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Crystallization and melting behaviour of plasticized poly(vinylidenechloride)

II. Fourier-transform infrared spectroscopy

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Summary

The kinetic of the crystallization process of slightly plasticized poly(vinylidenechloride) at room temperature (296 K) can be observed by FTIR spectroscopy. In dependence on the amount of plasticizer the half-time for crystallization decreases due to an increased segmental mobility of the stiff PVDC chains.

Introduction

Crystallization kinetics of semicrystalline polymers can be investigated by different methods, for instance by calorimetry, dilatometry, or light microscopy. The use of the respective method is limitated by its resolution in time with regard to the half-time of crystallization. Modern FTIR spectrometers produce spectra (scans) so rapidly that a real chance exists to follow up the crystallization process requiring some seconds or minutes if one or more crystallinity-sensitive bands within the IR spectra are observable.

Plasticizers can enhance the segmental mobility of the chain molecules, therefore, it might be interesting to investigate the influence of plasticizers on the crystallization kinetics of poly(vinylidenechloride) (PVDC).

Experimental

The PVDC under investigation was a copolymer containing vinylidenechloride (85 %), vinylchloride (12 %), and butylacrylate (3 %). Dibutylsebacate was used as plasticizer in percentages by weight of 3, 5, 7, and 10 %. Thin transparent films with a thickness of about 40 μm were prepared within a heating press (5 min at 170°C); after pressing the films were quenched down to -20 °C in order to obtain fully amorphous specimens.

The FTIR measurements were performed using a NicoletDX-10 apparatus. The recording time per scan was at about 2 sec, the number of scans per spectrum was fixed between 10 and 40. The temperature during the measurements was kept constant at 23 °C.

The thin films were picked up by a pincette from the quenching bath, wiped dry by a tissue and put immediately into the course of beam of spectrometer. The time interval between the removal from the quenching bath and the beginning of measurements was 10 sec for each sample. The spectra were stored on a magnetic disc and analysed by a special computer program.

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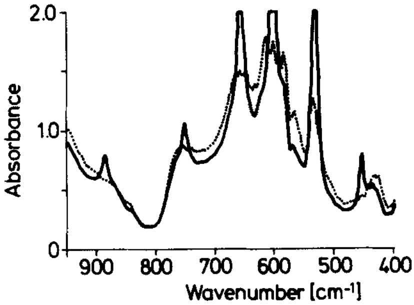

Figure 1: IR spectra of an amorphous (dotted line) and a semicrystalline (solid line) PVDC film.

Results and discussion

The IR spectrum of PVDC

Typical IR spectra of amorphous and semicrystalline PVDC are reproduced in Fig. 1. Crystallinity-sensitive bands at 884, 753, 653, 602, 530, and 453 cm^{-1} resp. are observed in accordance to the results reported by different authors (1 - 3). In this paper the bands at 1355 (reference band), 884, 753, and 453 cm^{-1} are used in order to get insight into the crystallization kinetics.

Band at 1355 cm^{-1}:	CH_2-wagging vibration (π -band) (3). This band serves as an internal standard.
Band at 884 cm^{-1} :	CH_2-rocking vibration (3) or skeletal C-C-stretching vibration (2)
Band at 753 cm^{-1} :	CH_2-stretching (2) or CCl_2-stretching (1) or C-C-C skeletal vibration (3).
Band at 453 cm^{-1} :	CCl_2-rocking vibration (3).

An elegant method for the elimination of the influence of film thickness consists in the application of an internal standard. It has been proven that the integral absorbance intensity of the band at 1355 cm^{-1} does not change during the course of the crystallization process. In this paper exclusively integral absorbance intensities are determined which are proportional to the area of the respective absorbance peaks. The underground intensity is separated by a linear base line.

Crystallization kinetics

The crystallization process in dependence on time at constant temperature is observed by measuring the integral absorbance intensities of the bands at 884, 753, and 453 cm^{-1} resp. normalized by the intensity of the 1355 cm^{-1} band. Fig. 2a reproduces a typical crystallization diagram; the normalized intensity of the 884 cm^{-1} band shows the well-known S-shaped

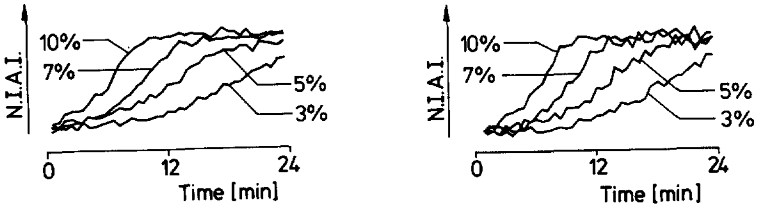

Figure 2: Normalized integral absorbance intensity (N.I.A.I.) of IR bands in dependence on crystallization time at 23 °C. The percentage represents the amount of plasticizer.

a) Band at 884 cm^{-1} (left side)
b) Band at 453 cm^{-1} (right side)

course of the curve. With increasing amount of plasticizer the crystallization curves shift to shorter times. Similar results have been obtained with the bands at 753 cm and 453 cm^{-1}, one of which is plotted in Fig. 2b.

From the crystallization curves a so-called half-time for crystallization can be obtained by taking the time at the point of curve inflection. The values listed in Tab. 1 prove that the half-time for crystallization decreases with increasing amount of plasticizer and that within the limits of experimental error an inverse proportionality between these two quantities exists. The unplasticized material does not crystallize at room temperature within the observation time of some minutes or hours.

Band [cm^{-1}] \ Percentage of plasticizer [%]	10	7	5	3
884	6,5	9,6	13,2	19,5
753	6,3	9,6	13,2	19,2
453	6,3	9,3	13,1	18,6
Average	6,4	9,5	13,1	19,1

Tab. 1: Half-time for crystallization (in sec) for plasticized PVDC

Obviously, the crystallization of PVDC at 296 K is supported by the presence of the used plasticizer DBS. This effect may be explained by an increase of segmental mobility of the relatively stiff PVDC chain molecule. The chosen crystallization temperature (296 K) is not far above the glass transition temperature of unplasticized PVDC which has been reported at 288 K (4) or 277 K (5) resp. The acceleration of the crystallization process by plasticizer at room temperature is in good agreement with the DTA-results of the crystallization process in the preceding paper (5).

Analogous results on poly(propyleneterephthalate) have been reported in a very recent publication by Bulkin et al. (6).

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