Kinetic study of crystallization of isotactic polypropylene and polypropylene fibres by means of infrared absorption spectroscopy. I.

Determination of the melting temperature of isotactic polypropylene by the use of infrared absorption spectroscopy

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Received 14 February 1980

Accepted for publication 26 May 1980

A method allowing to record continuously the transmittance for the temperature dependent absorption band of isotactic polypropylene (i-PP) at $\lambda = 11.89\ \mu m$ as a function of time and temperature is described. An abrupt change in transmittance on the continuous record transmittance — time at simultaneous temperature change is caused by a destruction of crystalline order in i-PP.

В работе описывается метод непрерывной регистрации изменений пропускной способности зависящей от температуры полосы поглощения изотактического полипропилена (и-ПП) при $\lambda = 11{,}89$ мкм при изменении температуры и времени. Резкое изменение пропускания на непрерывной записи пропускной способности во времени, при одновременном изменении температуры, сопряжено с исчезновением кристаллической структуры и-ПП.

As known, besides the absorption bands characteristic of chemical structure, there are in infrared absorption spectra of organic substances absorption bands which are related to the existence of crystalline arrangement. The process of melting of organic crystalline substances is thus accompanied by the extinguishment of crystalline order, which manifests itself by the disappearance of the corresponding absorption bands in the infrared absorption spectrum of the molten substance. A continuous tracking of the decrease in transmittance or the absorbance of a temperature dependent absorption band of organic substances enables us to observe the process of melting and determine the melting temperature from the corresponding records.

Like the infrared spectra of low-molecular organic substances, the infrared absorption spectra of polymers contain absorption bands corresponding to ordered (crystalline) regions which exhibit different degrees of arrangement. The application of continuous recording of the transmittance for absorption bands as a function of time and temperature enables us to observe not only the proper process of melting in polymer systems but also the different temperature transitions given by a change in molecular mobility of the segments of chains as well as the proper process of crystallization [1].

There are in literature some papers of similar character where the points and types of temperature transitions of polymers have been investigated by using multiple recording of structurally sensitive absorption bands at simultaneous temperature change [2, 3]. This kind of multiple repeated recording of a given absorption band at varying temperature gives reliable results only for slow processes, such as different temperature transitions (glassing temperature — T_g) of polymers. Fast processes, such as crystallization in the presence of nucleation agents cannot be observed by this method in polymer systems. For this purpose, we developed an experimental procedure for continuous recording of the transmittance as a function of time and temperature which we firstly applied to simpler low-molecular organic substances to observe the process of their melting.

In this paper (Part I), we present the results of measurements of the melting temperatures of i-PP and some low-molecular organic substances, *i.e.* phenacetine and benzanilide, obtained by the infrared absorption spectroscopy (IRAS). These substances were used as standards for comparison with the results obtained by other physical methods, *i.e.* light microscopy and calorimetry.

Experimental

The needed amount of the investigated substance (ascertained experimentally for obtaining the optimum spectrum) is homogenized with powdered KBr and pressed into the form of a tablet. This tablet is set in the holder of a heating chamber (commercial device supplied by Zeiss, Jena) which is put in a vacuum jacket. After perfect closure of the sample space in the vacuum jacket, the heating chamber is evacuated. Before subsequent switching of the heating, the transmission spectrum of the sample is recorded at room temperature for checking the quality of the prepared tablet. Afterwards, the wavelength is adjusted to the value corresponding to the maximum of the absorption band which exhibits the highest temperature sensitivity. Simultaneously with the switching of the electric heating (heating rate *ca.* 0.116 K s^{-1}) the paper advance and synchronous temperature recording are connected. All quantities are measured as a function of time. The temperature of the sample in the heating chamber is measured by means of a FeKo cell. The temporal change in temperature is recorded by the use of a suited compensation recorder (in our case, it was a recorder of the type Servogor). All spectral measurements were carried out on an infrared spectrophotometer UR-20 (Zeiss, Jena) in the region of NaCl prism. The calorimetric and light-microscopic determinations of melting temperatures were performed with a differential calorimeter DSC 1B (Perkin—Elmer) and a polarization microscope Zetopan-Pol equipped with a heating stage (Reichert) [4, 5].

Results and discussion

The determination of melting temperature of organic substances by the use of IRAS is, in principle, based on accomplishment of the following conditions: a) the presence of temperature sensitive absorption bands which disappear after melting of the sample; b) the determination of experimental conditions suited for continuous recording of the variation of absorption band transmittance with temperature and time.

Fig. 1 represents a direct continuous record of the variation of transmittance at the fixed wavelength $\lambda = 13.49$ μm for benzanilide in the temperature interval 298—473 K. It also gives the simultaneous change in temperature as a function of time.

Point *A* in this figure earmarks the spot from which the value corresponding to melting temperature of crystalline arrangement was read. The value of melting temperature thus obtained was 436.86 K.

A similar procedure was used for measuring the melting temperature of another organic substance, *i.e.* phenacetine which served as a standard for microscopic determination of the melting temperatures. By using IRAS, it was found that the absorption band at $\lambda = 11.84$ μm of phenacetine exhibited the maximum temperature sensitivity. On the basis of this procedure, it was found that the melting point of this substance was 407.06 K.

It appears that this value is in good agreement with the tabulated value of melting temperature of phenacetine obtained by the microscopic method (407.66 K) [5]. Table 1 gives the values of melting temperatures of standard substances determined by IRAS as well as the tabulated values obtained by the calorimetric and microscopic method.

The accuracy of the determination of melting temperature of phenacetine by IRAS is 407.66 ± 1 K and that of benzanilide is 436.16 ± 2 K. It is worth noticing that the precision and accuracy of the values measured is dependent on experimental conditions involving the simultaneous recording of transmittance for the corresponding absorption band and temperature in the course of time. At present,

Table 1

Melting temperatures of phenacetine and benzanilide
determined microscopically, calorimetrically,
and spectroscopically

Substance	$T_{\mathrm{m,micr}}$ K	$T_{\mathrm{m,DSC}}$ K	$T_{\mathrm{m,IRAS}}$ K
Phenacetine	407.66 [5]	406.16	407.06
Benzanilide	436.16 [5]	434.16	436.86

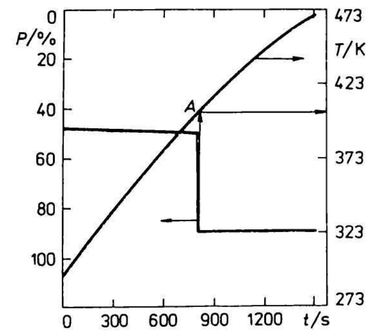

Fig. 1. Variation of transmittance (P) for the band at $\lambda = 11.84$ μm and variation of temperature (T) with time (t) for phenacetine.

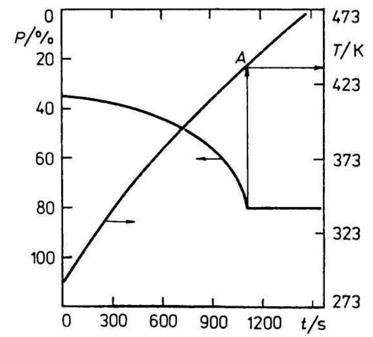

Fig. 2. Variation of transmittance (P) for the band at $\lambda = 11.89$ μm and variation of temperature (T) with time (t) for isotactic polypropylene.

there are available some infrared spectrophotometers with immediate recording of transmittance or absorbance as a function of time (Microlab 600, Beckman).

Though it seems that the determination of melting temperature of organic substances does not necessitate such instrumentally expensive experimental method as infrared absorption spectroscopy, we should like to allege that the use of the developed experimental procedure gives new pieces of knowledge in the field of physical chemistry of polymers, *e.g.* it allows to study the processes of crystallization of i-PP [6] and estimate the portion of crystalline arrangement in polypropylene fibres in the presence of modifying agents [7].

The continuous recording of transmittance of the temperature dependent absorption bands as a function of temperature and time was used for determining the melting temperature of i-PP. The temperature and time dependence of the absorption band at $\lambda = 11.89$ μm was investigated. The origin of this band is ascribed to vibrations of the segments of the polymer chain of i-PP consisting of 11—13 monomer units which form a helix structure [8]. The sample of polymer in the form of foil of about 30 μm width was closed between the windows of KBr. The procedure of determination was analogous to the procedure used for determining the melting temperature of low-molecular substances.

Fig. 2 represents the transmittance for the band at $\lambda = 11.89$ μm of i-PP as well as the temperature as a function of time. This figure shows that the melting process in polymer substances does not exhibit any abrupt change in transmittance at the wavelength used. A method of reading of $T_{\mathrm{m,IRAS}}$ (point A) based on correlation between the melting points of the i-PP samples obtained by the DSC method and the above change in transmittance at $\lambda = 11.89$ μm [9] is illustrated in Fig. 2. The values of $T_{\mathrm{m,IRAS}}$ thus obtained are in the best agreement with the melting points of i-PP determined by DSC.

The measured values of the melting temperature of i-PP are listed in Table 2. These results show that the melting temperature of this polymer may be determined by continuous recording of the transmittance at $\lambda = 11.89$ μm and the value thus obtained is sufficiently consistent with the values found microscopically or calorimetrically.

Table 2

Melting temperatures of isotactic polypropylene determined microscopically, calorimetrically, and spectroscopically

Type of polymer	$T_{\mathrm{m,micr}}$ K	$T_{\mathrm{m,DSC}}$ K	$T_{\mathrm{m,IRAS}}$ K
i-PP (TATREN HPF)	438.86	437.26	437.76
i-PP (TATREN HPE)	438.16	434.16	435.16
i-PP (MOSTEN)	437.36	432.96	433.16

Conclusion

The applicability of the IRAS method based on measurement at a fixed wavelength and allowing to observe the processes due to increasing temperature of the substance was verified for low-molecular organic substances. In this way, the melting temperatures of benzanilide and phenacetine were determined. This procedure was analogously applied to the investigation of melting process in i-PP. The presence of the absorption bands due to the presence of ordered crystalline regions in i-PP was confirmed by determining the melting temperature of this polymer which is in good agreement with the values obtained by the microscopic and calorimetric method.

On the basis of the results of the experimental studies concerning the determination of the melting temperature of i-PP, we used the continuous recording of transmittance at a fixed wavelength in other studies for investigating the processes taking place in the course of solidification of this polymer [6, 7]. We employed the knowledge obtained from the study of the process of isothermal crystallization of i-PP for interpretation of fine structure of the fibres prepared from this polymer.

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Translated by R. Domanský