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Accelerated crystal growth in cryogenic mechanically milled polymers and polymer blends

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Abstract

Previous comparative studies on the impact of cryogenic mechanical milling (CMM) of polymers showed significantly changed thermal and mechanical properties and—in the case of some polymer blends (e.g., PMMA/PVDF) an improved miscibility. Those changes were mainly attributed to a reduction of the molecular weight average during the milling process.

The crystallization process in macromolecular systems is strongly affected by any small change of the initial chain structure like the chain conformation, the presence of branches and of course a decrease of the molecular weight average. Therefore, the aim of this paper was a comparative study of isothermal crystallization of cryogenic mechanically milled and original (unmilled) polymers and polymer blends. The overall crystal growth rates were determined and the development of the spherulitic morphology was studied in detail by means of hot stage polarized light microscopy. Isothermal crystallization of bulk samples was also investigated using differential scanning calorimetry (DSC).

The average spherulite growth rates of the milled homo-polymer as well as the blends were significantly higher than in unmilled samples; even when all experiments started from the molten state. Moreover, the increase in crystal growth was almost independent of the chosen crystallization temperature and thus the degree of undercooling.

Keywords: Cryogenic mechanical milling; PVDF; Blends; Crystallization

1. Introduction

The problem of how chain folded polymer crystals grow from a metastable melt and how growth is related the chain architecture as well as the molecular weight [1] has attracted great interest since the work of Lauritzen and Hoffman (LH) [2] and further generalizations of their model [3–5]. After primary nucleation at a sufficient degree of undercooling, growth occurs via crossing another nucleation barrier associated with the formation of one stem of the polymer followed by lateral spreading by other stems. Regarding the temperature dependence of crystal growth two generally opposite factors has to be considered. The sequential attachment of further polymer molecules to the growth front is a very complex process involving polymer diffusion as well as entanglement effects in the undercooled melt [6] which are the crystallization rate controlling factors at high undercooling since melt viscosity is also high. In contrast to that, at low undercooling the proposed rate determining step of growth at the crystalline interface is adsorption of a chain suitable segment that is assumed to occur by a "molecular nucleation" process, called secondary nucleation [2], followed by addition of further chain segments and accompanied by the conformational rearrangement of the macromolecules. Under isothermal crystallization conditions a time proportional crystal growth is expected [7] whereby the linear growth rate is inversely proportional to the average molecular weight of the polymer, independent of the undercooling [8]. In this investigation we evaluated changes in the crystallization kinetics of neat PVDF as well as PVDF/PMMA blends after cryogenic mechanical milling, which is expected to decrease the average molecular weight of the initial polymers due to breaking of covalent bonds chain rupture [9,10], as a probe for the chain length reduction after milling.

2. Experimental

2.1. Sample preparation

CMM was applied on polyvinylidenefluoride (PVDF)/polymethylmethacrylate (PMMA) 50/50 (wt.%) blends as well as on neat PVDF. A mass of 1 g in total was placed in a hardened steel grinding vial together with a 32 g

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steel impactor. After cooling the vial assembly to liquid nitrogen temperature in a SPEX Certiprep 6850 Freezer/Mill, the materials were pulverized by shuttling the steel impactor back and forth magnetically. All samples were milled for a constant milling time of 30 min at a milling frequency of 30 Hz (30 impacts per s). A detailed description of the milling process is given elsewhere [10]. Neat PVDF was used as delivered and unmilled PVDF/PMMA were prepared by melt blending at 220 °C for 5 min in an mini-lab extruder.

2.2. *Differential scanning calorimetry (DSC)*

Isothermal crystallization experiments were carried out in a DSC-2910 (TA-Instruments), temperature calibrated with Ga, In and Sn to be ±0.5 K in error. Each sample was heated from 30 to 220 °C at a heating rate of 10 K/min and kept isothermally for 5 min in order to erase the previous thermal and "mechanical" history. After that, a temperature jump from the homogeneous melt (220 °C) to the particular crystallization temperature of interest was performed and the release of heat of crystallization isothermal conditions was monitored. To ensure a good thermal conductivity, all samples were put in standard aluminum sample pans and additional aluminum lids were used to compact the powders. Sample weights were 7 ± 0.2 mg and all DSC-scans were performed under nitrogen atmosphere in order to prevent oxidation during long time crystallization experiments.

2.3. *Polarized optical microscopy (POM)*

One drop of a 2 wt.% Polymer/DMF solution was casted on a microscopy glass slide which was preheated to 50 °C, allowing the solvent to evaporate quickly. The resultant thin films (about 20 μm for PVDF and PVDF/PMMA blends) were transferred to a hot plate and molten at a 220 °C for 3 min to destroy possible crystal seeds. After that, the slides were immediately put into the preheated hot stage of the microscope and the spherulite growth from the homogeneous melt was monitored *in situ* for various isothermal crystallization temperatures. All micrographs were taken by means of polarized light (POM) after 2 h of isothermal crystallization.

3. Results and discussion

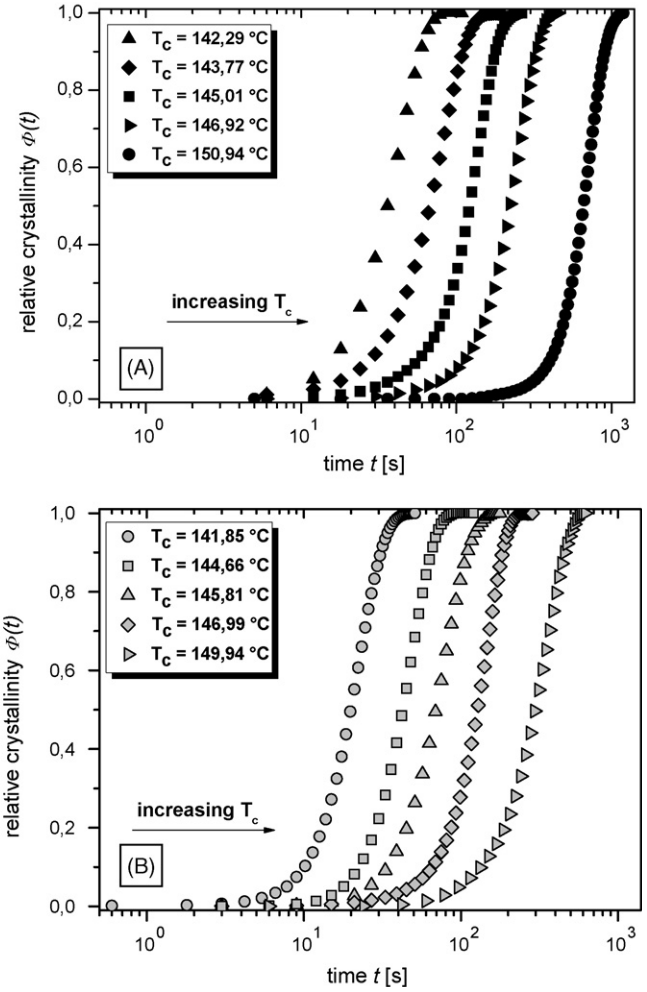

Fig. 1. DSC: relative crystallinities of unmilled (A) and milled (B) PVDF, calculated by integration of the exotherms for various crystallization temperatures.

Fig. 1 shows the increase of relative crystallinities with time for various isothermal crystallization temperatures, calculated by integrating the crystallization exotherms of neat PVDF (Fig. 1A) and PVDF milled for 30 min (Fig. 1B). Both plots indicate that the crystallization kinetics for the temperature range studied are predominately governed by nucleation instead of diffusion processes, therefore crystallization is delayed with increasing temperature.

As measure for the overall crystallization rate the crystallization half time values $\tau_{0.5}$ (50% relative crystallinity) were taken to point out the differences between the unmilled and milled PVDF samples. Apparently there is a great influence of the milling treatment on the crystallization kinetics, namely the $\tau_{0.5}$ values are nearly two times lower for the milled materials and independent of the degree of undercooling ΔT (see Table 1). Since the evolution of relative crystallinity represents the sum of all thermal events during isothermal crystallization, given by the growth rates of individual crystals but also by the number (primary nucleation density) of growing crystals, POM on milled and unmilled samples was performed. Exemplary for the investigated temperature range, the morphologies of unmilled (Fig. 2A) and milled PVDF samples (Fig. 2B) isothermally crystallized at 150 °C for 2 h are shown. A significant increase in the number of spherulites can be observed for the milled sample compared to the original material, indicating a higher nucleation density. Since both unmilled and milled PVDF crystallize to fast to resolve the growth rates of isolated spherulites *in situ* by means of hot stage POM, we only can report the observation that the spherulites in milled PVDF grow significantly faster until they impinge. This observation gives clear evidence for the fact that the increase of the overall crystallization rate for milled PVDF, as measured by DSC, is not only due to a higher primary nucleation density, but also due an acceleration of crystal growth which is attributed to the so called "molecular nucleation process" according to Lauritzen and Hoffmann [2].

A more detailed investigation of the growth kinetics of isolated PVDF spherulites is becoming possible by adding a miscible amorphous diluent to the PVDF melt. It is well known

Table 1
Half time of crystallization values for neat PVDF, obtained from DSC for milled and unmilled samples

T_c (°C)	ΔT (°C)	$\tau_{0.5}$ (s) unmilled	$\tau_{0.5}$ (s) milled	$\Delta\tau_{0.5}$ (%) rel. decrease after milling
142	38	36	19	47
147	33	222	127	43
150	30	660	294	55

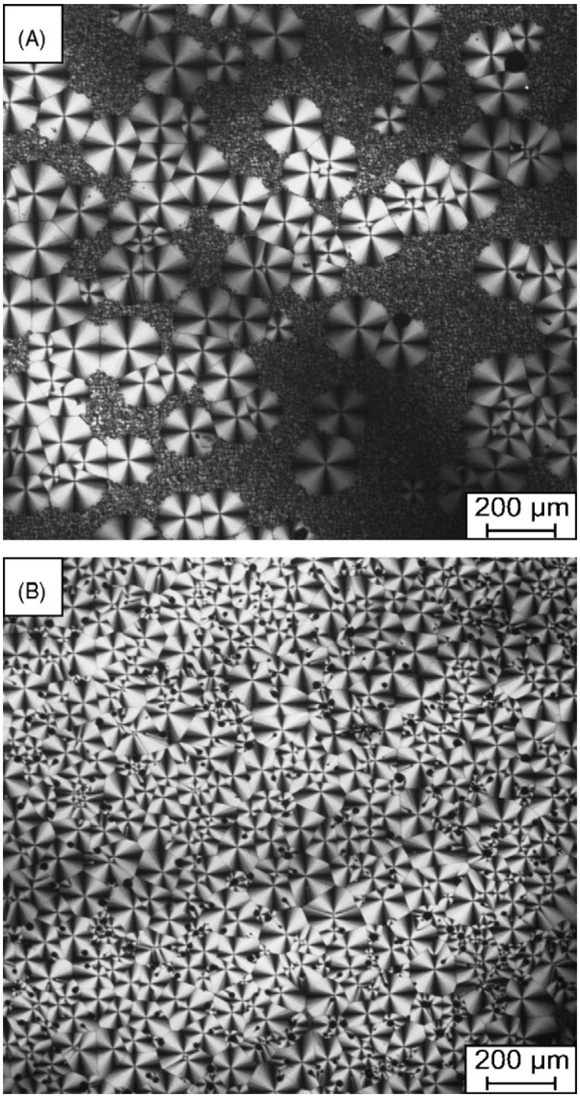

Fig. 2. POM: spherulitic morphologies and number of spherulites after isothermal crystallization at 150 °C for 2 h. (A) Unmilled and (B) milled PVDF sample.

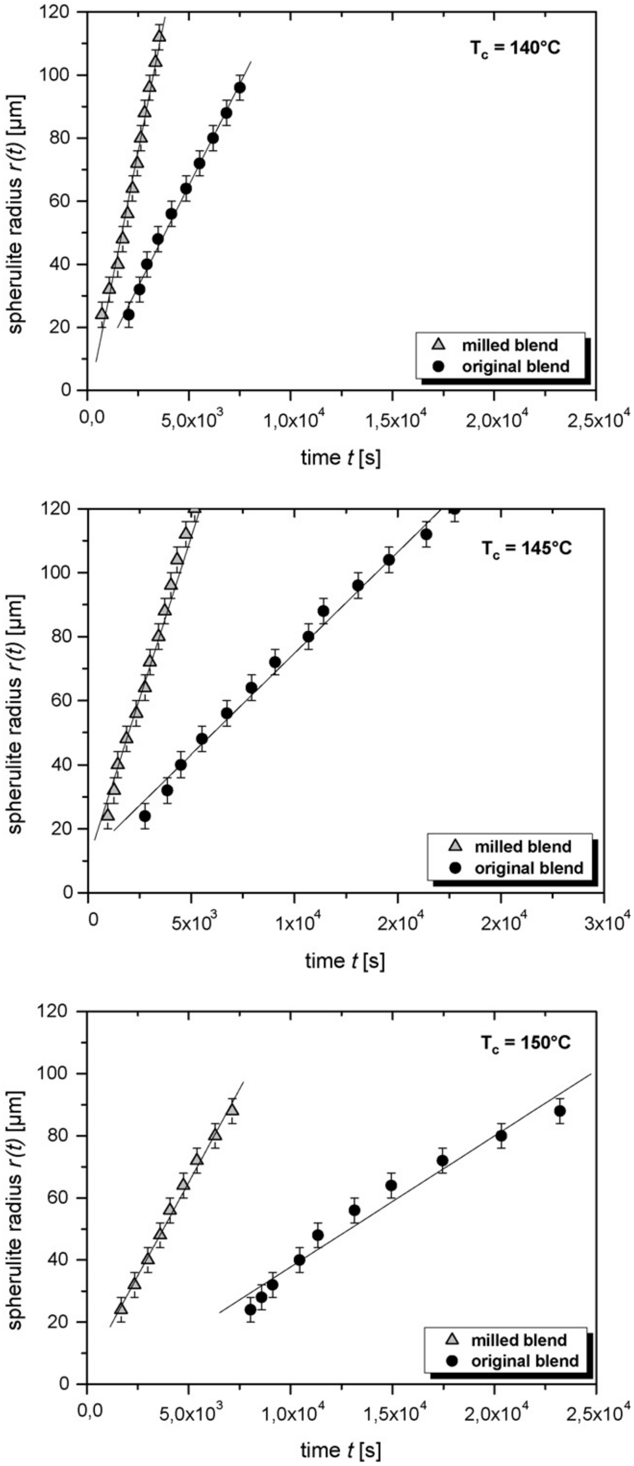

Fig. 3. POM: increase in PVDF spherulite radius with time (50:50, wt.% PVDF/PMMA blend) during isothermal crystallization at crystallization temperatures indicated.

that PMMA is miscible with PVDF in the molten state [11] and thus leads to a decrease of PVDF spherulite growth rates in PMMA/PVDF blends. For the 50:50 (wt.%) blend the time scale of crystallization at low ΔT is becoming very long compared to neat PVDF, allowing to measure the growth of isolated single spherulites by means of POM. Fig. 3 shows the increase of PVDF spherulite radii with time for unmilled as well as milled blends during isothermal crystallization. In good agreement with the DSC results, an apparent acceleration of the spherulite growth rates of the milled materials can be observed, resulting in an increase of nearly three times faster growth (see Table 2). From this results it is quiet evident that milling is leading to noticeable increase in crystal growth rates. Growth of typical folded chain polymer crystals proceeds via several selection mechanisms that are governed by the chain configuration and the conformational state of the macromolecules which are going to be incorporated in the growing crystals. Therefore, the average chain length (molecular weight) and the number of chain defects along the whole macromolecule have great impact on the crystallization ability of a particular macromolecule as well as on the growth kinetics since these processes are very sensitive to the average molecular weight. In this study the chosen isothermal crystallization temperatures were high enough (low ΔT) to ensure sufficient fast transport of macromolecules to the growth front; therefore, the rate determining step for the

Table 2
PVDF spherulite growth rates in PMMA/PVDF 50:50 (wt.%) blends for milled and unmilled materials as determined by POM

T_c (°C)	ΔT (°C)	$\dot{u}$ (t) (μm/s) unmilled	$\dot{u}$ (t) (μm/s) milled	$\Delta\dot{u}$ (t) (%) rel. increase after milling
140	40	12.1×10^{-3}	34.5×10^{-3}	185
145	35	6.5×10^{-3}	20.2×10^{-3}	211
150	30	4.2×10^{-3}	12.3×10^{-3}	193

formation of typical chain folded lamella-crystals should be the incorporation of the suitable chain segments. We conclude that a reduction of the average molecular weight, owing from the cleavage of covalent bonds due to the mechanical impact during milling, is mainly responsible for the accelerated crystal growth in the milled materials.

4. Conclusion

Isothermal crystallization kinetics of milled and original PVDF was determined by DSC, showing a significant overall crystallization rates in the milled materials. This increase was found to be almost independent of the degree of undercooling in the temperature range studied. The examination of the morphologies by POM revealed that the milled samples show a higher nucleation density, resulting in a lager number of spherulites after identical crystallization conditions. Similar to the increase of the crystallization rates in neat PVDF, the spherulite growth rate in PVDF/PMMA blends is three times faster than in the original materials and also independent of the undercooling. Since growth of isolated individual spherulites was measured *in situ* by means of hot stage POM, it can be concluded that the observed higher crystallization rates in the DSC experiments are not only originating from an increased number of primary nuclei. The rate determining step for the formation of chain folded lamella-crystals at low undercooling ΔT is the incorporation of macromolecules into the growing crystals. This process is very sensitive to the average molecular weight, since chain-folding is accompanied by a conformational rearrangement along the whole polymer chain and might be significantly accelerated by a decrease of the PVDF molecular weight due to the cryogenic mechanical milling

In the case of the blends a more detailed study on the influence of the PMMA content on the PVDF spherulite growth is planed to study the influence of possible de-mixing processes near the spherulite growth front which might be superimposed and therefore could delay crystal growth.

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