FAST DYNAMICS OF REVERSIBLE CRYSTALLIZATION AND MELTING OF POLYMERS : A COMBINED PHOTOACOUSTIC DSC INVESTIGATION.

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Dynamic thermal properties of polymers such as the complex heat capacity thermal diffusivity and thermal effusivity are known to show frequency dependence not only at the glass transition but also in the following temperature interval up to main melting. Reversible surface melting and crystallization and other reversible and irreversible processes of reorganization could contribute to these properties. However mainly due to limited frequency range (below 0.1Hz) of commercial temperature modulated differential scanning calorimeters (TMDSC) they was considered as a relatively slow process with characteristic times up to 1 second. It was suggested also that such processes could contribute to dynamic thermal properties only relatively close below (30-40K) the melting /crystallization interval.

During the last fifteen 15 years we develop a thermal wave technique based on photoacoustic (PA) cell build on a standard commercial DDSC7 Perkin Elmer called combined PA-DSC. It uses laser heating as a modulated heat source and microphone detection coupled with lock-in amplifier, thus overcoming all troubles with thermal contacts. PADSC allows registering both PA and DSC signals simultaneously. Photoacoustic signal is inversely proportional to square root of thermal effusivity $e=\rho k C_p$ and measurements could be done from several Hz to several kHz. Our measurements demonstrates that polymers of different type such as HDPE, PCL and iPP show pronounced frequency dependence of the thermal effusivity in the interval 20Hz -1kHz, even far below melting/ crystallization region. Moreover, it was found that except frequency there exist temperature amplitude, temperature wave length $\mu=\sqrt{\alpha}/\sqrt{\omega}$ and thermal history dependences. Measurements were performed at different fixed frequency on heating and cooling with constant heating rate of 5K/min. Several types of experiments were carried out in order to reveal the relative significance of temperature amplitude and length of generated thermal waves, DC heating and thermal history on thermal effusivity.

From results obtained one can conclude that processes which contribute to frequency dependence are even faster than the highest frequency we used since the signal did not show any saturation.

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