CRYSTALLIZATION AND MELTING BEHAVIOUR OF POLY(FERROCENYLSILANES)

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Abstract: A series of poly(ferrocenyldimethylsilanes) was prepared anionically in order to study their melting behaviour. The DSC traces of these polymers displayed multiple endotherms that could be assigned to melting of lamellae with varying thicknesses. Upon heating, thinner lamellae are converted into thicker ones in a continuous melting-recrystallization process.

INTRODUCTION

The development and study of polymers containing inorganic elements is an area of growing interest because of the special properties displayed by such polymers.[1] Poly(ferrocenylsilanes) possess an unusual main chain which consists of alternating ferrocene groups and silicon atoms. High molecular weight poly(ferrocenylsilanes) can be obtained by thermal ring-opening[2] or transition-metal catalyzed polymerizations[3] of silicon bridged ferrocenes (ferrocenylsilanes). Anionic ring-opening polymerization[4] can be used for the preparation of narrow polymers with controlled MWs and low polydispersities. Furthermore, this technique provides the opportunity to produce well-defined novel block copolymers. In this work, the still unexplored thermal properties of poly(ferrocenyldimethylsilanes) are described.

RESULTS AND DISCUSSION

The poly(ferrocenyldimethylsilanes) were prepared in THF at room temperature, using *n*-butyllithium as initiator (Tab. 1). The thermal behaviour of the polymers was investigated by means of DSC. Two main melting transitions were observed. The first endotherm, the lower temperature transition, was observed only upon heating a sample that was previously crystallized at a specific holding temperature. The position of the first endotherm shifted to higher temperatures if a higher holding temperature was applied, while the position of the second endotherm did not change (Fig. 1a).

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Tab. 1. Characteristics of the poly(ferrocenyldimethylsilanes).

Polymer[a)]	$\overline{M}_w$, g/mol [b)]	$\overline{M}_n$, g/mol [b)]	$\overline{M}_w/\overline{M}_n$
DP 25	7100	6600	1.09
DP 50	12400	11400	1.09
DP 100	26200	21500	1.09
DP 200	49500	44900	1.10
DP 350	87000	76700	1.14

[a)]Degree of polymerization, from [M]/[I]; [b)]GPC in THF, relative to polystyrene.

The second endotherm decreased in intensity with higher scanning rates and an exotherm was observed between the endotherms, indicating the presence of a melting-recrystallization process.

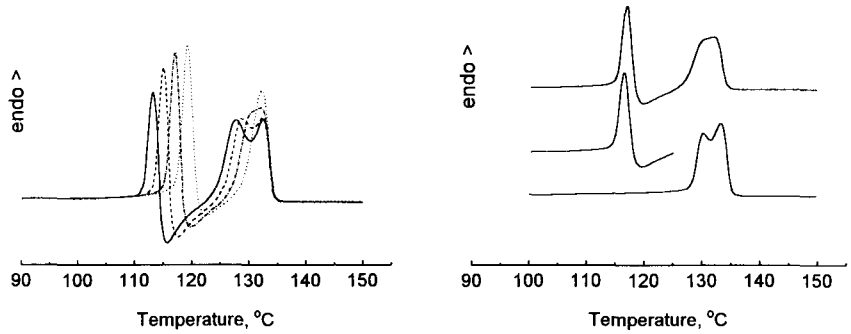

Fig. 1 a. (left): DSC trace of poly(ferrocenyldimethylsilane) DP 25, crystallized at holding temperatures: — 80 °C, --- 85 °C, -.- 90 °C, ... 95 °C;
b. (right): Irreversible transformation of thin lamellae into thicker ones for DP 25.

A striking feature in the DSC traces is that the first endotherm belongs to an irreversible transition, as is shown in Fig. 1b. The top scan was taken after the sample was crystallized at 90 °C. The middle scan was taken after the same treatment, but it was scanned to 125 °C, cooled to 90 °C, and reheated. In this scan, the first endotherm is no longer observed. Complete melting and crystallization is required to make it reappear. The first endotherm is associated with the melting of thin lamellae. Upon further heating, these are converted into thicker ones in a continuous melting-recrystallization process, until the temperature becomes so high that recrystallization is no longer possible and the thicker lamellae finally melt in the second endotherm. A similar thermal behaviour has been observed for poly(ethylene terephthalate).[5] An

equilibrium melting temperature of 143 °C was found for all polymers, except for the lowest member DP 25 (139 °C). The polymers have a Tg at 33.5 °C. Even though several melting transitions were observed, no evidence was found for the existence of different crystal modifications. Temperature-dependent WAXS experiments showed a single diffraction pattern which vanished upon going through the second melting transition. SAXS showed that the long period increased with a step in the discussed thermal region (Fig. 2), which can be indicative of thin lamellae being transformed into thicker ones.

The degree of crystallinity of these semicrystalline polymers was estimated by WAXS; DP 100 for example has a crystallinity of 30%. From the heat of fusion found for the poly(ferrocenyldimethylsilanes), the melting enthalpy for 100% crystalline polymer was calculated (42 J/g). AFM showed that the poly(ferrocenylsilanes) crystallize as spherulites (diameter 10 μm).

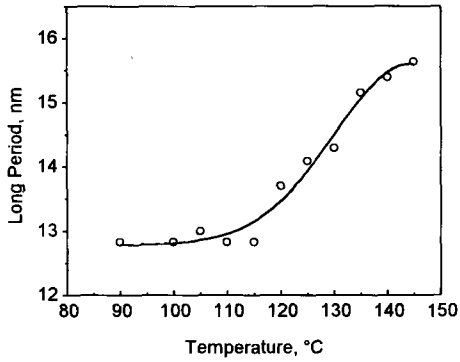

Fig. 2. SAXS of poly(ferrocenyldimethylsilane) DP 25 showing a step in the long-period.

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