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Application of infrared ATR spectroscopy to in situ reaction monitoring

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Abstract

The infrared horizontal ATR technique was adapted to be applied for in situ reaction monitoring even at high pressure and high temperature. Different types of reactors and flow cells were built which can be used for recording IR ATR spectra at pressures up to 200 bar and temperatures up to 300°C.

The use of the horizontal ATR technique is shown by the following application examples:

- addition reaction of *n*-butyl isocyanate with butyric alcohol;
- investigation of the equilibrium of isocyanate, HCl and carbamic acid chloride at elevated pressure and temperature;
- monitoring the polycondensation of bifunctional alcohols and carbonic acids;
- recording spectra of polymer melts at 280°C.

Keywords: Attenuated total reflection (ATR); IR-ATR spectra; Horizontal ATR technique; Reaction monitoring

1. Introduction

Infrared spectroscopy is a valuable tool for in situ monitoring of chemical reactions, because functional groups which are reacting or are produced during reaction show characteristic fingerprints in the IR spectrum.

However, in most cases it is not useful to record transmission spectra if reactions shall be followed by means of IR spectroscopy because the spectral path length and thus the optical density is too large. So quantitative concentration data cannot be derived from the mean peaks of the IR spectrum.

To overcome this problem the ATR (attenuated total reflection) technique, a well-known technique for recording the IR spectra of organic substances [1], was used. The IR radiation is directed into the ATR crystal and is totally reflected within the crystal. The sample is brought into contact with the ATR crystal. In the contact area, because of the wave property of the IR radiation, the IR radiation penetrates the sample resulting in the IR-ATR spectrum.

The horizontal ATR design was invented by Messerschmidt [2]. It enables high throughput of the IR radiation and good reproducibility of the IR spectra without the need for optical realignment when

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changing crystals and samples. The reflection angle is simply determined by the grinding angle of the reflecting planes at the end of the crystal. These are coated with a reflecting metal layer. The sample is brought into contact with the crystal only at its upper side.

The effective penetration depth d_p depends on the wavelength λ of the IR radiation, the reflection angle θ and the refractive indices of the ATR crystal material n_1 and the sample n_2. It can be calculated according to the following formula [3]:

$$d_p = \frac{\lambda/n_1}{2\pi(\sin^2\theta - (n_2/n_1)^2)^{1/2}}.$$

In most cases, the effective penetration depth in the IR is between 0.5 and 5 μm. This penetration depth is suitable for recording the IR spectra of organic materials and to realize maximum sensitivity for the quantitative determination of concentrations.

Because of practical advantages of the horizontal ATR design, we chose this design for reaction monitoring experiments.

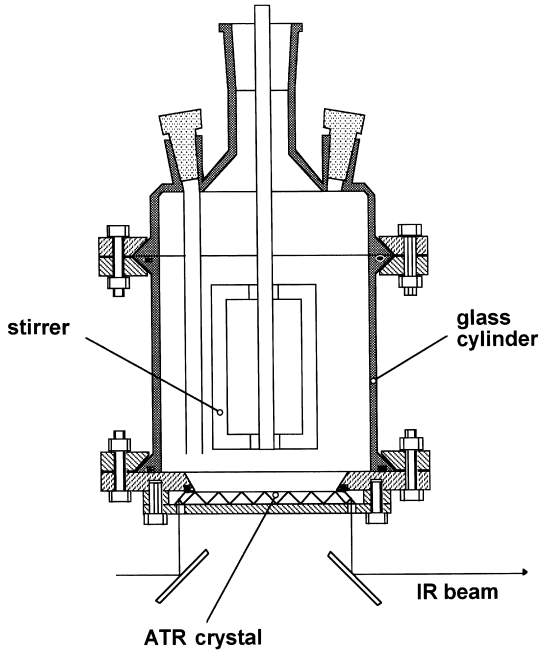

Fig. 1. Schematic diagram of the horizontal ATR laboratory reactor.

2. Horizontal ATR laboratory reactor

The stirred reactor which we have used for reaction monitoring is schematically shown in Fig. 1. The horizontal ATR crystal is mounted in the bottom plate of the reactor. A similar reactor design was published by Sting [4]. Differences exist in the type of mounting and sealing of the ATR crystal. Another way for applying ATR spectroscopy to a laboratory reactor is based upon cylindrical internal reflectance [5,6]. Beyond that, reactions can be followed by means of ATR probes which are commercially available.

The low pressure horizontal ATR reactor can be used for monitoring noncatalyzed or homogeneous or even heterogeneous catalyzed reactions. Aqueous or organic systems can be monitored, and also reactions in emulsions can be followed. The reactor content can be well stirred during the reaction. Because of the well-protected mounting of the ATR crystal, a mechanical damage of the crystal during stirring is unlikely.

The ATR crystal is sealed against the liquid within the reactor by elastomeric seal. In order to avoid absorption peaks due to the seal the upper flat side of the ATR crystal is coated with gold where the seal touches the crystal.

The ATR crystal is pressed from below against the seal by a flat metal plate. This metal plate stays in direct contact with the bottom side of the ATR crystal but it does not produce an IR spectrum because it is purely reflecting. Alternatively, the bottom side of the ATR crystal can be coated with a reflecting layer. So no distortion of the ATR spectra to be measured only from the upper side of the ATR crystal occurs. The ATR crystal can be changed by loosening the metal plate at the lower side of the ATR crystal.

The choice of the ATR crystal material is determined by the requirements of chemical resistance and free spectral range. A material with a good alkali resistance is ZnS, whereas good resistance against acids can be achieved with Si or Ge. A broad spectral range is given by the standard material ZnSe. An extreme chemical resistance and hardness shows ZrO_2, but this material has a limited spectral range of greater than 2000 cm^{-1}. However, for the investigation of OH-, CH- and NCO-groups this material is the first choice. Good spectral properties and chemical resistance has diamond.

The reactor is placed upon the horizontal ATR optical bench attachment which is placed into the sample compartment of the spectrometer. A commercially available optical stage manufactured by Spectra Tech is used.

The wet side of the ATR crystal is accessible and can easily be cleaned after an experiment is finished without demounting the ATR crystal. Before the next experiment is run, the reactor with clean ATR crystal is set upon the optical stage and a background spectrum is taken. So the horizontal ATR reactor is easy to handle and is a productive instrument in a laboratory where reaction kinetics are investigated.

Most spectra were taken with Nicolet FT-IR-Spektrometers equipped with a liquid nitrogen cooled MCT detector. If no high time resolution is required, FT-IR-Spectra can be taken automatically in constant time intervals and be stored while the reaction is carried out.

If a high time resolution is required, it is useful to registrate and store only interferograms. The Fourier transformation can be performed later on when the reaction is finished. In a rapid scan mode, typically up to 50 scans per second can be recorded. However, this high time resolution of the spectrometer is not required for reaction monitoring in stirred reactors because the reactants cannot be mixed so fast. A typical mixing time of about 1 s can be assumed. If faster reactions shall be investigated, the application of the stopped flow technique is recommended.

2.1. Application example

The following application example of the low pressure ATR reactor concerns with the addition reaction of *n*-butyl isocyanate with butyric alcohol at normal pressure in the temperature range 51–84°C which is running noncatalyzed. The reaction starts immediately by injecting *n*-butyl isocyanate into the well-temperated reactor containing butyric alcohol in excess. The spectra recorded with a time interval of 1 min show the decrease of the NCO band at 2275 cm^{-1} and the increase of the urethane carbonyl band at 1702 cm^{-1} (Fig. 2). As expected the reaction rate increases with increasing temperature Fig. 3.

A plot of the logarithm of the NCO concentration versus time shows a strongly linear relationship (Fig. 4).

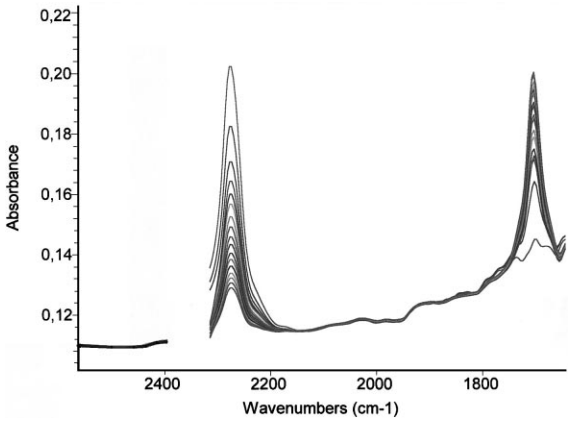

Fig. 2. IR-ATR spectra of a mixture of *n*-butyl isocyanate in excess of butyric alcohol at elevated temperature showing the decrease of the isocyanate band at 2275 cm^{-1} and the increase of the urethane band at 1702 cm^{-1}. The spectra were recorded in a time interval of 1 min.

Therefore the kinetic model applied is of first order (linear relationship, *n*-butyric alcohol in 25-fold excess). The rate constant and the activation energy were derived from the Arrhenius plot (Fig. 5).

3. High pressure horizontal ATR reactor

In order to achieve a high pressure resistance, the reactor arrangement was strongly reinforced and slightly changed (Fig. 6). The seal which is attached to the ATR crystal is an O-Ring surrounding the wet area of the ATR crystal. The crystal width is 20 mm and the length 44 mm. The O-Ring is fixed by a groove within the bottom plate of the reactor. Again the ATR crystal is placed upon a massive metal base.

The pressure resistance of the reactor was designed to be 200 bar. Successful pressure tests were carried out at 280 bar.

3.1. Application example

The equilibrium of isocyanate, HCl and carbamic acid chloride was investigated using the high pressure horizontal ATR reactor.

$$R-N=C=O + HCl \Leftrightarrow R-NH-COCl$$

Fig. 7 shows an ATR-spectrum of both substances. The absorption at 1771 cm^{-1} refers to the carbamic acid chloride.

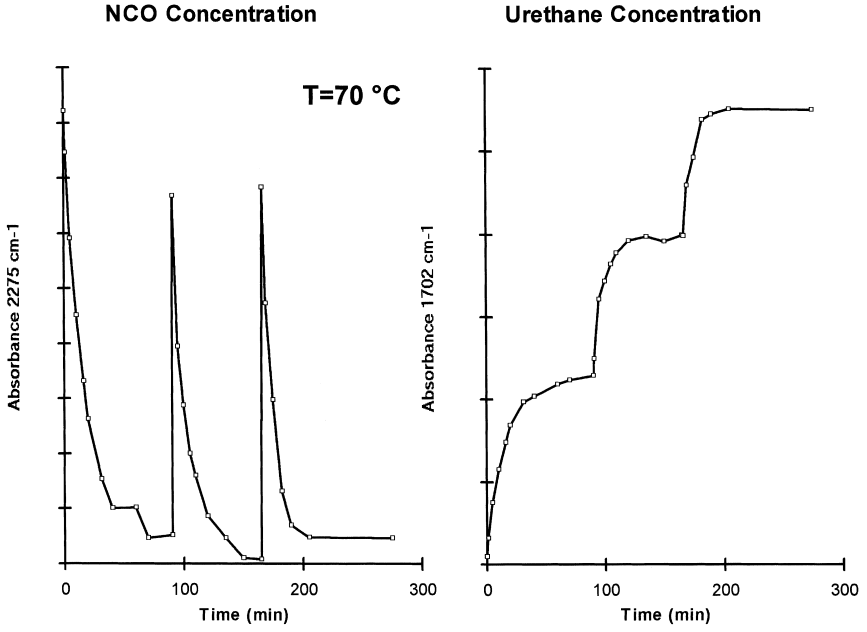

Fig. 3. Time dependence of the absorption at 2275 cm^{-1} (NCO concentration) and 1702 cm^{-1} (urethane concentration) after multiple adding of *n*-butyl isocyanate to butyric alcohol.

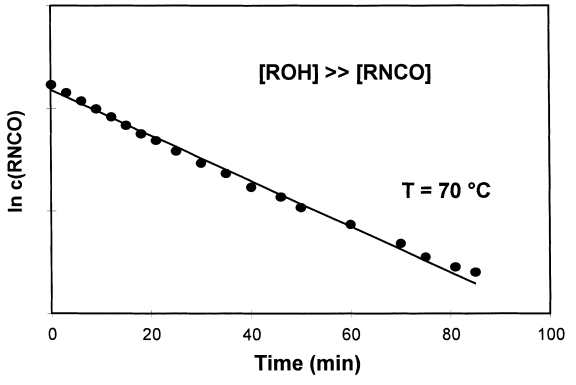

Fig. 4. Time dependence of the logarithm of the concentration of NCO groups as measured from the NCO absorption at 2275 cm^{-1}.

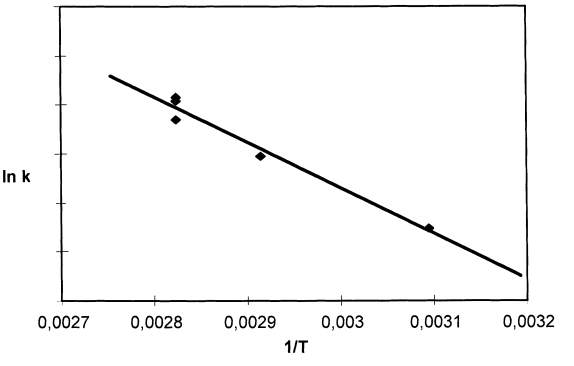

Fig. 5. Arrhenius plot of the reaction of *n*-butyl isocyanate in butyric alcohol being in excess.

The unknown equilibrium constant K_{eq} is

$$K_{eq} = [R{-}NH{-}COCl]_{eq}/([R{-}NCO]_{eq} \cdot [HCl]_{sol}). \quad (1)$$

The solubility of HCl in the isocyanate and the carbamic acid chloride cannot be determined by conventional phase equilibrium measurements. It was derived from the measurements taking into account the mass balance, the measured pressure and the ratio $[R–NH–COCl]_o/[R–NH–COCl]_{eq}$ being proportional to the quotient of the absorption at 1771 cm^{-1} in the original mixture and in the equilibrium. Henry's equation was found to hold for the solubility

$$[HCl]_{sol} = p(HCl)/H(HCl), \quad (2)$$

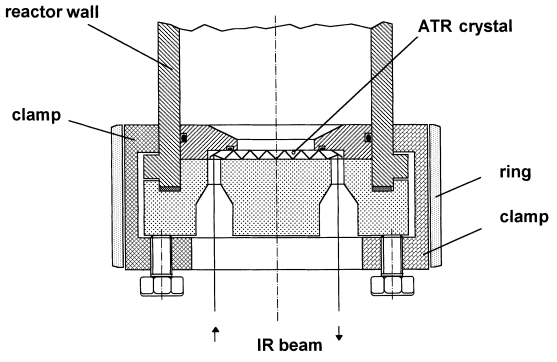

Fig. 6. Schematic diagram of the high pressure horizontal ATR laboratory reactor.

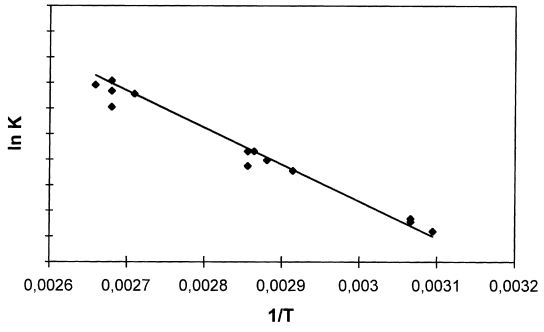

Fig. 8. Arrhenius plot of isocyanate and carbamic acid chloride.

where H(HCl) is Henry's constant. Eq. (1) can be converted to

$$K_{eq} = ([R{-}NH{-}COCl]_{eq} \cdot H(HCl))/([R{-}NCO]_{eq} \cdot p(HCl)). \quad (3)$$

The experiments for the determination of the equilibrium constant were carried out as follows. Different amounts of isocyanate and carbamic acid chloride were injected into the high pressure horizontal ATR reactor. The reaction mixture reached the final temperature very quickly. The pressure within the reactor was registrated. In different experiments the pressure due to gaseous HCl rose up to 25 bar.

At room temperature the decay of the concentration of the carbamic acid chloride is very slow, i.e. the absorption peak at 1771 cm^{-1} can be calibrated by taking spectra immediately after heating the mixture very quickly to the final temperature, e.g. 100°C. ATR-spectra and pressure were then measured along time. After a certain time the pressure and the ATR-signals stayed constant.

The ratio $[R–NH–COCl]_o/[R–NH–COCl]_{eq}$ was used for the determination of the equilibrium constant

$$K = ([R{-}NH{-}COCl]_{eq} \cdot H(HCl))/([R{-}NCO]_o + ([R{-}NH{-}COCl]_o - [R{-}NH{-}COCl]_{eq})) \cdot p(HCl). \quad (4)$$

From a plot of ln K_{eq} versus $1/T$ (Fig. 8) we determined the reaction enthalpy.

4. Low pressure horizontal ATR flow cell

With a flow cell, reactions can be monitored in a bypass to an intermediate scale or a large scale reactor.

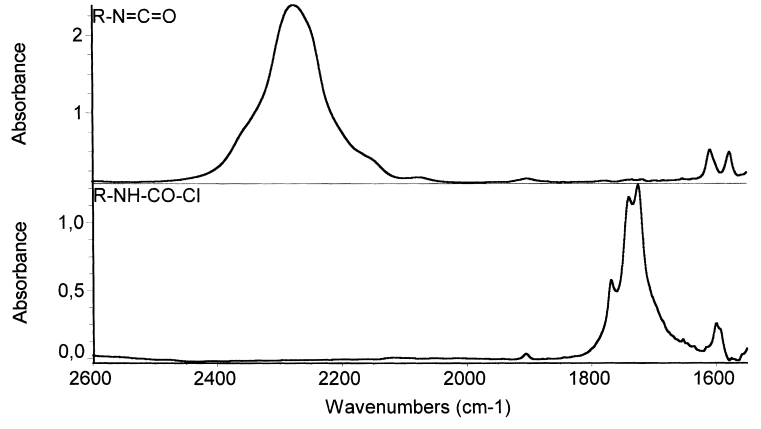

Fig. 7. IR-ATR spectra of an isocyanate and the corresponding carbamic acid chloride.

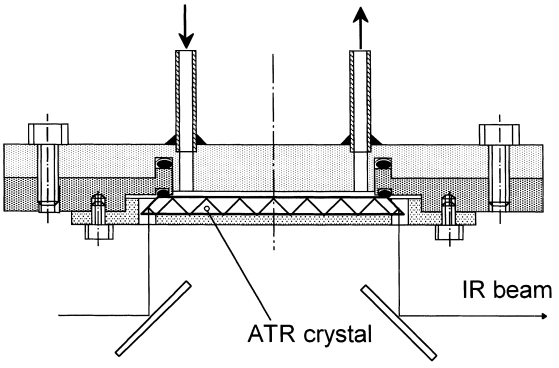

Fig. 9. Schematic diagram of the low pressure horizontal ATR flow cell.

The information of the IR-ATR spectra can be used for process development or process control.

The flow cell which we used for reaction monitoring in a bypass is built analogous to the low pressure ATR reactor and is shown in Fig. 9. Again the ATR crystal is sealed by an elastomer and can be changed. The wet side of the ATR crystal can be cleaned easily after loosening only four screws and opening the ATR flow cell.

4.1. Application example

The low pressure ATR flow cell was applied for monitoring the polycondensation of bifunctional alcohols and carbonic acids.

In the case of polycondensation reaction the functional groups reacting with each other must stay in the correct stoichiometric balance in order to obtain the desired molecular weights. The concentration of end groups are represented by the hydroxyl and acid numbers which can be measured by titration.

The ATR spectra show a decrease of the absorption in the OH region from 2200 to 3700 cm^{-1} during the reaction (Fig. 10). The absorption of alcoholic hydroxyl groups is shifted against the carbonic acid groups. The constant C–H stretching band is superimposed. The reaction is run at a temperature around 150°C.

The hydroxyl and acid numbers were derived from the IR-ATR spectra measured on-line [7]. The precision of the measurement was tested over time in a pilot plant. The hydroxyl and acid numbers derived from the IR-ATR spectra are in a good agreement with the reference values determined by titration (Fig. 11).

This shows that the hydoxyl and acid numbers determined on-line can be used for process development and process control.

5. High pressure horizontal ATR flow cell

The high pressure ATR flow cell (Fig. 12) withstands pressures up to 200 bar. The temperature resistance is limited by the seal materials applied and by the temperature dependent transmission of the ATR crystal. For instance, for applications at elevated temperatures germanium is not recommended as

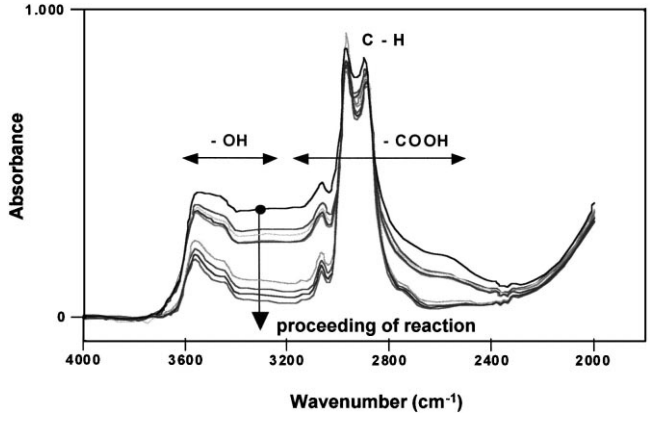

Fig. 10. IR-ATR spectra measured during polycondensation of a bifunctional alcohol and carbonic acid at a temperature of 150°C showing the decrease of hydroxyl and carbamic acid groups.

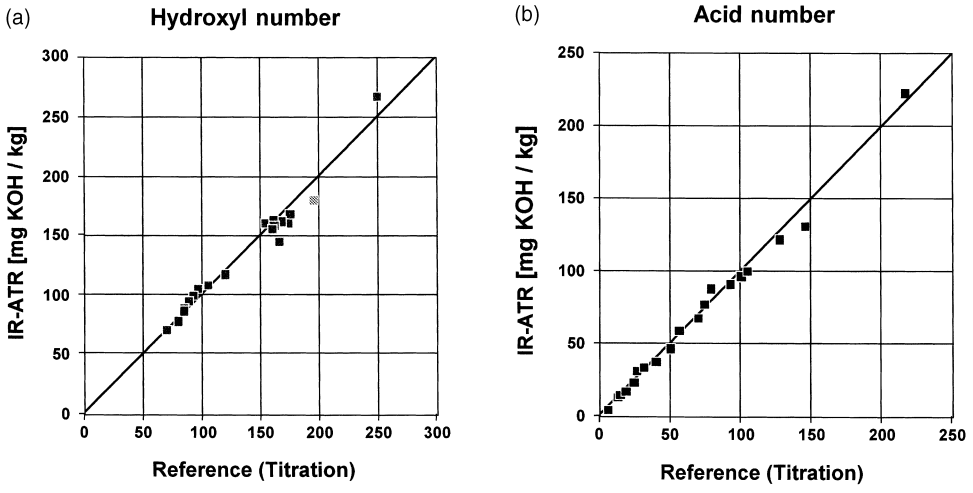

Fig. 11. Comparison of hydroxyl numbers (a) and acid numbers (b) determined from the IR-ATR spectra with reference values determined by titration.

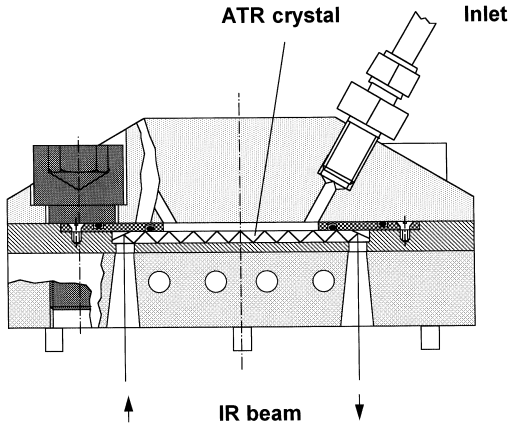

Fig. 12. Schematic diagram of the high pressure horizontal ATR flow cell.

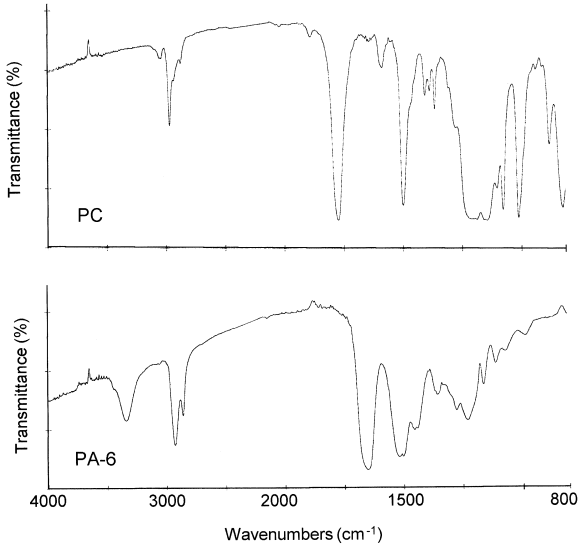

Fig. 13. IR-ATR spectra measured from polymer melts at 280°C using the high pressure horizontal ATR flow cell coupled to a laboratory extruder.

ATR crystal material, because the electronic band gap of germanium is low and thus free carriers which absorb IR radiation are produced at elevated temperature.

The kinetics of the material exchange at the surface of the ATR crystal can be influenced by the width of the product channel and by the throughput.

5.1. Application example

IR-ATR spectra of polymer melts were recorded at 280°C with the high pressure ATR flow cell. The cell was directly coupled to the outlet of a laboratory extruder. The polymer throughput was around 1 kg/h.

IR-ATR spectra of polycarbonate and polyamide-6 were recorded using a ZnS crystal (Fig. 13). No reactions were carried out, but the application example shows that even high viscous systems can be monitored by means of IR-ATR spectroscopy at high temperatures.

6. Conclusion

It is shown that the horizontal ATR principle can be used for in situ reaction monitoring and reaction control even at high pressure and high temperature. By proper choice of ATR crystal, seals and cell body materials additionally a high chemical resistance can be achieved.

The horizontal ATR reactors and flow cells are easy to handle and are a productive instrument in an industrial laboratory where reaction kinetics are investigated.

The application examples of noncatalyzed reactions demonstrate the use of ATR spectroscopy for reaction monitoring.

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