

## A new method for on-line monitoring of non isothermal crystallization kinetics of polymers

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### Summary

Detailed knowledge of polymer crystallization kinetics is a mandatory requirement in modeling of transformation processes. On the other hand, techniques for investigation of crystallization kinetics are limited to cooling rates much lower than those experienced by the materials in industrial processes. A method suitable to investigate crystallinity evolution during cooling procedures carried out adopting rates comparable with those experienced by the polymer during industrial processes is thus extremely attractive.

In this work a method is proposed, based on fast cooling of thin samples by means of air/water sprays and optical detection of the crystallization phenomenon. Preliminary results of crystallization temperatures detected with a device based on such a method are presented and, in the low cooling rate range, are compared favorably with calorimetric results. The comparison of experimental crystallization temperature with results of a kinetics model previously developed leads to satisfactory agreement.

### Introduction

Crystallization kinetics of polymers has been widely investigated with a large theoretical and experimental effort, because of its relevance in the evaluation and modeling of polymer transformation processes. Detailed knowledge of crystallization kinetics under isothermal and non isothermal conditions is strictly required to evaluate all other variables characterizing a polymer transformation process (pressure, kinematics, external forces, ...). Experimental crystallinity evolution is accessible only in a narrow window of external conditions. In particular, DSC calorimeters, currently adopted for the study of crystallization kinetics, can be operated under isothermal conditions with a limited degree of undercoolings and under constant cooling rates up to about  $1\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$ . An optical method, previously suggested by Ding and Spruiell [1-2], and before by Magill [3-4], can be adopted to measure crystallinity evolution during cooling experiments carried out at cooling rates larger than those allowed by DSC apparatuses. In the last years, researchers of the University of Palermo [5, 6] developed and adopted an experimental procedure to investigate the crystallization of polymers under very fast cooling. Thin polymer samples held between two copper plates were quenched by water sprays, and temperature histories during quenching procedure were measured by a suitable thermocouple connected to a

data acquisition system. Unfortunately, this device does not allow monitoring the crystallinity *during* the cooling. A similar device, with the quench zone optically accessible through two windows, should be able to realize high cooling rates while monitoring crystallinity evolution. The aim of this work was the design, the development of such an apparatus and the analysis of preliminary experimental results.

### **Material and methods**

The resin adopted for the experiments performed in this work is a commercial iPP supplied by Montell (T30G,  $M_w = 481000$ ,  $M_n = 75000$ , tacticity = 87.6%*mmmm*). Quiescent crystallization kinetics of the resin was already satisfactory described by a slight modification of the model proposed by Ziabicki [8], as modified by Lamberti and Titomanlio [7].

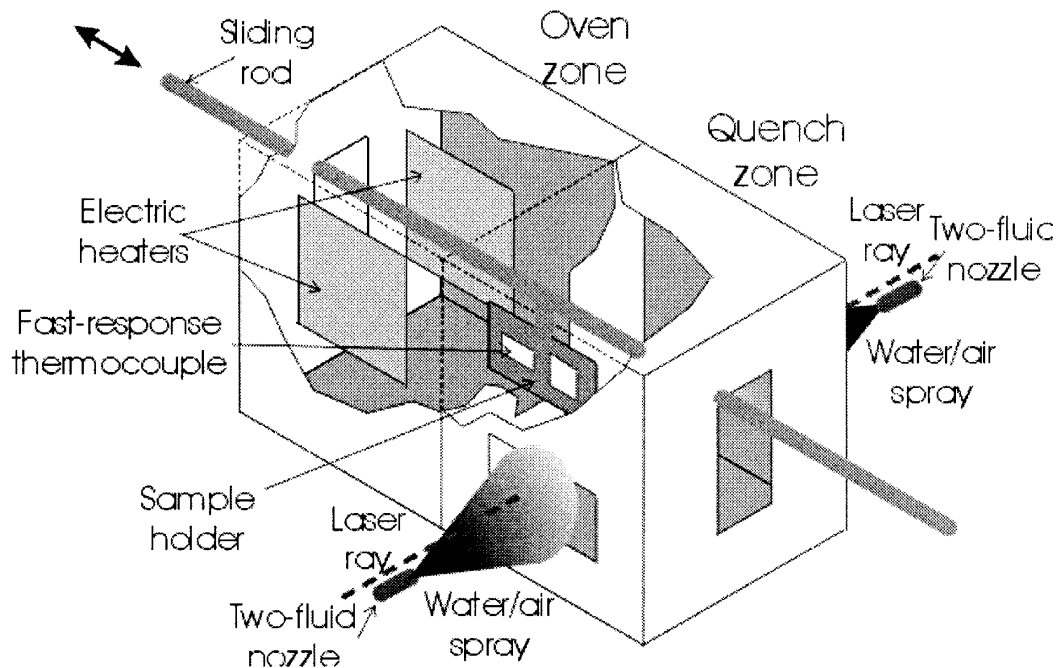
#### *Apparatus description*

An apparatus for quenching thin polymer samples (typically, 50-100 microns thickness), and monitoring crystallization during the quench was developed. A scheme of the apparatus is shown in Figure 1. The apparatus includes a hot (oven zone) section and a cold (quench zone) section and is equipped with a sample holder device suitable for fast transfer of the sample from the hot to the cold section. Temperature data are measured by a fast response K-type thermocouple (Omega CO1-K, response time of 10 ms), located close to the polymer sample. Its signal is sampled and recorded by a data acquisition system (National Instruments, PCI 1200). The cooling system, based on nozzles spraying gas or gas-liquid (typically air and water) operated nozzles (Spraying System, SUJ4B) on the sample allowed to obtain cooling rates up to several hundreds of °C/s.

The real time crystallinity measurement set up is schematically shown in Figure 2. It was made of a polarized light source (Melles Griot, HeNe Laser,  $\lambda = 632.8$  nm, 5 mW max output) and a photo-resistance acting as light intensity detector. The output of the photo-resistance is sampled and recorded by the same data acquisition system adopted for acquisition of temperature. A specific software code (based on National Instruments LabView 5.0.1, G programming language) was developed to synchronize the recording of both temperature and light intensity data.

#### *Experimental procedure*

Thin polymeric films were confined between two thin glass windows. Also the thermocouple was located between the two glass windows very close to the polymer, and the sandwich was fastened to the traveling sample holder. In order to erase the effect of any previous history, the polymer was molten and annealed in the oven section of the apparatus at 240°C for 30 min. After annealing of the polymer, the sample holder was moved quickly to the quench section, where it was spray cooled, while temperature and light intensity were recorded.



**Figure 1.** A scheme of the quenching device

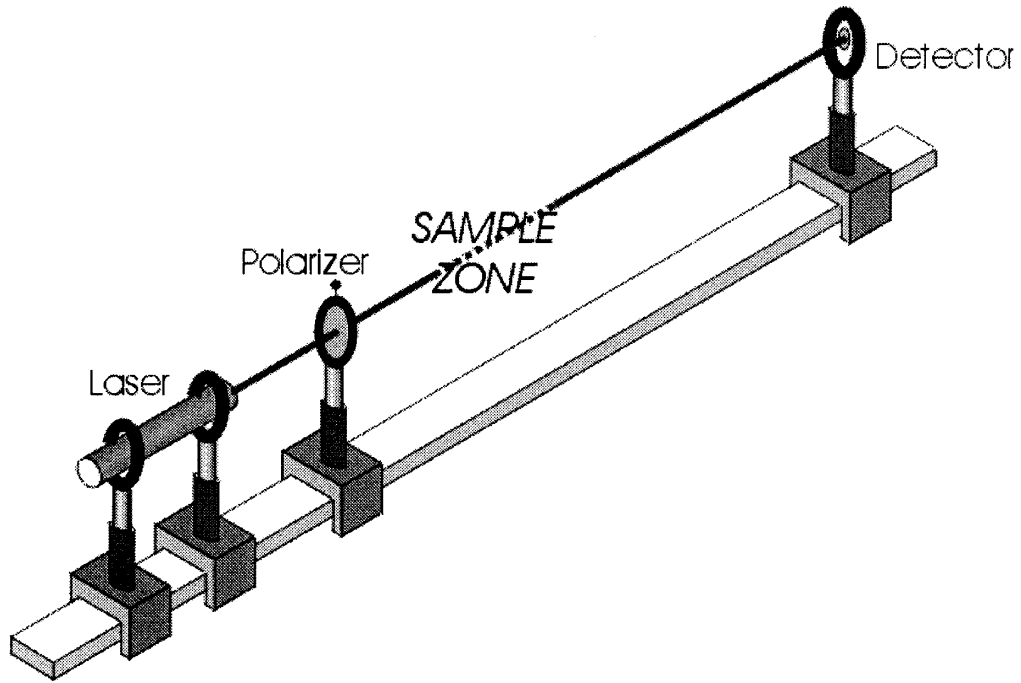
## Results and discussion

Figure 3 shows temperature and corresponding synchronized optical signals as function of time for some runs, characterized by cooling rates in the range 0.1-50 °C/s. Cooling histories show exponential-like decays, in agreement with the well-known behaviour of a slab cooling without relevant heat generation. Optical signal exhibits a peak related to the crystallization phenomenon [1-2, 9].

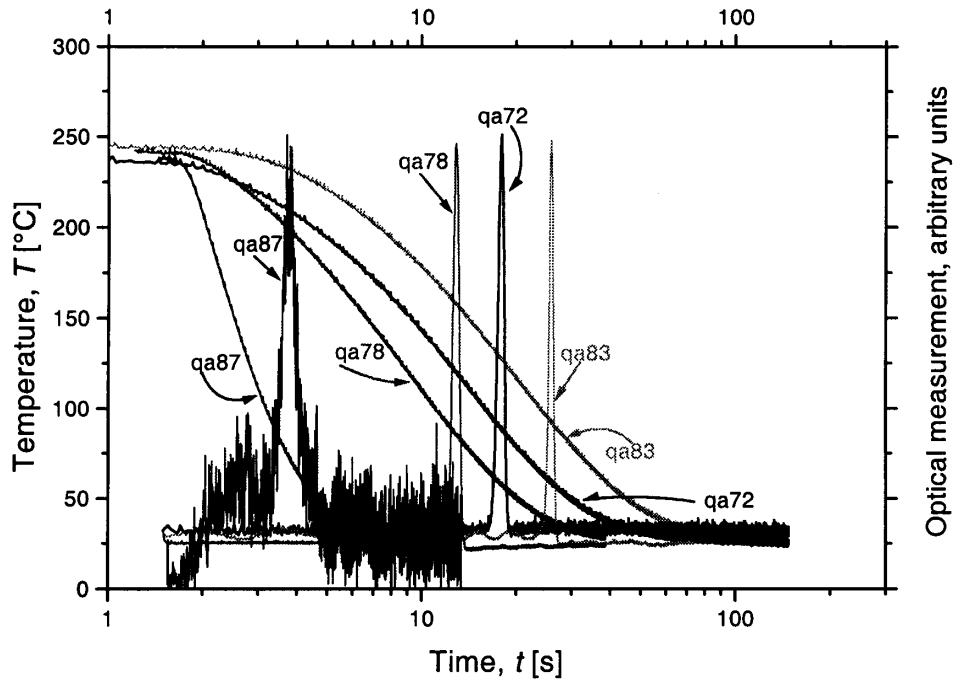
The light intensity scattered from the beam passed impinging on the polymer sample first increases, as the spherulites increase in size, and then decreases as destructive interferences set in, when the growing units impinge each other [1]. Peaks position roughly identify temperatures at which crystallization rates attain maximum value.

When the samples were cooled by air the optical signal was very well defined, see results of runs qa83, 72 and 78 in Figure 3 (increase in cooling rates is due to increase in air flow rate). When the nozzles were operated with gas/liquid mixtures, as to attain higher cooling rates, liquid droplets interfered with the light to be detected. However, the interaction was kept to a low level by minimizing droplet size, thus the sampled signals allowed to identify crystallinity evolution as shown in Figure 3 for run qa87 (air/water cooling).

Piccarolo *et al.* [10] suggested that cooling rate at 70°C has to be adopted to characterize cooling history of iPP samples. Thus, temperatures of the optical peaks and half crystallization temperatures obtained with different techniques (DSC on same resin carried out in a DSC Mettler TC11 and Light Depolarizing Method on a different iPP, [1]) are reported in Figure 4 versus the cooling rate at 70°C. All data, obtained by



**Figure 2.** Details of optical instruments



**Figure 3.** Thermal histories and optical signal measurements during some cooling experiments

different experiments, plotted versus characteristic cooling rate, outline a reasonable decreasing pattern as cooling rate increases and show good mutual agreement. In the range 0.1-1 °C/s data of half crystallization temperature, as obtained by DSC, nicely agree with peaks temperatures of transmitted light intensity detected with the apparatus developed in this work.

Maximum crystallization rate temperatures, predicted by the crystallization kinetics model proposed in [7] and based on final crystallinity of fast cooled samples data are also reported in Figure 4. Model prediction relay experimentally determined thermal histories. Since the same characteristic cooling rates can be drawn from different thermal histories, different prediction for crystallization temperature can be obtained for the same cooling rate, as for runs qa70 and qa78. The comparison between experimental data and model predictions is good.

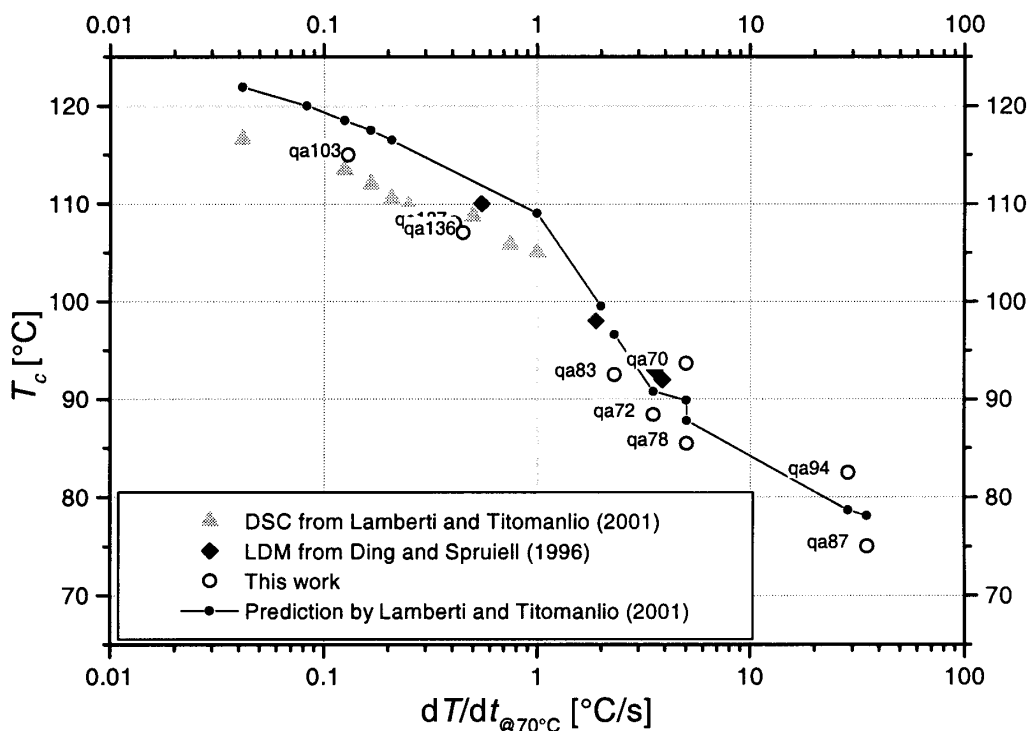
## Conclusions

A technique useful to monitor the crystallinity evolution during cooling runs from the melt has been proposed. A set-up has been built to carry out these runs, and some experiments have been performed. Crystallization temperatures have been measured at various characteristic cooling rates, measured values well compare with DSC data and previous Ding and Spruiell measurements.

A crystallization kinetics model previously proposed proved able to predict in a satisfactory way the experimental data behavior, namely the effect of cooling rate on crystallization temperature.

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**Figure 4.** Crystallization temperature versus characteristic cooling rate from different experiments. Comparison with model prediction by Lamberti and Titomanlio (2001) [7].

**Reference**

1. Ding, Z.; Spruiell, J.E.; *J. Polym. Sci. Part B*, **34**, 2783 (1996)
2. Ding, Z.; Spruiell, J.E.; *J. Polym. Sci. Part B*, **35**, 1077 (1997)
3. Magill, J.H.; *Polymer*, **2**, 221 (1961)
4. Magill, J.H.; *Polymer*, **3**, 35 (1962)
5. Brucato, V.; Crippa, G.; Piccarolo, S.; Titomanlio, G.; *Polym. Eng. Sci.*, **31**, 1411 (1991)
6. Piccarolo, S.; Saiu, M.; Brucato, V.; Titomanlio, G.; *J. Appl. Pol. Sci.*, **46**, 625 (1992)
7. Lamberti, G.; Titomanlio, G.; *Polym. Bulletin*, **46**, 231 (2001)
8. Ziabicki, A.; *Colloid Polym. Sci.*, **274**, 209 (1996); *ibidem*. **274**, 705 (1996)
9. Hawkins, S. W., Richards, R.B.; *J. Polym. Sci.*, **4**, 515 (1949)
10. Piccarolo, S.; Alessi, S.; Brucato, V.; Titomanlio, G.; in *Crystallization of Polymers*, Ed. M. Dosière, NATO ASI Series, Kluwer Academic Publisher, 475, (1993)