MORPHOLOGY CONTROL OF POLY(VINYLIDENE FLUORIDE) OBTAINED FROM SURFACTANT-FREE HOMOGENEOUS PHASE POLYMERIZATION IN SUPERCRITICAL CO$_2$

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ABSTRACT

Poly(vinylidene fluoride) (PVDF) samples obtained from surfactant-free homogeneous phase polymerization in supercritical CO$_2$ were analyzed with respect to end groups, morphology, degree of crystallinity and the type of polymorphs present. For polymers with end groups originating from the initiator *di-tert*-butyl peroxide (DTBP) and M_n = 2400 g·mol^{-1} it was found that expansion of the reaction mixture containing 73 wt.% CO$_2$ results in stack-type particles with diameters around 10 μm. Contrary, polymers of similar M_n but end groups originating from the chain transfer agent C$_6$F$_{13}$I yield a sponge-type morphology upon expansion of the reaction mixture. The degree of crystallinity is also strongly affected by the end groups. For PVDF with DTBP-derived end groups a crystallinity of 13.4 % and for PVDF with C$_6$F$_{13}$I-derived end groups 45.7 % were found. The amount of β crystal phase material is the lowest for PVDF with C$_6$F$_{13}$I-derived end groups.

INTRODUCTION

Fluorinated polymers gained large interest for technical applications due to their unique properties, e.g., excellent chemical, thermal and mechanical stability as well as electroactivity.[1] Frequently, these polymers are synthesized in heterogeneous phase employing fluorinated stabilizers, which have a high potential for bioaccumulation. Supercritical carbon dioxide (scCO$_2$) has emerged as an attractive alternate solvent.[2,3,4] Besides being environmentally benign interesting features of scCO$_2$ for polymer applications are reduction in viscosity, easy separation from polymeric products under mild conditions and particle generation upon expansion of the reaction mixture.[5] To avoid the use of surfactants homogeneous phase polymerizations of vinylidene fluoride in scCO$_2$ were studied using *di-tert*-butyl peroxide (DTBP) as initiator.[6] The homogeneous nature of the reaction and monomer conversion as a function of time were monitored by in-line Fourier-Transform Near Infrared (FT-NIR) spectroscopy.
Poy(vinylidene fluoride) (PVDF) is a semi-crystalline polymer, which may occur in five different polymorphs, the so-called α, β, γ, δ, and ε crystal phase.[7] The crystal form of PVDF may be affected by the polymerization and processing conditions. Further, CO$_2$ may alter the PVDF polymorphs.[8] The different crystal phases are associated with widely varying polymer properties, e.g. the β phase has piezo- and pyroelectric properties.[9]
In this contribution we show that polymer end groups originating either from the chain transfer agents, such as bromotrichloromethane and perfluorinated hexyl iodide, or from the initiator DTBP also have a significant influence on the crystallinity of the polymer.

EXPERIMENTAL PART

Polymerizations of vinylidene fluoride were carried out at 120 and 140 °C in solution with 73 wt.% of CO$_2$ at 1500 bar. In all cases the reactions were chemically initiated using DTBP. Partly, VDF

polymerizations were carried out in the presence of either bromotrichloromthane or perfluorinated hexyl iodide as chain transfer agent. The reaction mixtures were prepared as detailed in ref. 6. In all cases the number average molecular weights were between 2000 and 7000 $g\cdot mol^{-1}$. All polymerizations were carried out in homogeneous phase up to high degree of monomer conversion as determined by quantitative in-line FT-NIR spectroscopy.[6,10]

After complete monomer conversion was reached expansion of the reaction mixture to ambient conditions resulted in white polymer particles, which were analyzed by Scanning Electron Microscopy (SEM). Molecular weight distributions were obtained from size-exclusion chromatography using N, N-dimethylacetamide (DMAc) containing 0.1 % LiBr as eluent and polystyrene standards for calibration. Polymer end groups were identified by ^{1}H-NMR and Electrospray Ionization – Mass Spectrometry (ESI-MS). The polymers obtained are given in Table 1 and Table 2. Rather broad molecular weight distributions with polydispersities between 3.1 and 4.5 were obtained for reactions in which molecular weights were controlled by the initiation. For polymers originating from reactions with MW control via a chain transfer agent (CTA) small polydispersities around 1.5 were measured.

The degree of crystallinity and the melting temperatures were estimated from differential scanning calorimetry (DSC). Fourrier Transform Infrared (FT-IR) and wide angle X-ray diffraction (WAXD) were employed to study the PVDF polymorphs.

Sample	$c_{DTBP}/$ mmol$\cdot$L^{-1}	$M_n/$g$\cdot$mol^{-1}	M_w/M_n	end groups
PVDF-1	310	2200	4.5	CH_3, $(CH_3)_3CO$
PVDF-2	77	6800	3.1	

Table 1: Poly(vinylidene fluoride) samples from polymerizations at 140 °C and 1500 bar. Number average molecular weights, M_n, and weight average molecular weights, M_w, were obtained from size exclusion chromatography with polystyrene calibration.

Sample	CTA	$c_{CTA}/$ mmol$\cdot$L^{-1}	$M_n/$ g$\cdot$mol^{-1}	M_w/M_n	end groups
PVDF-3	$C_6F_{13}I$	150	2400	1.4	I, $CF_3(CF_2)_5$
PVDF-4		50	6700	1.5	
PVDF-5	CCl_3Br	920	2100	1.6	Br, CCl_3
PVDF-6		230	6000	1.6	

Table 2: Poly(vinylidene fluoride) samples from polymerizations at 120 °C and 1500 bar with 61 mmol$\cdot$L^{-1} DTBP as initiator and the chain transfer agents indicated. Number average molecular weights, M_n, and weight average molecular weights, M_w, were obtained from size exclusion chromatography with polystyrene calibration.

RESULTS AND DISCUSSION

With the exception of sample PVDF-5 upon expansion of the homogeneous reaction mixtures containing 73 wt.% CO_2 dry polymer particles were obtained. The visual appearance of these particles, however, was different. To determine whether the morphology was affected by the type of end groups and by the molecular weight, SEM images were measured for the samples listed in Tables 1 and 2. The SEM images indicate that stack-type particles are obtained for DTBP-derived end groups, whereas spongy material is found in case of $C_6F_{13}I$-derived end groups. Finally, the higher molecular weight sample with CCl_3Br-derived end groups shows rose patel like structures.

It is well known that the crystallinity and the type of PVDF polymorph may be affected by various factors, e.g. such as the polymerization conditions and polymer processing. Thus, we were interested in studying whether and to what extend crystallinity and and the type of crystal phases may also be affected by the end groups. Differential scanning calorimetry was carried out to determine the degree of crystallinity. To test whether the expansion of the reaction mixture does affect crystallinity, three DSC cycles were carried out. As expected, the endotherms resulting from the first heating cycles are broader than the curves obtained during the second and third heating cycles. For further discussion, the the second heating curves were considered. With the exception of sample PVDF-5, which shows a very broad multimodal peak, the endotherms are bimodal. As an example, Figure 1 gives the DSC curves for the two PVDF samples with DTBP-derived end groups. It is evident that the peak maxima of sample PVDF-2 are shifted to higher temperatures as compared to PVDF-1. The most prominent melting temperatures indicated by an asterix in the Figure 1 are listed in Table 3. In case of $C_6F_{13}I$-derived end groups (samples PVDF-3, PVDF-4) the melting temperatures are only slightly enhanced upon increasing molecular weight. The data given in Table 3 indicate, too, that the type of end groups strongly affect the melting temperatures. Generally, the melting temperatures are lower for PVDF with DTBP-derived end groups, whereas $C_6F_{13}I$-derived end groups lead to higher melting temperatures.
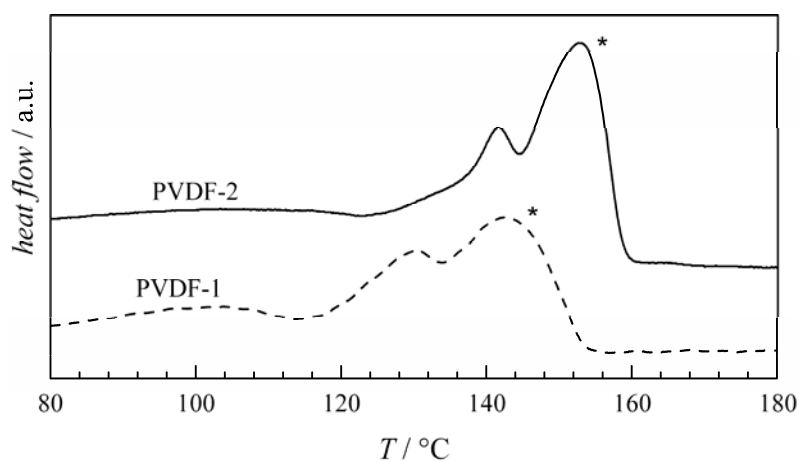

Figure 1: DSC results for poly(vinylidene fluoride) samples with DTBP-derived end groups (PVDF-1, PVDF-2). For further details refer to text.

Sample	T_m / °C	X (%)
PVDF-1	142.7	13.4
PVDF-2	152.6	20.6
PVDF-3	156.7	45.7
PVDF-4	158.9	54.6
PVDF-5	-[a]	30.9
PVDF-6	163.5	39.8

Table 1: Melting temperatures, T_m, and degrees of crystallinity, X, determined from the second DSC heating curves. The notation PVDF-1 to PVDF-6 refers to Tables 1 and 2. [a]: multimodal distribution. For further details refer to the text.

The DSC results allow for the calculation of the degree of crystallinity, X. According to $X = \Delta H_m / \Delta H_c$ the crystallinity is accessible from the melting enthalpy, ΔH_m, determined by integration of the DSC curve of the second heating cycle and from $\Delta H_c = 104.5$ J·g^{-1} for perfectly crystalline PVDF.[11] For the low MW samples, the highest melting enthalpy of 47.8 J·g^{-1} associated with a crystallinity degree of 45.7 % is found for PVDF-3, whereas for DTBP-derived end groups (PVDF-1) a melting enthalpy of 14.0 J·g^{-1} and a degree of crystallinity of 13.4 % was derived. For a given end group, the crystallinity is enhanced upon increasing molecular weights. The crystallinity values of all samples are contained in Table 3. It is interesting to note that the most massive and heavy chain end groups (C_6F_{13}I-derived) give rise to the highest melting temperature. The finding suggests that the entropy of melting decreases with an increase in weight of the chain end group, because of a suppression of the chain mobility.

To determine the type of polymorph present in the different samples, FT-IR and WAXD measurements were carried out. Generally, the amount of β phase material is higher for lower degrees of crystallinity: Samples PVDF-3 and PVDF-4 with C_6F_{13}I-derived end groups contain the lowest amount of β phase material. The samples obtained from polymerizations without any chain transfer agent and thus only DTBP-derived end groups show the highest amount of β phase material.

CONCLUSIONS

The morphology of PVDF with number average molecular weights between 2000 and 7000 g·mol^{-1} may be changed by the choice of polymer end groups. Generally, DTBP-derived end groups yield comparably low degrees of crystalliniy ($\leq 21\%$) and the highest amount of β phase material. The C_6F_{13}I-derived end groups lead to the highest degrees of crystallinity and the smallest amount of β phase material. The differences are not due to the presence of CO_2 during polymerization and expansion of the reaction mixture, which is concluded from the fact that the differences remain in the second and third DSC heating cycle.

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