with β = 2, 3.5 and 5 K/min; MED range with β = 7, 10 and 12 K/min; HIGH range with β = 15, 17 and 20 K/min. According to this ranges kinetic parameters were calculated at different reaction extent. Figure 1 represents such calculation as an example for a LOW heating range.

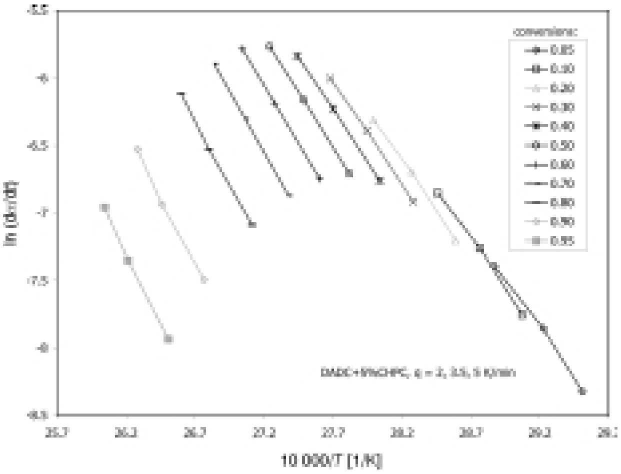

Fig. 1 – *Model free determination of Ea,app at different α according to Friedman, LOW range of β*

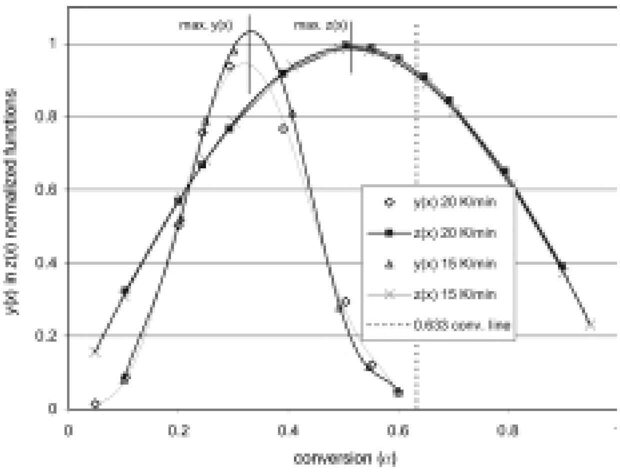

Fig. 2 – *Plot of the y(x) and z(x) auxiliary functions for testing the reliability of ROn model*

In the next step we need to test the consistency of use of a single step reaction model ROn to (EQ 3) fit the kinetic curve data. Known calculation procedure proposed by *Málek* et al.,[13] represented in detail also in previous work,[11] gives as a result of a plot of two auxiliary concave functions *y(α)* and *z(α)* which maximums should be in certain order to indicate the consistency of use of the ROn reaction model. First must be the maximum of a *y(α)*, than *z(α)* function and both should be at less than reference line at 0.633 of whole conversion. In Figure 2 such a procedure is represented for a reaction system under consideration, the reliability of use of the ROn model was confirmed.

Reaction order *n* in the selected reaction model was calculated as the average value from the whole range of heating rates. SHR and multilinear regression method was applied (Eq. 4) on each set of experimental data. As shown in Figure 3 an average value of 1.33 was selected.

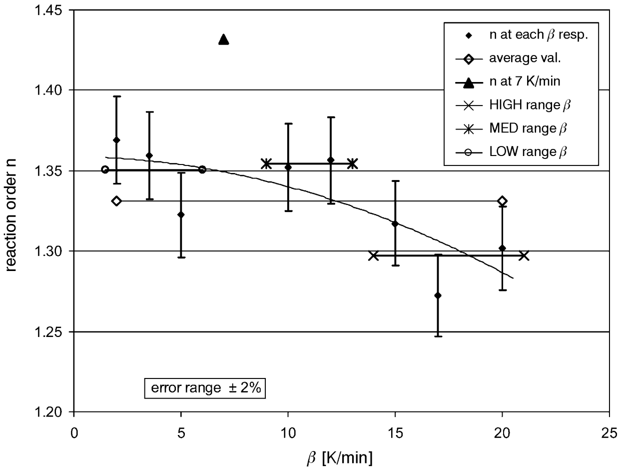

Fig. 3 – *Reaction order n at different β calc. with SHR and multilinear regression method*

With definition of reaction order *n* all elements for the final calculation of the reaction kinetic data are available. Results of the Friedman isoconversional analysis at different extent of the reaction (*α*) are represented in Figure 4.

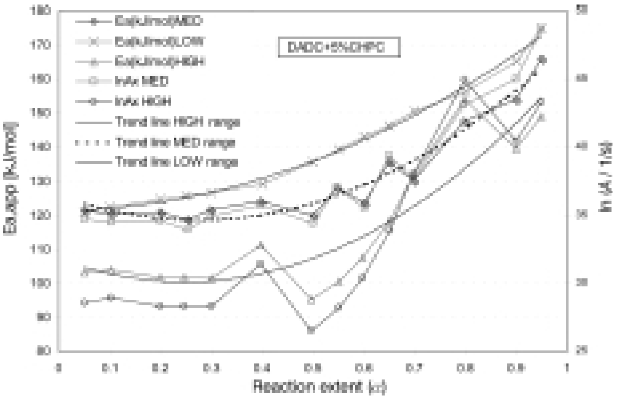

Fig. 4 – *Results of the isoconversional analysis of the kinetic parameters at different β and reaction extent (α)*

From the results represented in a Fig. 4 it can be concluded that the polymerization of the DADC with 5 % of CHPC at nonisothermal conditions (β = 2–20 K/min) is a typical complex and multi-step reaction system.[14]

With the defined kinetic parameters for each conversion it is possible to express the IKR or compensation effect for a nonisothermal curing process. At each conversion three points were taken from LOW, MED and HIGH group of heating rates (*β*) to get IKR lines. Lines were extended to the whole range of Ea to be comparable with each other. Results in a Figure 5 show linear relationship and tendency to converge to one point except the line at high (*α* = 0.95) conversion. Lines do not intersect but form a narrowest point signed as NP. The point at *Ea,app* = 128.23 kJ/mol and *lnA* = 37.133 ($1.34 \cdot 10^{16}$ s^{-1}) was taken as a common point for all

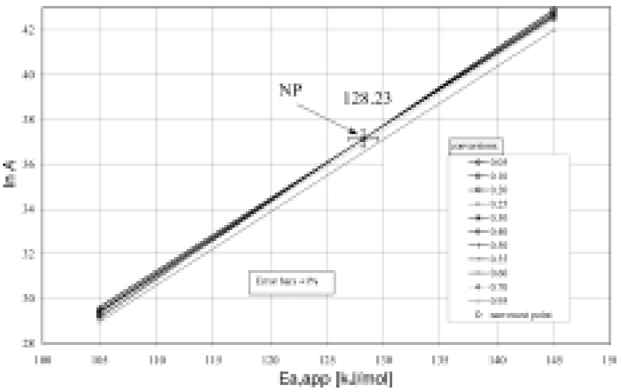

Fig. 5 – *IKR lines for nonisothermal curing process for each α from LOW, MED and HIGH β*

nonisothermal experiments. For the purposes to test the reliability of parameters at NP point the correlation among simulated (calculated) and experimental conversion data was calculated.

Results of the correlation between calculated and simulated data for three typical heating rates (2, 10 and 20 K/min) are collected in the Table 1.

Analysis of the data from Table 1 clearly shows that parameters correlate best in the mid of the whole range of β. The correlation is better for low heating rates than at high ones, but deviation is still very good and acceptable for projecting the industrial curing cycles. For the practical comparison reaction times are also represented. In industrial practice low heating rates are usually used to avoid auto-accelerating effect (due to poor heat transfer) in the centre of product shape.

Isothermal and SHR method

Isothermal curing method is basically important because a huge part of the industrial curing cycles consist of isothermal segments (in average 80 % of curing time). To predict conversion accurately or correct curing rates some relevant kinetic data are needed. It was discussed above that allyl polymerization systems are very slow and express no Trommsdorff effect. These are the main reasons that direct isothermal measurements in DSC are not possible. Indirect method was applied. Samples are isothermally precured and nonisothermally scanned (at β = 10 K/min) for residual heat. Results can be expressed as $\alpha = f(t)$ function. Conversion as a function of time curves was fitted with the selected reaction model (Eq. 3) in the same range of *Ea,app*, as in nonisothermal case, to get best preexponential factors *Ao*. Calculated pairs of *Ea,app* and *lnA* represent IKR relationship for isothermal curing regime and can be compared with nonisothermal one for each temperature, respectively. Results are collected in a Table 2.

International "ICTAC" kinetics project[15] formulate in the year 2000 a message about SHR method: "With the ready availability of … good analysis programs, kinetic analysis using single heating rate methods should no longer be considered in the thermal analysis community". That means SHR method should be avoided in kinetic studies. But chemical engineers and technologists still apply SHR method in some industrial applications because of its simplicity and still enough accurate results[16,17] in some cases. Our intention is to compare SHR results with isoconversional results to find out discrepancies among them and probably the reasons for this.

Table 2 – *IKR calculated parameters for isothermal precured samples*

IKR relat. ln $A = a$ Ea + b

Temp. °C	a	b	Ea,app.	ln A	Ao
50	0.37241	–10.6207	128.23	37.270	1.5352E+16
60	0.36097	– 9.0170	128.23	37.133	1.3386E+16

Isothermal method II (residual heat) DADC + 5 % CHPC

With the multilinear regression of the experimental results (Eq. 4) for each heating rate some SHR kinetic parameters can be calculated. Results from the Table 3 are separated in three groups. First group of β from 2–10 K/min expresses perfect linear IKR relation, 10 and 12 K/min behave like transition to next line representing 17 and 20 K/min samples. IKR relationship was calculated for both groups (Table 3) and can be compared with other results.

Finally, we compare all calculated results together in one diagram in Figure 6. Interesting results appear, parameters at nonisothermal narrowest – NP point covers almost all results, isothermal IKR line at 50 °C even crosses the NP point. SHR line for samples 2–10 K/min lies on the 10 K/min line

Table 1 – *Correlation among simulated (calculated) and experimental conversion data with NP parameters*

Kinetic parameters at NP point	heating rate K min^{-1}	correlation r^2	Reaction time for a = 0.4		
			calculated s	experimental s	difference s
Ea,app = 128.23, kJ mol^{-1}	2	0.999282	234	240	6
Ao = 1.34 E16, s–1	10	0.999978	–	–	–
	20	0.996065	1766	1782	16

correl. for whole range a (0.05–0.95)

Table 3 – *Kinetic results from multilinear regression – SHR method*

Heating rate K min^{-1}	Ea,app kJ mol^{-1}	ln A	Ao s^{-1}	Reaction order n
20	129.43	37.2733	1.540E+16	1.3016
17	125.61	36.0527	4.544E+15	1.2726
15	127.07	36.5867	7.752E+15	1.3172
12	128.81	37.2133	1.450E+16	1.3564
10	128.85	37.3140	1.604E+16	1.3521
7	131.21	38.0639	3.396E+16	1.4319
5	124.55	35.9242	3.997E+15	1.3225
3.5	120.28	34.5071	9.688E+14	1.3597
2	118.50	33.8417	4.980E+14	1.3692

$\ln A = a\,\mathrm{Ea} + b$ for 2–10 K min^{-1} $a = 0.3306$ and $b = -5.283$

$\ln A = a\,\mathrm{Ea} + b$ for 17–20 K min^{-1} $a = 0.3195$ and $b = -4.0827$

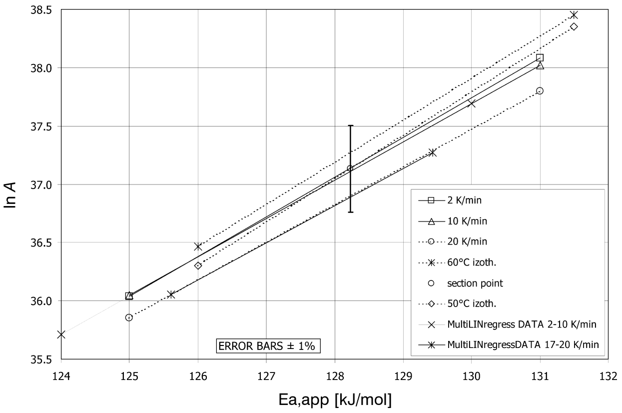

Fig. 6 – *IKR for nonisothermal conditions, for isothermally precured samples and SHR method*

calculated with isoconversional method and both go very close to the NP point. Lines for high heating rates are almost the same no matter of the calculation method; their deviation from NP is not significant. Correlations for the isothermal lines at 50 °C and 60 °C are $r^2 = 0.999332$ and $r^2 = 0.99544$, respectively, with the simulations from NP parameters. This means the NP point can be applied as a common point. It can be used for both curing regimes in a proposed quasi one step reaction model.

Conclusions

The overall or apparent kinetics of the DADC polymerization with 5 % CHPC were established using DSC. Isoconversional multiple-heating rate method (MHR), residual heat analysis of isothermally precured samples, and single heat method (SHR) were applied to determine the kinetic parameters. With the single step reaction model (ROn-type) a complex and multistep reaction system can be approximated. With the proposed procedure based on a "compensation effect" all three groups of the kinetic results can be unified in one common kinetic triplet.

Kinetic triplet from the common point $Ea,app = 128.23$ kJ/mol, $lnA = 37.133$ ($1.3410 \cdot 10^{16}$ s^{-1}) and $f(\alpha) = (1-\alpha)^{1.33}$ can be successfully used for the simulations of nonisothermal and isothermal curing processes as a quasi single step reaction model. Kinetic parameters can be applied to model the polymerization process in terms of the temperature distribution for different shapes and sizes of the lenses at different experimental conditions, which is important for the production of the products with almost perfect optical homogeneous structure.

Symbols

MHR – multiple heating rate method
SHR – single heating rate method
DADC – diethylene glycol bis(allyl carbonate)
CHPC – dicyclohexyl peroxy dicarbonate
Ea,app – apparent activation energy, kJ mol^{-1}
Ao – preexponential factor, 1 s^{-1}
lnA – natural logarithm of Ao
DSC – differential scanning calorimetry
a – slope of the linear equation (Eq. 7)
b – intercept of the linear equation (Eq. 7)
R – gas constant, J mol^{-1} K^{-1}
T – temperature, K
n – order of the reaction
α – conversion, reaction extent
ξ – factor producing a change in Arrhenius parameters
β – heating rate [K/min]
IKR – isokinetic relationship (compensation effect)
NP – narrowest point
r^2 – square of the correlation coefficient
MLIN – multilinear regression
ROn – reaction model of type – $(1-\alpha)^n$

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