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INVESTIGATION OF THE INFLUENCE OF DIFFUSION CONTROL ON THE CURING REACTION USING DSC AND TEMPERATURE MODULATED DSC

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Abstract

The curing reaction of a thermosetting system is investigated by DSC and temperature modulated DSC (TMDSC). When the material vitrifies during curing, the reaction becomes diffusion controlled. The phase shift signal measured by TMDSC includes direct information on the reaction kinetics. For long periods the phase shift is approximately proportional to the partial temperature derivative of the reaction rate. This signal is very sensitive for changes in the reaction kinetics. In the present paper an approach to determine the diffusion control influence on the reaction kinetics from the measured phase shift is developed. The results are compared with experimental data. Further applications of this method for other reactions are proposed.

Keywords: curing, diffusion controlled reaction, kinetics, thermosetting systems

Introduction

During curing reaction the system transforms from a low molecular liquid mixture of the epoxy resin and the curing agent into a three dimensional cross-linked macromolecule. In this process dramatical changes in the molecular dynamics and the macroscopic behavior of the material occur. Its clear indication is the increase of the glass transition temperature. If the isothermal reaction temperature is below the glass transition temperature of the fully cured material or the heating rate is relative low, the glass transition temperature of the reactive system can pass the actual sample temperature. In such a case the molecular mobility is reduced and the further reaction becomes diffusion controlled. This process is widely studied by DSC [1 and references within]. However, the investigation of vitrification processes in conventional DSC are extensive, because, the heat capacity change during reaction is masked by the large exothermal reaction peak. Therefore, the change of the glass transition must be measured separately.

Gobrecht *et al.* was the first to propose to use temperature modulation to measure the heat capacity change and the heat flow due to the reaction simultaneously [2]. The first systematical investigation of the glass transition during reaction by temperature modulated DSC (TMDSC) were carried out by Cassettari *et al.* [3, 4]. Van

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Assche *et al.* introduced a method for a direct description of the diffusion control using the heat capacity signal measured by TMDSC [5, 6]. As shown by Ferrari *et al.* the heat capacity change during reaction can be understood as a response of the thermal relaxation process [7]. Consequently, the heat capacity signal is frequency dependent. This was experimentally shown in references [8]. As a result, the Van Assche [5, 6] approach of the description of diffusion control delivers a frequency dependent diffusion control contribution on the reaction kinetics.

In the present paper these facts are discussed and a new determination method of the influence of diffusion control using the phase shift is introduced.

Experimental

Sample

The thermosetting system of investigation is diglycidylether of bisphenol A (DGEBA) (Shell Chemical, Epikote 828) and diaminodiphenyl methane (DDM) (Aldrich). The substances were mixed in the stoichiometric ratio of 2 mol DGEBA and 1 mol DDM and heated up to 120°C for 20 s. During this time the sample was stirred to get a homogeneous mixture. The mixture was then rapidly cooled to room temperature and approximately 3 mg samples were prepared in aluminum crucibles. The samples were stored at –35°C. At this temperature the samples are stable for several months. This was checked by a weekly measurement of the glass transition temperature (–14.8°C), the heat of reaction (406 J g^{-1}) and the maximum temperature of the reaction peak (160°C) by DSC. During the investigation time no significant deviations of this properties could be measured.

Instrumentation

The measurements were performed on a Mettler-Toledo DSC 821^e with intracooler using the 'ADSC' and the 'Model free kinetics' software option for temperature modulation and kinetic evaluation, respectively. The instrument was temperature calibrated using the melting peaks of water, indium and tin measured at 0.5, 1, 2, 5 and 10 K min^{-1}. Indium was used for the heat flow calibration.

In the TMDSC measurements the underlying temperature program is superimposed by a periodical temperature perturbation. The temperature amplitude T_a was 0.5 K. For all calculations blank corrected data (sample run subtracted by empty pan run) were used.

The calibrated heat flow Φ in the TMDSC can be described by

$$\Phi = \Phi_u + \omega T_a m|c|\cos(\omega t - \varphi) \qquad (1)$$

where Φ_u is the underlying heat flow (related to the conventional DSC curve), $\omega(=2\pi/t_p)$ is the angular frequency, t_p is the period, T_a the temperature amplitude, m the sample mass, $|c|$ is the modulus of the apparent specific complex heat capacity, t the time and φ is the phase shift. For the present application $|c|$ is in a good approximation equal to the real part of the apparent specific complex heat capacity $c'=|c|\cos\varphi$. Its imaginary part is $c''=|c|\sin\varphi$.

Result and discussion

Figure 1 shows normalized DSC curves of uncured material measured at different heating rates β_0. After the glass transition around –15°C the curing reaction starts. The reaction peak shifts to higher temperature with increasing heating rate. At β_0=1 K min^{-1} on the high temperature side of the reaction peak a small shoulder occurs. This is an indication for a change of the reaction kinetics due to diffusion control as a result of vitrification.

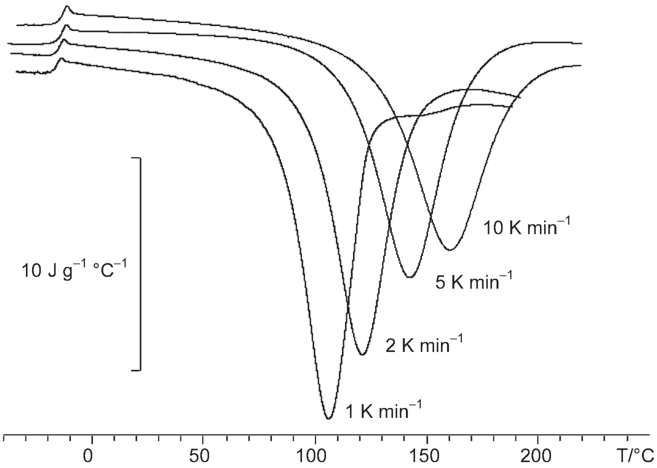

Fig. 1 DSC curves of uncured epoxy thermoset measured at different heating rates. The curves are normalized in heat capacity units

An indication that the sample vitrified delivers a TMDSC experiment with different heating rates [6]. The used epoxy system exhibits no significant vitrification at an underlying heating rate of 2 K min^{-1} or more. In agreement with the results of model free kinetics (Fig. 2) the TMDSC measurements indicate vitrification at underlying heating with 1 K min^{-1} [9].

From the curves in Fig.1 we can determine the apparent activation energy E_a as a function of conversion using the model free kinetics approached developed by Vyazovkin [10, 11]. For this procedure at least three curves measured with different heating rates are necessary. The dashed curve in Fig. 2 represents the apparent activation energy plot determined from the curves measured at 2, 5, 10 K min^{-1}. The nearly constant activation energy (E_a≈52 kJ mol^{-1}) describes the chemically controlled reaction. The black curve in Fig. 2 is the result from the curves measured at 1, 2, 5 K min^{-1}. Here the apparent activation energy shows a significant increase at approx. 90% conversion. This is also an indication for changing the reaction kinetics at $\beta_0\leq$1 K min^{-1}.

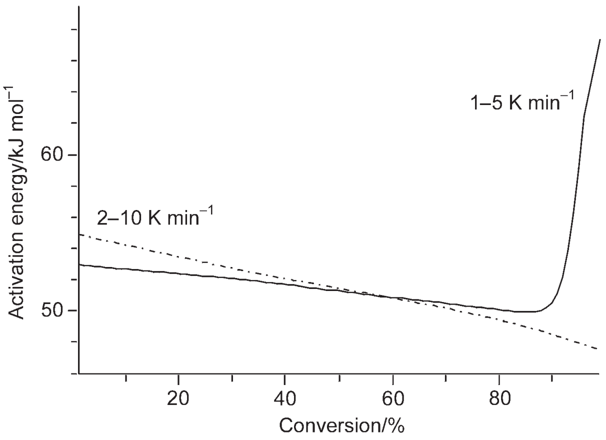

Fig. 2 Apparent activation energy as a function of conversion calculated from the curves in Fig. 1 using the 'Model-Free Kinetic' option of the Mettler-Toledo STAR^e-Software. For the dashed curve the data from the measurements at heating rates of 2, 5 and 10 K min^{-1} are used. The black curve is calculated from the 1, 2 and 5 K min^{-1} measurements

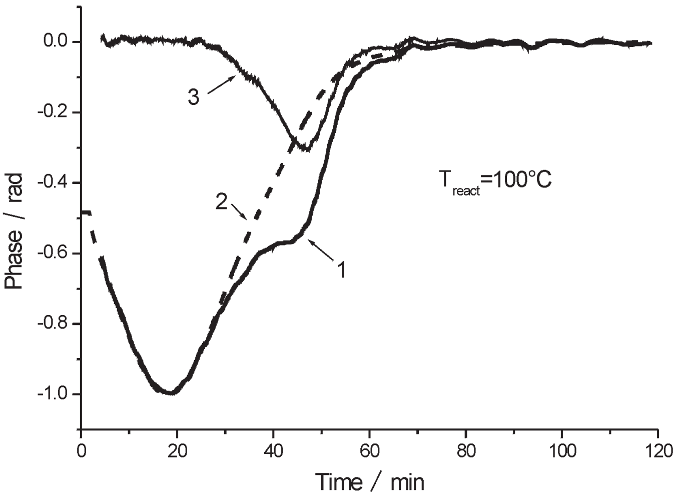

Fig. 3 Illustration of the determination procedure for $(\partial f_d/\partial t)_{T_u}$ using the phase shift and Φ_u, at 100°C (1 – measured phase shift φ, 2 – normalized heat flow $a_1\Phi_u$, 3 – subtracted curve). The period is 210 s

One possibility for description the kinetics of curing reaction is the introduction of a 'diffusion controlled function' f_d [12]. Than the observed rate of reaction ν can be expressed as:

$$\nu = \frac{d\xi}{dt} = \nu_{ch} f_d(\xi) \tag{2}$$

where ξ is the conversion and ν_{ch} the reaction rate of the fully chemically controlled reaction. For the epoxy-amine reaction an often used model function for the reaction rate is [13]:

$$\nu_{ch} = (k_1 + k_2 \xi^m)(1-\xi)^n \tag{3}$$

where k_1 and k_2 are rate constants, n and m are empirical reaction orders. Also for f_d model functions are described in the literature [12]. An application of this type of kinetics on the system of investigation is discussed in Ref. [14].

For fitting the experimental data with model functions a large number of parameters are necessary. Therefore, it is useful to reduce the number of fit-parameter by application of additional experiments. Van Assche *et al.* [5, 6] introduced an approach for determination of the diffusion controlled function with TMDSC. In this approach it is assumed that the stepwise decrease of the measured heat capacity signal $|c|$ during reaction describes the vitrification and it was suggested to determine f_d from the $|c|$- (or c'-) curve:

$$f_d = \frac{c_l(t,T) - |c(t,T)|}{c_l(t,T) - c_g(t,T)} \tag{4}$$

where $c_l(t,T)$ is the heat capacity curve of the liquid and $c_g(t,T)$ denotes the specific heat capacity of the glassy state. $|c(t,T)|$ is the measured curve.

As shown in [8] and discussed in details in [15, 16] the measured heat capacity signal is frequency dependent. Consequently, Eq. (4) delivers a frequency dependent

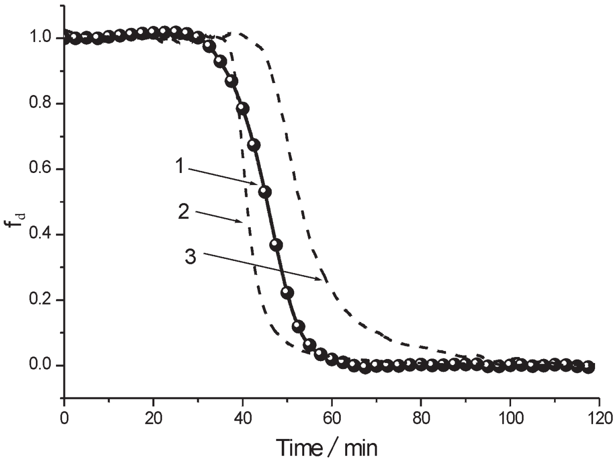

Fig. 4 Diffusing controlled functions for 100°C determined from different approaches. ($f_{d,\varphi}$: calculated from the phase shift according to step (i) to (iv) at t_p=210 s, $f_{d,c24}$ and $f_{d,c210}$ determined from the heat capacity curves measured at a period of 24 and 210 s, respectively, according to Eq. (4)

diffusion controlled function, as it is shown in the dashed curves in Fig. 4. However, a frequency dependent reaction kinetics is not in agreement with the experimental results. This disadvantage is our motivation to develop a different approach using direct information of the kinetics.

From literature it is well known that the phase shift φ (or c'') depends on the temperature derivative of the reaction rate [17–21]. According to [8] the phase shift subtracted by the contribution of the heat transfer path in the instrument can be described by

$$\varphi=\varphi_{\mathrm{relax}}+a\Delta h_{\mathrm{r}}t_{\mathrm{p}}\left(\frac{\partial\nu}{\partial T}\right)_{\mathrm{T_u}}+\frac{b}{t_{\mathrm{p}}}\Delta|c| \tag{5}$$

where a and b are constants, Δh_{r} the specific enthalpy of reaction, $(\partial\nu/\partial T)_{\mathrm{T_u}}$ the temperature derivative of the reaction rate around the underlying temperature T_{u} and $\Delta|c|$ the change of $|c|$ during relaxation. φ_{relax} denotes the phase shift due to relaxation. The first term in Eq. (5) is due to the thermal relaxation, the second term includes the information of the reaction kinetics and the third term describes the influence of the changes in the heat transfer conditions. Because the second term is proportional to the period and the third term is proportional to $1/t_{\mathrm{p}}$, the measured phase at long periods is mainly determined by the second term. For such conditions φ_{relax} is neglectably small. Therefore, we assume that the measured phase is proportional to the temperature derivative of the heating rate for long periods:

$$\varphi\propto\left(\frac{\partial\nu}{\partial T}\right)_{\mathrm{T_u}} \tag{6}$$

or

$$\varphi=a\left(\frac{\partial\nu}{\partial T}\right)_{\mathrm{T_u}} \tag{7}$$

In a good approximation of Eq. (7) is

$$\left(\frac{\partial\nu}{\partial T}\right)_{\mathrm{T_u}}=b\nu_{\mathrm{ch}}f_{\mathrm{d}}(\xi)+b_1\left(\frac{\partial f_{\mathrm{d}}}{\partial t}\right)_{\mathrm{T_u}} \tag{8}$$

where b and b_1 are constants. An explanation of the used approximation is given in the appendix.

The underlying heat flow Φ_{u} is proportional to the rate of reaction:

$$\Phi_{\mathrm{u}}=m\Delta h_{\mathrm{r}}\nu=m\Delta h_{\mathrm{r}}\nu_{\mathrm{ch}}f_{\mathrm{d}}(\xi) \tag{9}$$

By inserting of the Eqs (8) and (9) in (7) we receive

$$\varphi=a_1\Phi_{\mathrm{u}}+b_1\left(\frac{\partial f_{\mathrm{d}}}{\partial t}\right)_{\mathrm{T_u}} \tag{10}$$

where the constant a_1 is $a_1 = b/(m\Delta h_r)$. We get the diffusion controlled function by integration and normalization:

$$f_d(t) = 1 - \frac{\int_0^t (\varphi(t') - a_1\Phi_u(t'))\mathrm{d}t'}{\int_0^\infty (\varphi(t') - a_1\Phi_u(t'))\mathrm{d}t'} \tag{11}$$

Thus the determination algorithm of the diffusion controlled function from the phase shift signal includes four steps:

(i) TMDSC measurements at large periods and evaluation of the underlying (total) heat flow and the phase shift.

(ii) Determination of the maximum time and height of the reaction peak in Φ_u and calculation of the proportionality factor:

$$a_1 = \varphi(t_{\max})/(\Phi_u(t_{\max}) - \Phi_u(t_\infty)) \tag{12}$$

where $t_{\max}$ is the peak time of the Φ_u-peak and t_∞ characterizes a long time at which the reaction rate is practically zero.

(iii) Subtraction of the normalized heat flow from the phase.

(iv) Integration of the resulted peak to determine f_d using Eq. (11).

This procedure is illustrated in Fig. 3. The calculated diffusion controlled function is shown in Fig. 4 (solid line with circles). In addition, f_d determined from the heat capacity curves at periods of 24 and 210 s according to Eq. (4) are drawn as dashed curves in this figure for comparison.

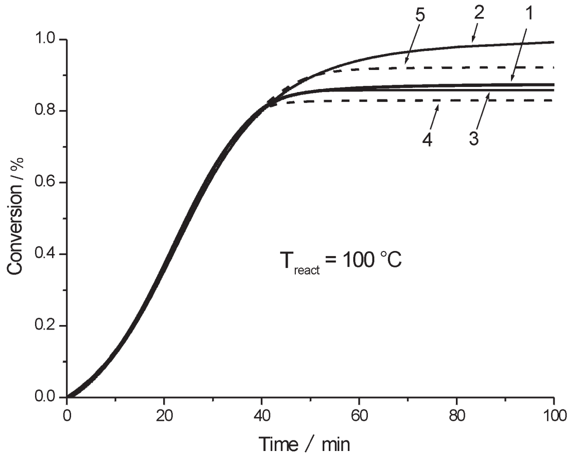

Fig. 5 Conversion curves of the isothermal curing of the thermoset at 100°C (1 – measured curve $\xi(t)$, 2 – curve without diffusion control ξ_{ch} determined by model free kinetics. 3 – calculated using curve 2 and $f_{d,\varphi}$, 4 – determined from curve 2 and $f_{d,c24}$, 5 – determined from curve 2 and $f_{d,c210}$)

The validity of the different diffusion controlled functions can be discussed using Fig. 5 by comparison of calculated results (Eq. (2)) with experimental data. The chemically controlled reaction rate ν_{ch} is determined by the apparent activation energy curve from the model-free kinetics using the heating curves above 1 K min^{-1} (dashed curve in Fig. 2). In the region without an important influence of diffusion ($\xi \leq 0.8$) the result of the model free kinetics is practically identical to the measured curve.

The modeled curves are calculated from Eq. (2) and following integration. As diffusion controlled functions all curves from Fig. 4 are used. The results are plotted in Fig. 5. The new approach, which uses the kinetic information of the phase shift ($f_{\mathrm{d},\varphi}$) delivers result with a very good agreement with the experimental data. In contrast, the heat capacity approach ($f_{\mathrm{d,c24}}$ and $f_{\mathrm{d,c210}}$) has a large uncertainty in the description of the diffusion control influence on the reaction kinetics. The reason of this is the frequency dependent heat capacity. The heat capacity measured by TMDSC does not describe the vitrification exactly.

Conclusions

The phase signal of the TMDSC measurements during curing of thermosetting systems includes information of the reaction kinetics. This is superimposed with contributions of relaxation and heat transfer. However, at measurements with long periods the reaction part becomes dominant. For such conditions the phase shift is proportional to the partial temperature derivative of the reaction rate.

If the reaction kinetics does not change during reaction, the measured phase shift is proportional to the underlying (total) heat flow signal. Otherwise changes in the reaction kinetics occur. In the case of curing reactions this is the contribution of diffusion control. In the presented approach this effect is used to determine the diffusion controlled function. For other chemical reactions the comparison of the phase shift and the total heat flow curve should be a simple and useful method to detect changes in reaction kinetics.

Appendix

It follows from Eq. (5) that the phase shift measured at long periods is proportional to the temperature derivative of the reaction rate

$$\varphi \propto \left(\frac{\partial \nu}{\partial T}\right)_{\mathrm{T_u}} \tag{A1}$$

We will find an approximation for the partial derivative $(\partial\nu/\partial t)_{\mathrm{T_u}}$. The rate of reaction is given in Eq. (2) to be $\nu=\nu_{\mathrm{ch}} f_{\mathrm{d}}(\xi)$. By temperature derivation follows:

$$\left(\frac{\partial \nu}{\partial T}\right)_{\mathrm{T_u}} = \left(\frac{\partial \nu_{\mathrm{ch}}}{\partial T}\right)_{\mathrm{T_u}} f_{\mathrm{d}}(\xi) + \nu_{\mathrm{ch}} \left(\frac{\partial f_{\mathrm{d}}}{\partial T}\right)_{\mathrm{T_u}} \tag{A2}$$

For an approximation of Eq. (A2) we will discuss this equation in two steps.

In the first step we solve the temperature derivative of the chemical controlled reaction rate of the first summand in Eq. (A2).

Chemical reactions usually are described by

$$\nu_{\mathrm{ch}}=k(T)f(\xi_{\mathrm{ch}}) \tag{A3}$$

where the conversion ξ is a function of the reaction time, k is the temperature dependent rate constant and $f(\xi)$ is the conversion function which is a model function dependent on the reaction mechanism. According to the Arrhenius equation the rate constant is given by:

$$k(T)=k_0\exp\left(-\frac{E}{RT}\right) \tag{A4}$$

where k_0 is the pre-exponential factor, E the activation energy and R is the gas constant.

Since $f(\xi_{\mathrm{ch}})$ is assumed to be temperature independent for the small temperature variation due to the temperature amplitude, the temperature dependence of the reaction rate is

$$\left(\frac{\partial\nu_{\mathrm{ch}}}{\partial T}\right)_{\mathrm{T_u}}=\left(\frac{\partial k}{\partial T}\right)_{\mathrm{T_u}}f(\xi_{\mathrm{ch}})=\frac{E}{RT_{\mathrm{u}}^2}f(\xi_{\mathrm{ch}})k(T_{\mathrm{u}})=\frac{E}{RT_{\mathrm{u}}^2}\nu_{\mathrm{ch}} \tag{A5}$$

From of Eq. (A5) it follows for the first summand of Eq. (A2):

$$\left(\frac{\partial\nu_{\mathrm{ch}}}{\partial T}\right)_{\mathrm{T_u}}f_{\mathrm{d}}(\xi)=b\nu_{\mathrm{ch}}f_{\mathrm{d}}(\xi) \tag{A6}$$

where $b=E/(RT_{\mathrm{u}}^2)$ is a proportional constant.

In the second step we discuss the second summand of Eq. (A2). We can write:

$$\nu_{\mathrm{ch}}\left(\frac{\partial f_{\mathrm{d}}}{\partial T}\right)_{\mathrm{T_u}}=\left(\frac{\partial\xi_{\mathrm{ch}}}{\partial t}\right)_{\mathrm{T_u}}\left(\frac{\partial f_{\mathrm{d}}}{\partial T}\right)_{\mathrm{T_u}}=\left(\frac{\partial\xi_{\mathrm{ch}}}{\partial T}\right)_{\mathrm{T_u}}\left(\frac{\partial f_{\mathrm{d}}}{\partial t}\right)_{\mathrm{T_u}} \tag{A7}$$

In the relevant range of reaction we assume $(\partial\xi_{\mathrm{ch}}/\partial T)_{\mathrm{T_u}}$ to be a constant b_1.

By introducing of Eqs (A6) and (A7) into (A2) we receive for the temperature dependence of the reaction rate around the actual underlying temperature:

$$\left(\frac{\partial\nu}{\partial T}\right)_{\mathrm{T_u}}=b\nu_{\mathrm{ch}}f_{\mathrm{d}}(\xi)+b_1\left(\frac{\partial f_{\mathrm{d}}}{\partial t}\right)_{\mathrm{T_u}} \tag{A8}$$

References

1 R. B. Prime, Thermosets, In: E. A. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic Press, San Diego 1997, p. 1380.

2 H. Gobrecht, K. Hamann and G. Willers, J. Phys. E: Sci. Instrum., 4 (1971) 21.

3 M. Cassettari, G. Salvetti, E. Tombari, S. Veronesi and G. P. Johari, Il Nuovo Cimento, 14D (1992) 763.
4 M. Cassettari, F. Papucci, G. Salvetti, E. Tombari, S. Veronesi and G. P. Johari, Rev. Sci. Instrum., 64 (1993) 1076.
5 G. Van Assche, A. Van Hemelrijck, H. Rahier and B. Van Mele, Thermochim. Acta, 268 (1995) 121.
6 G. Van Assche, A. Van Hemelrijck, H. Rahier and B. Van Mele, Thermochim. Acta, 304/305 (1997) 317.
7 C. Ferrari, G. Salvetti, E. Tombari and G. P. Johari, Phys. Rev. E, 54 (1996) R1058.
8 J. E. K. Schawe, Thermochim. Acta, 361 (2000) 97.
9 J. E. K. Schawe, in preparation.
10 S. Vyazovkin and C. A. Wight, Annu. Rev. Phys. Chem., 48 (1997) 129.
11 S. Vyazovkin, J. Thermal Anal., 49 (1997) 1493.
12 J. Fournier, G. Williams, C. Duch and G. A. Aldridge, Macromolecules, 29 (1996) 7097.
13 M. R. Kamal, Polym. Eng. Sci., 14 (1974) 231.
14 W. Jenninger, J. E. K. Schawe and I. Alig, Polymer, 41 (2000) 1577.
15 J. E. K. Schawe and I. Alig, Colloid Polym. Sci. submitted.
16 J. E. K. Schawe and I. Alig, J. Chem. Phys., submitted.
17 A. Toda, T. Oda, M. Hikosaka and Y. Saruyama, Polymer, 38 (1997) 231.
18 A. Toda, C. Tomita, M. Hikosaka and Y. Saruyama, Polymer, 38 (1997) 2849.
19 A. Toda, T. Arita, C. Tomita and M. Hikosaka, Thermochim. Acta, 330 (1999) 75.
20 A. A. Lacey, C. Nikolopoulos and M. Reading, J. Thermal Anal., 50 (1997) 267.
21 J. E. K. Schawe and G. R. Strobl, Polymer, 39 (1998) 3745.