

# **DEVELOPMENT OF A UNIVERSAL SAMPLE CONTROLLED THERMAL ANALYSIS (SCTA) SYSTEM FOR BEING USED WITH ANY THERMOANALYTICAL INSTRUMENT**

J.M. Criado, L.A. Pérez-Maqueda, M.J. Diáñez and P.E. Sánchez-Jiménez  
Instituto de Ciencia de Materiales de Sevilla, Centro Mixto Universidad de Sevilla-C.S.I.C.,  
Avda. Américo Vespucio s/n, 41092 Sevilla (Spain)

## **ABSTRACT**

The SCTA method implies to control the temperature in such a way that the reaction rate changes with the time according to a function previously defined by the user. Constant Rate Thermal Analysis (CRTA) is one of the most commonly used SCTA methods and implies achieving a temperature profile at which the reaction rate remains constant all over the process at a value previously selected by the user. This method permits to minimize the influence of heat and mass transfer phenomena on the forward reaction. The scope of this work is to develop a universal CRTA temperature controller that could be adapted to any thermoanalytical device. The thermoanalytical signal is programmed to follow a preset linear trend by means of a conventional controller that at the time controls a second conventional temperature programmer that forces the temperature to change for achieving the trend programmed for the thermoanalytical signal. Examples of the performance of this control system with a Thermobalance and a Thermomechanical Analyser (TMA) are given.

Keywords: SCTA, CRTA, TG, TMA, PVC, BaTiO<sub>3</sub>

## **INTRODUCTION**

The study of the kinetics of solid state reactions continues attracting the attention of researchers as shown by the large number of recent articles on the topic (1-24). Sample Controlled Thermal Analysis (SCTA) methods have proven to be more effective than conventional rising temperature experiments for obtaining reliable kinetic data of thermal decomposition of solids (25-42). This is because the ability of SCTA for performing a direct or indirect control of both the partial pressure of the gases generated in the reaction and the heat evolution proportional to the reaction rate, minimizing the influence of heat and mass transfer phenomena on the forward reaction. This advantage has been also used for synthesising materials with controlled texture and structure (43-57). The scope of this work is to develop a new SCTA control system that does not require a control signal directly proportional to the rate of the process like in the SCTA controllers previously developed and, therefore, would be easily adapted to any thermoanalytical instruments.

## **EXPERIMENTAL**

High purity Polyvinyl chloride (PVC) and Barium Titanate samples supplied by Aldrich have been used.

A CI Electronic thermobalance that allows sample weights up to 5 g has been used. The thermobalance can be operated under vacuum or flow of gases. The thermal decomposition of PVC has been carried out using a starting weight of sample of 80 mg and a flow rate of nitrogen of 80 cc/min.

A Themomechanical Analyser (TMA) equipment developed by us has been used. The variation in length of the sample is measured with a LVDT transducer from RDP, model D5 100AG. The LVDT is provided with a guide armature fitted to an alumina pushrod that can be displaced until contacting the sample by means of a micrometric screw. This TMA device can be operated under high vacuum or controlled atmosphere. The shrinkage of BaTiO<sub>3</sub> pellets has been followed under air atmosphere. The pellets were prepared from powder samples of 500 mg that were uniaxially pressed into a disc of 13 mm in diameter under a pressure of 660 MPa.

## RESULTS AND DISCUSSION

Fig. 1 shows the CRTA control system. It is constituted by a conventional Eurotherm programmer, model 2408, which receives the analog output of the thermocouple and controls the temperature of the sample placed in the Thermoanalytical Instrument (TAI) under either isothermal or rising temperature conditions at a temperature or heating rate previously selected. A second Eurotherm programmer, model 2408, was used for programming the profile of the analog output supplied by the TAI as a function of the time. It is noteworthy to point out that a single programmer cannot control the temperature such that the TAI signal follows a linear profile because the Proportional Integral Differential (PID) control requires the value of the control parameter (the sample weight or the total change in length in our case) to be reversible as a function of the parameter to be controlled (i.e.; the temperature). This condition is fulfilled by differential signals, such as decomposition rate or sintering rate, but not by integral signal, such as sample weight (in the case of a TG) or shrinkage (in the case of TMA), because these integral parameters are not reversible. The control of the reaction rate is achieved by connecting the control relay of the TAI programmer to the digital input, LA, of the temperature programmer. CRTA control is performed by selecting from the menu of the digital input a command that allows one to move the temperature program from a preset heating rate when the TAI control relay is closed, to a preset cooling rate when the TAI control relay is open. In other words, the temperature increases if the output signal supplied by the TAI is higher than the programmed setpoint and decreases if it is lower than the setpoint. The Holdback command of the TAI programmer must be activated all over the process in order to stop the program when the TAI signal is lower than the programmed value and to resume again when the input is higher than the setpoint.

Fig. 2 shows the percentage of weight loss and the temperature as a function of the time obtained for the thermal dehydrochlorination of PVC under CRTA control. The weight signal schedule was programmed in the TAI programmer outlined in Fig. 1 for a weight decrease rate of  $3 \cdot 10^{-2}$  mg/min. The temperature controller was programmed such that either a heating or cooling rate of  $2^{\circ}\text{C}/\text{min}$  was selected depending on whether the weight output of the electrobalance was higher or lower, respectively, than the weight setpoint. The percentage of weight loss versus temperature determined from the CRTA plots of Fig. 2 is shown in Fig. 3 together with a the TG curve obtained at a heating rate of  $2^{\circ}\text{C}/\text{min}$ . It can be observed that CRTA provides a better discrimination

of the two steps observed in the thermal degradation of PVC than conventional TG. It is quite clear that the CRTA curve of the first step of the dehydrochlorination of PVC falls back on itself upon achieving the preset constant rate, indicating that this reaction follows either an Avrami-Erofeev kinetics (33), as we suggested in a previous paper (58), or a mechanism controlled by the random scission of the main chain of the polymer (59), instead of obeying a “n order” kinetics as commonly proposed in literature (60-).

Fig. 4 shows the change of the dimension and the temperature as a function of the time obtained for BaTiO<sub>3</sub> with the TMA developed by us under CRTA control at a constant shrinkage rate  $C=0.258 \mu\text{m}/\text{min}$ . In this case the analogical output corresponding to the total change of length supplied by the LVDT transducer was used as input of the TAI signal programmer on the device outlined in Fig. 1 following the procedure previously described for the electrobalance. The shrinkage data taken from Fig. 4 have been plotted as a function of the corresponding temperatures in Fig. 5 together with the shrinkage plot obtained at linear heating of 5°C/min. These results clearly point out that the densification attained by BaTiO<sub>3</sub> under CRTA control of temperature is considerably higher than under linear heating control.

## CONCLUSIONS

1. It has been developed a universal control system that can be easily adapted to any Thermoanalytical Instrument (TG, TMA, Dilatometer, etc.) that supplies to this control system a signal input directly proportional to the total progress of the reaction, without requiring an input representative of the reaction rate.
2. The **CRTA** control system developed here has been successfully applied to the study of *a*) the thermal decomposition of PVC by means of a conventional electrobalance and *b*) the sintering of BaTiO<sub>3</sub> by means of a TMA equipment developed by us.

## REFERENCES

1. L.A. Pérez-Maqueda, P.E. Sánchez-Jiménez and J.M. Criado, Int. J. Chem. Kinet., 37 (2005) 658
2. J. Shánelová, J. Málek, M.D. Alcalá and J.M. Criado, J. Non-Cryst. Solids, 351 (2005) 557

3. L.A. Pérez-Maqueda, P.E. Sánchez-Jiménez and J.M. Criado, *Polymer*, 46 (2005) 2950
4. P. Budugreac, J.M. Criado, F.J. Gotor, J. Málek, L.A. Pérez-Maqueda and E. Segal, *Intern. J. Chem. Kinetics*, 36 (2004) 309
5. D. Svadlák, J. Shánelová, J. Málek, L.A. Pérez-Maqueda, J.M. Criado and T. Mitsuhashi, *Thermochim. Acta*, 414 (2004) 137
6. L.A. Pérez-Maqueda, F.J. Gotor, J. Málek and N. Koga, *J. Thermal anal. Calorim.*, 72 (2003) 901
7. L.A. Pérez-Maqueda, J.M. Criado and C. Real, *J. Am. Ceram. Soc.*, 85 (2002) 763
8. J. Málek, T. Mitsuhashi and J.M. Criado, *J. Mater. Res.*, 16 (2001) 1862
9. F.J. Gotor, J.M. Criado and J. Málek, *J. Am. Ceram. Soc.*, 84 (2001) 1797
10. P.P. Papageorgiou, D.S. Achilias, D.N. Bikiaris and G.P. Karayannidis, *J. Thermal Anal. Calorim.*, 84 (2006) 85
11. Y. Cheng, H.N. Xiao, W.M. Guo and W.M. Guo, *Thermochim. Acta*, 444 (2006) 173
12. B. Saha, A.K. Maiti and A.K. Ghoshal, *Thermochim. Acta*, 444 (2006) 46
13. L.C.S. Sides, A.A.S. Araujo, M. Santos-Filho and J.R. Matos, *J. Thermal Anal. Calorim.*, 84 (2006) 441
14. F. Liu, G.C. Yang, H.F. Wang, Z. Chen and Y.H. Zhou, *Thermochim. Acta*, 443 (2006) 212
15. N. Mehta and A. Kumar, *J. Thermal Anal. Calorim.*, 83 (2006) 669
16. S. Vyazovkin, *J. Thermal Anal. Calorim.*, 83 (2006) 45
17. B.A. Howell, *J. Thermal Anal. Calorim.*, 83 (2006) 53
18. P. Simon, E. Illekova and S.C. Mojundar, *J. Thermal Anal. Calorim.*, 83 (2006) 67
19. K. Pielichowski and B. Swierz-Motysia, *J. Thermal Anal. Calorim.*, 83 (2006) 207
20. P. Simon, *J. Thermal Anal. Calorim.*, 82 (2005) 651
21. M.E. Brown, *J. Thermal Anal. Calorim.*, 82 (2005) 651
22. T. Ozawa, *J. Thermal Anal. Calorim.*, 82 (2005) 687
23. I.M.K. Ismail and T. Hawkins, *Thermochim. Acta*, 439 (2005) 32
24. J.M. Wang, M.P.G. Laborie and M.P. Wolcott, *Thermochim. Acta*, 439 (2005) 68

25. J. Rouquerol, *Thermochim. Acta*, 144 (1988) 209
26. M. Reading, D. Dollimore, , J. Rouquerol and F. Rouquerol, *J. Thermal Anal.*, 37 (1989) 775
27. F. Rouquerol, Y. Laureiro and J. Rouquerol, *Solid State Ionics*, 63 (1993) 363
28. S. Bordère, F. Rouquerol, P.L. Lawellin and J. Rouquerol, *Thermochim. Acta*, 282 (1996) 1
29. J.M. Criado, F. Rouquerol and J. Rouquerol, *Thermochim. Acta*, 38 (1980) 117
30. M. Reading, in: P.K. Gallagher (Ed.), *Handbook of Thermal Analysis and Calorimetry*, Elsevier, Amsterdam 1998, Vol.1, p 423
31. N. Koga and J.M. Criado,, *Int. J. Chem. Kinetics*, 30 (1998) 737
32. L.A. Pérez-Maqueda, J.M. Criado and F.J. Gotor, *Int. J. Chem. Kinet.*, 34 (2002) 184
33. J.M. Criado, A. Ortega and F.J. Gotor, *Thermochim. Acta*, 157 (1990) 171
34. F.J. Gotor, M. Macías, A. Ortega and J.M. Criado, *Phys. Chem. Miner.*, 27 (2000) 495
35. F.J. Gotor, J.M. Criado, J. Málek and N. Koga, *J. Phys. Chem. A* 104 (2000) 10777
36. L.A. Pérez-Maqueda, J.M. Criado, F.J. Gotor and J. Málek, *J. Phys. Chem. A* 106 (2002) 2862
37. P.A. Barnes, G.M.B. Parkes, D.R. Brown and E.L. Charsley, *Thermochim. Acta*, 269 (1995) 665
38. E. Baden, P. Llewellyn, J.M. Falconis, C. Jourdan, S. Veessler, R. Boistelle and F. Rouquerol, *J. Solid State Chem.*, 139 (1998) 37
39. S. Ichihara, A. Endo and T. Aarii, *Thermochim. Acta*, 360 (2000) 179
40. M.J. Tiernan, P.A. Barnes and G.M.B. Parkes, *J. Phys. Chem. B* 105 (2001) 220
41. K. Nahdi, P. Llewellyn, F. Rouquerol,, J. Rouquerol, N.K. Ariguib and M.T. Ayedi, *Thermochim. Acta*, 390 (2002) 123
42. J.M. Criado and L.A. Pérez-Maqueda, in: O.T. Sorensen and J. Rouquerol (Eds), *Sample Controlled Thermal Analysis*, Chapter 4 (“SCTA and Kinetics”), p 62, Kluwer Academic Publishers, Dordrecht (The Netherland) 2003, p 62
43. M.H. Stacey, *Langmuir*, 3 (1987) 681
44. L.A. Pérez-Maqueda, J.M. Criado, C. Real, J. Subrt and J. Boháček, *J. Mater. Chem.*, 9 (1999) 1839

45. L.A. Pérez-Maqueda, J.M. Criado, J. Subrt and C. Real, *Catal. Lett.*, 60 (1999) 151
46. G.S. Chopra, C. Real, M.D. Alcalá, L.A. Pérez-Maqueda, J. Subrt and J.M. Criado, *Chem. Mater.*, 11 (1999) 1128
47. G. Agarwall, R.F. Speyer, and W.S. Hakenberger, *J. Mater. Res.*, 11 (1996) 671
48. G. Agarwall and R.F. Speyer, *J. Mater. Res.*, 11 (1996) 671
49. F. Chehimi-Moumen, P. Llewellyn, F. Rouquerol, G. Vacquier, D.B. Hassem-Chehimi, M. Ferid and M. Trabelsi-Ayadi, *J. Thermal anal. Calorim.*, 82 (2005) 783
50. P.Llewellyn and J. Rouquerol, *J. Thermal anal Calorim.*, 72 (2003) 1099
51. E.A. Fesenko, P.A. Barnes, G.M.B. Parkes, D.R. Brown and M. Naderi, *J. Thermal Anal. Calorim.*, 72 (2003) 1103
52. O. Monnereau, L. Tortet, P. Llewellyn, F. Rouquerol, and G. Vackier, *Solid State Ionics*, 157 (2003) 163
53. E.A. Dawson, G.M.B. Parkes,, P.A. Barnes and M.J. Chinn, *Carbon*, 41 (2003) 571
54. E.A. Dawson, G.M.B. Parkes,, P.A. Barnes, M.J. Chinn, L.A. Pears and C.J. Hindmmarsh, *Carbon*, 40 (2002) 2897
55. E.A. Fesenko, P.A. Barnes, G.N.B. Parkes, E.A. Dawson and M.J. Tiernan, *Topics in Catalysts*, 19 (2002) 283
56. C. Real, M.D. Alcalá and J.M. Criado, *J. Am. Ceram. Soc.*, 87 (2004) 75
57. M.D. Alcalá, J.M. Criado, F.J. Gotor and C. Real, *J. Mater. Sci.*, 41 (2006) 1993
58. P. Budugreac, E. Segal, L.A. Pérez-Maqueda and J.M. Criado, *Polym. Degrad. Stabil.*, 84 (2004) 311
59. T. Aarii, S. Ichihara, H. Nakagawa and N. Fujii, *Thermochim. Acta*, 319 (1998) 139
60. S. Kim,, *Waste Manage. Res.*, 21 (2001) 609
61. A. Jiménez, V. Berenguer, J. López and A. Sánchez, *J. Appl. Polym. Sci.*, , 50 (1993) 1565
62. A. Marcilla and M. Beltrán, *Polym. Degrad. Stab.*, 64 (1999) 127
63. M.J.P. Spalak, J.M.N. van Kasten and A.A.H. Drinkenburg, *Comput. Theor. Polym. Sci.*, 10 (2000) 481
64. R. Miranda, J. Yang, C. Roi and C. Vasile, *Polym. Degrad. Stab.*, 72 (2001) 469

65. T. Karayildirim, J. Yanik, M. Yuksel, M. Saglam, C. Vasile and H. Bockhorn, J. Anal. Appl. Pyrolysis, 75 (2006) 112



## CAPTIONS OF FIGURES

Figure 1. Scheme of the CRTA system developed for controlling the reaction temperature through the input supplied by any Thermoanalytical Instrument (TAI).

Figure 2. Plots of mass loss percentage and temperature as a function of the time for the thermal dehydrochlorination of PVC at a constant decomposition rate  $C = 3 \cdot 10^{-2}$  mg/min.

Figure 3. CRTA and TG plots recorded for the thermal decomposition of PVC under decomposition rate  $C = 3 \cdot 10^{-2}$  mg/min and a heating rate of  $2^{\circ}\text{C}/\text{min}$ , respectively.

Figure 4. Rate Controlled TMA of a  $\text{BaTiO}_3$  pellet under a constant shrinkage rate equal to  $0.258 \mu\text{m}/\text{min}$ .

Figure 5. TMA of  $\text{BaTiO}_3$  pellets recorded under a linear heating rate of  $5^{\circ}\text{C}/\text{min}$  and under a constant shrinkage rate of  $0.25899999 \mu\text{m}/\text{min}$ , respectively.

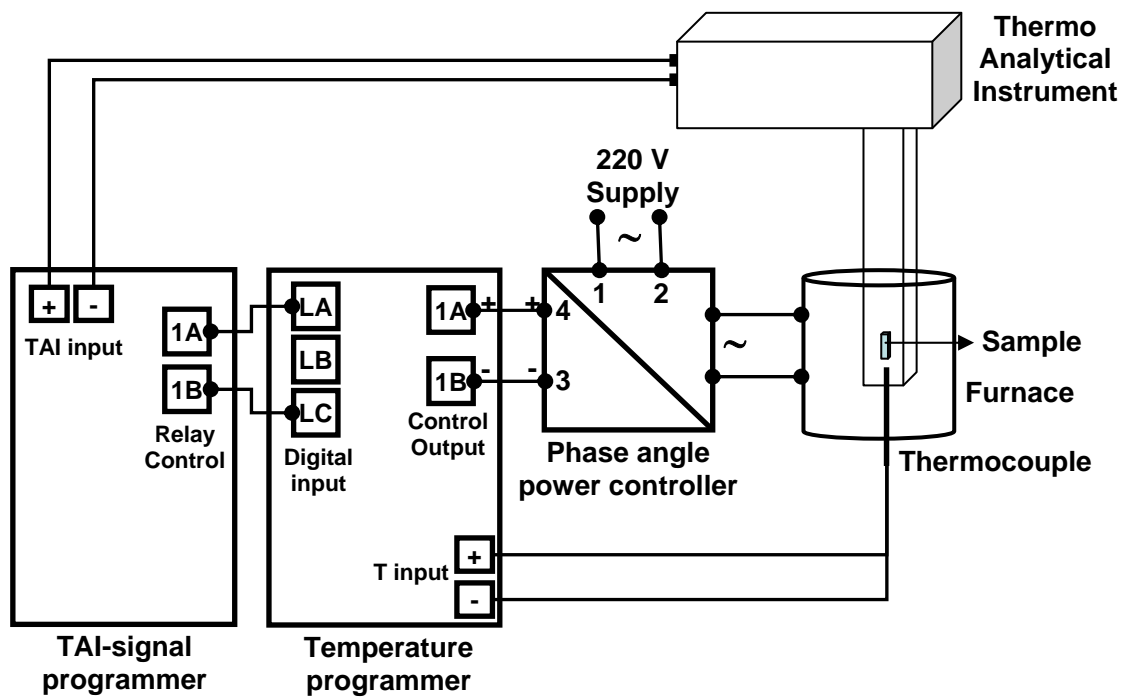


Fig. 1

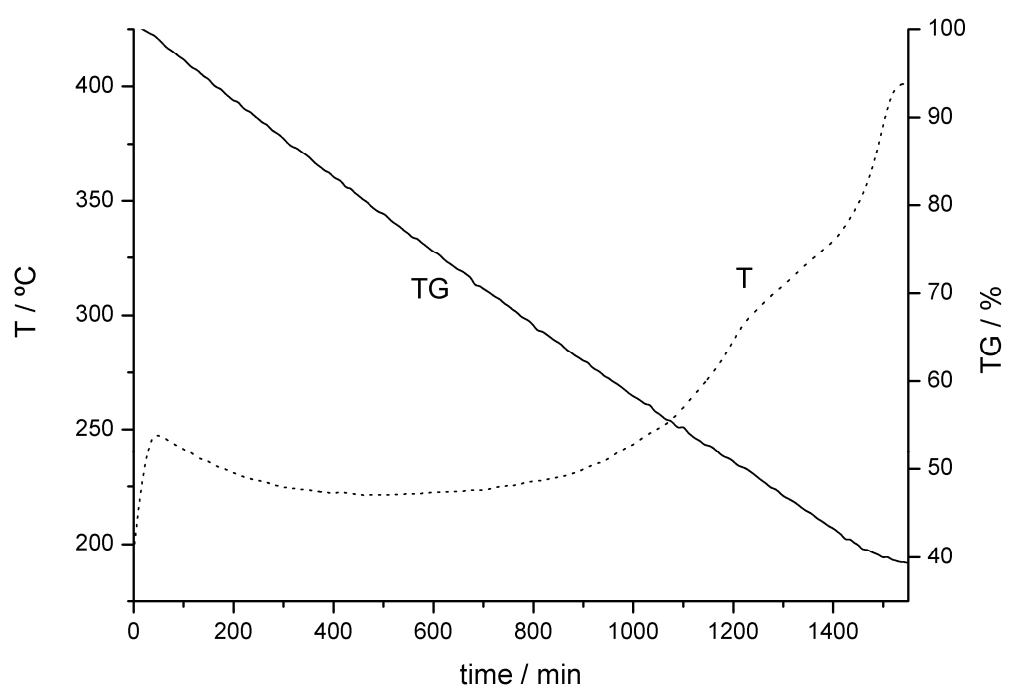


Fig. 2

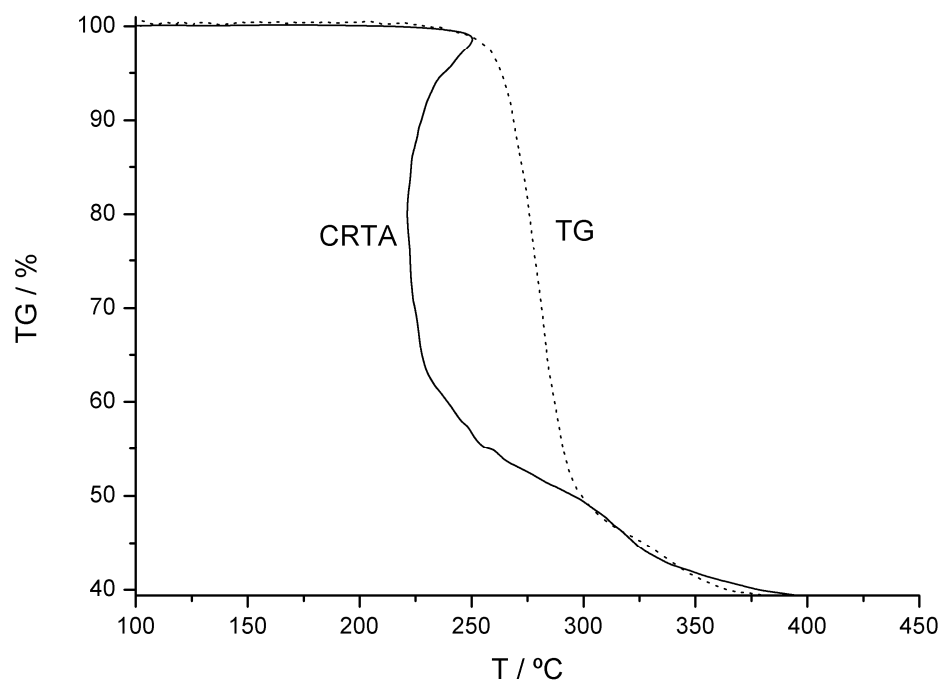


Fig. 3

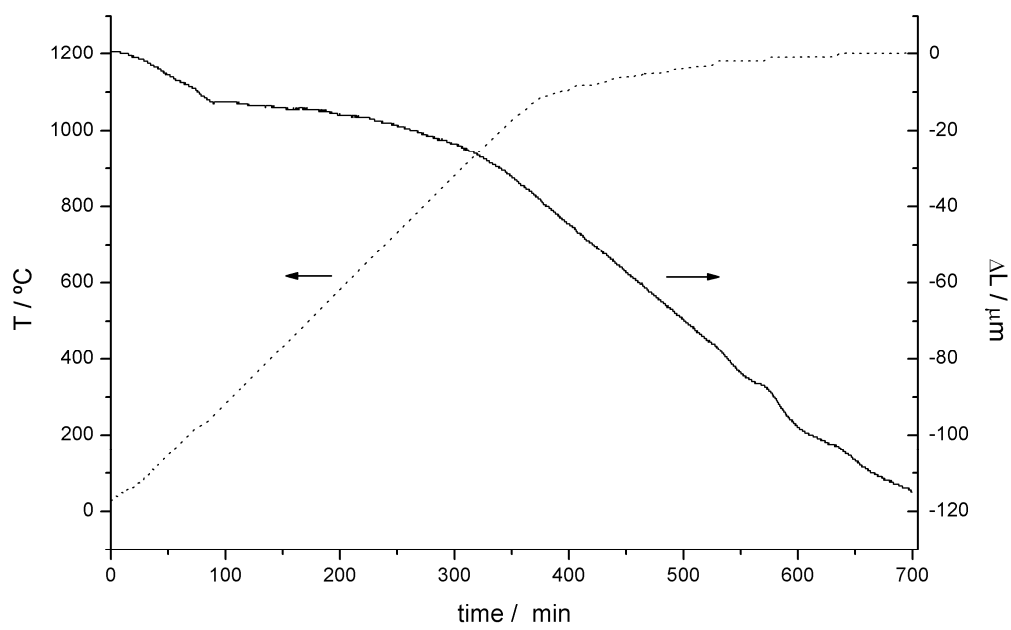


Fig4

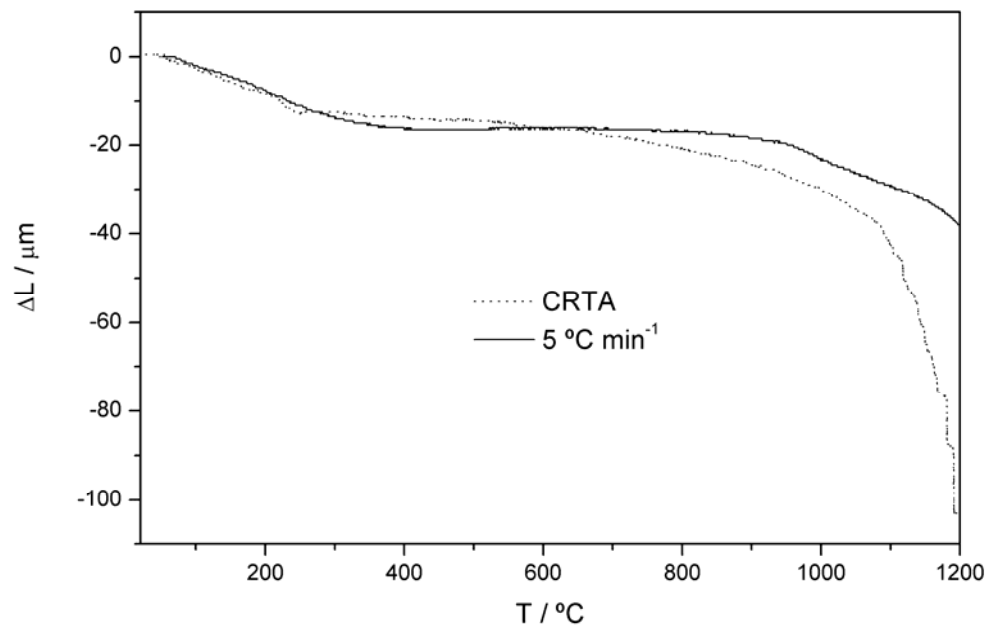


Fig. 5