# Monitoring of Chemical Reactions during Polymer Synthesis by Real-Time Attenuated Total Reflection (ATR)–FTIR Spectroscopy

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**ABSTRACT:** The present study demonstrates *in situ* real-time attenuated total reflection (ATR)–FTIR spectroscopy as a powerful tool for monitoring and analyzing different polymerization and polymer modification reactions. Thus, a metallocene catalyzed copolymerization of propene and 10-undecene-1-ol, a polycondensation reaction towards polysulfone, and a modification reaction of OH end groups of hyperbranched poly(urea-urethane) were investigated successfully. The interpretation of the development of FTIR spectra was carried out on the basis of typical vibration bands of chemical groups of the corresponding monomers and polymers in each case, e.g. of the C=C double bond of 10-undecene-1-ol during the copolymerization, the new C—O—C group of polysulfone, and the new urethane end group of poly(urea-urethane). Kinetics prediction is also under consideration. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1374–1380, 2006

**Key words:** FTIR spectroscopy; metallocene catalyzed copolymerization; polycondensation; modification of hyperbranched polymers

## INTRODUCTION

New rapid monitoring techniques were developed for high-speed validation and analysis of several processes in chemical industry in recent years. Real-time measurements of chemical processes allow to provide an insight into the reaction pathways of chemical syntheses under actual reaction conditions that are often harsh and susceptible to trouble. Therefore, corresponding technologies have evolved to an essential integral part of production line control in the chemical industry. So, the so-called "ReactIR" technology as an important tool was created. This means that the use of Real-Time Attenuated Total Reflection (ATR)–FTIR spectroscopy together with the individually adapted robust ATR probes allow both the monitoring and analysis of reaction processes. The method enables to detect changes in chemical structures and to determine reaction rates by using the highly specific mid-infrared range (4000–650 cm$^{-1}$). Thus, kinetic data as well as information about chemical conversions and reaction mechanisms can be obtained.[1–6]

In the previous work,[7] a special ATR "dipper" probe was adapted to a twin-screw extruder for in-line monitoring of reactive extrusion of polymer melts. Now, we report on the use of a real-time ATR–FTIR technique to monitor different polyreactions *in situ* in organic solvents, which are performed under stirring in well known state-of-the-art lab reactors:

1. Metallocene catalyzed copolymerization of propene and 10-undecene-1-ol.
2. Polycondensation of 2,2'-bis(4-hydroxyphenyl) propane (bisphenol A) and 4,4'-dichlorodiphenyl sulfone to polysulfone (PSU).
3. Modification by addition reaction of OH end groups of hyperbranched poly(urea-urethane)s (HBP).

The specific goal was to identify irregularities and side reactions during the particular polymeric reactions. Moreover, the results should verify the variable application of this special ATR–FTIR technique in complex polymer-solvent systems.

### Real-time ATR–FTIR spectroscopy

A ReactIR™ 4000 system (Mettler-Toledo) was used.[8] The ReactIR on-line monitoring system is based on the well-known ATR–FTIR technique.

This technique allows to investigate the surface-near area of substances by direct contact with the ATR measuring crystal. The infrared beam passes through
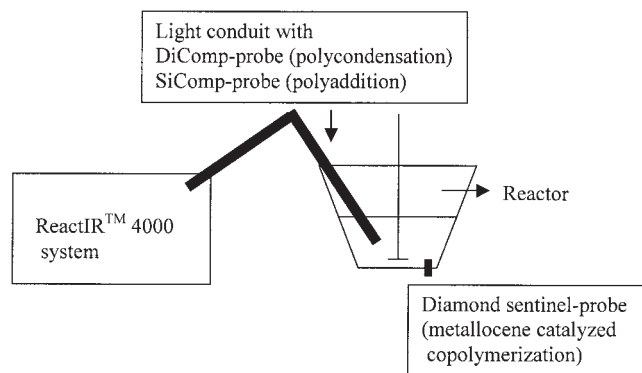
**Figure 1** Principle of ATR–FTIR spectroscopic equipment for three different polyreactions followed.

the crystal. Under defined physical conditions, it penetrates marginally into the substance and is then totally reflected. And so, the refractive index $n_2$ of the substance has to be less than $n_1$ of the measuring crystal, and the angle of incidence has to be greater than the critical angle in order that total reflection is obtained. The penetration depths of the IR beam in silicon or diamond crystals amount to 210–1400 or 500–3300 nm in the mid-infrared range (angle of incidence: 45°).

The ATR principle was used for the development of both the diamond and silicon testers and the special diamond sentinel probe of the ReactIR system. These utilized ATR measuring crystals possess more than six reflections. The build-up of the probes ensures a thermal stability up to 250°C, chemical resistance, and a maximum pressure limit of 7 bar (see Fig. 1).

The probes are connected via optimized light conduit (adjustable mirror arms) with the FTIR spectrometer. The FTIR spectrometer is equipped with a common Michelson interferometer and a MCT detector. The measurements are carried out in the mid-infrared range. The so-called IR spectroscopic fingerprint characterizes the changes of molecular compositions as a function of time during the chemical reaction.

## EXPERIMENTAL

### Materials

Copolymerization

Toluene (Fluka, p.a.) was sodium/potassium-dried and distilled prior to use. Propene 2.8 grade (Riessner-Gase) was purified by R3–11 copper oxide catalysts (BASF) followed by passing through 3-Å molecular sieves. The metallocene rac-Et[Ind)]$_2$ZrCl$_2$, methylaluminoxane (MAO) (10 wt % solution in toluene), and triisobutyl aluminum (TIBA) (all from Crompton GmbH, Germany) were used as received. 10-undecene-1-ol (Aldrich) was distilled and then stored over

molecular sieve before being used in copolymerization.

Polycondensation

Toluene (Acros) was dried with sodium, and N-methyl-2-pyrrolidone NMP (Fluka) was dried with calcium hydride and both solvents were distilled prior to use. Both monomers were recrystallized twice with either 2,2′-bis(4-hydroxyphenyl) propane (bisphenol A) (Avocado) from ethanol/water in (1:1) or 4,4′-dichlorodiphenyl sulfone (Aldrich) from toluene, and vacuum dried prior to use. Potassium carbonate (Fluka) was used as received.

Polyaddition

A hyperbranched poly(urea-urethane) synthesized from 2,4-toluylene diisocyanate (BASF AG) and diethanol amine (BASF AG) with OH end groups was used for end group reaction with phenyl isocyanate (Fluka). The synthesis of the hyperbranched poly(urea-urethane) is fully described in ref. 9.

### Chemical reactions and monitoring parameters

Metallocene catalyzed copolymerization of propene and 10-undecene-1-ol

This type of copolymerization permits to functionalize polyolefinic structures by incorporating the comonomer 10-undecene-1-ol into the propene backbone chain. Well-defined stereospecific polymer structures of polypropene with hydrophilic side chains are aimed for.

Copolymerizations were carried out in toluene in a 1 L steel autoclave (Büchi). The polymerization temperature, the stirring speed, and the total pressure were held constant at 30°C, 800 rpm, and 1.2 bar. The reactor was first charged with toluene, cocatalyst (MAO), and the comonomer pre-reacted with TIBA. The copolymerization was initiated by injecting the metallocene catalyst solution into the reactor. The catalyst concentration was $3.2 \times 10^{-5}$ mol/L and the added comonomer concentration was 236 mmol/L 10-undecene-1-ol. Termination of the polymerization, precipitation, and purification was carried out as described earlier.[10,11]

For the FTIR measurements, a special diamond sentinel$^{TM}$ ATR probe (Mettler-Toledo) fixed and screwed at the bottom of reactor was used. The probe was linked via mirror arms with the spectrometer. IR spectra were recorded continuously per minute within 2.5–3 h during copolymerization. The resolution amounts to 2 cm$^{-1}$; 50 scans were coadded for each spectrum. So, 150–180 spectra per experiment were obtained. Corresponding background spectrum was
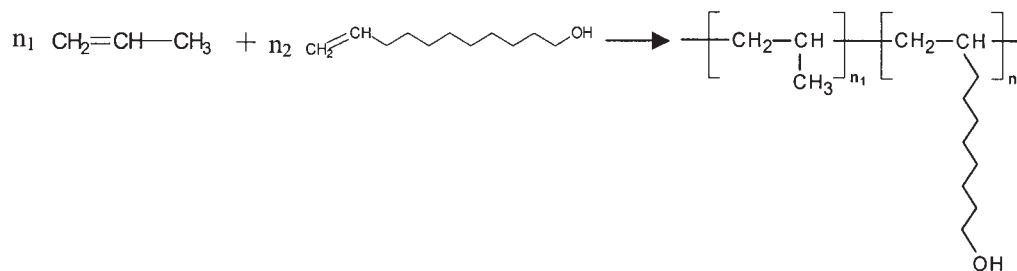
**Figure 2** Reaction scheme of the propene copolymerization.

assembled for toluene/MAO/triisobutyl aluminum spectra. The propene spectrum was also included in this background.

^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer. The samples were measured at 120°C in $C_2D_2Cl_4$, which was also used as reference and lock.

Polycondensation of bisphenol A and 4,4′ -dichlorodiphenylsulfone to polysulfone

The nucleophilic aromatic substitution polycondensation reaction was performed to obtain polysulfone according to refs. 12–15. The synthesis was performed in a 2.3-L Juchheim stainless steel reactor with an equimolar ratio of the bisphenol A to 4,4′-dichlorodiphenylsulfone (0.351 mol) under constant stream of nitrogen, stirring, and normal pressure. Toluene (300 mL) was applied to remove the water (~6 mL) formed during polycondensation by azeotropic distillation. In the first reaction step, potassium carbonate was used to generate the phenoxide ion of the bisphenol A *in situ*. Subsequently, the azeotropic distillation step of the polycondensation was carried out at 145°C for 4.5 h, and later, the main volume of toluene was distilled off. In the second polycondensation step, after removal of toluene by increasing the reaction temperature to 180°C, the phenoxide ion of bisphenol A reacted with the 4,4′-dichlorodiphenylsulfone in 600 mL NMP for further 4 h.

The polyethersulfone was characterized by ^{1}H NMR spectroscopy (Bruker DRX 500) in $CDCl_3$, by SEC (Knauer) in chloroform with narrowly distributed PS standards and by DSC (Perkin-Elmer) using half-step method; second heating run with 20 K/min.

IR spectra were recorded continuously every 4 min within 9 h during the polycondensation reaction. One hundred and fifty scans were coadded with resolution of 2 cm$^{-1}$ for each spectrum. The ATR probe Di-Comp™ (Mettler-Toledo) as diamond composite dipper was fixed at the top cover of the reactor and connected again via mirror arms with the spectrometer.

Modification by addition reaction of OH end groups of hyperbranched poly(urea-urethane)s

The chemical reaction of the OH end groups of poly(urea-urethane)s with phenyl isocyanate was used to obtain a well-defined hyperbranched chemical structure with specific end functions; in this case phenyl groups. The use of the highly reactive phenyl isocyanate should ensure the complete modification of the end groups. The polymer structures of unmodified and modified poly(urea-urethane)s were characterized by FTIR spectroscopy, ^{1}H NMR and SEC. ^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer. DMSO-$d_6$ as solvent was used. The SEC measurements were carried out with an instrument of Knauer. The calibration was performed with linear poly(vinylpyridine) standards.[9,16]

During the infrared spectroscopic measurements, the modification reaction was carried out in a common three-necked 250-mL glass flask under Argon atmosphere at room temperature, under stirring. Pure phenyl isocyanate (0.62 g) was added dropwise to 0.5 g dissolved polyurethane in 100 mL DMSO.

IR spectra were collected every minute within 3 h with a resolution of 4 cm$^{-1}$ and 32 scans for each spectrum. The SiComp™ (Mettler-Toledo) as a silicon composite ATR dipping probe was inserted in the flask and connected with the spectrometer accordingly, as described earlier. Solvent used in this experiment was DMSO which has no amide groups to overlap with the urethane bands of HBP.

## RESULTS AND DISCUSSION

### Metallocene catalyzed copolymerization of propene and 10-undecene-1-ol

ATR–FTIR spectroscopy was utilized to provide an insight in some details of the metallocene catalyzed copolymerization as it is proposed (Fig. 2). In our investigations 10-undecene-1-ol was chosen as comonomer example. The propene is dosed continuously, but the comonomer is filled-in only before the start of polymerization. This copolymerization is already described in numerous articles.[17–20] However,
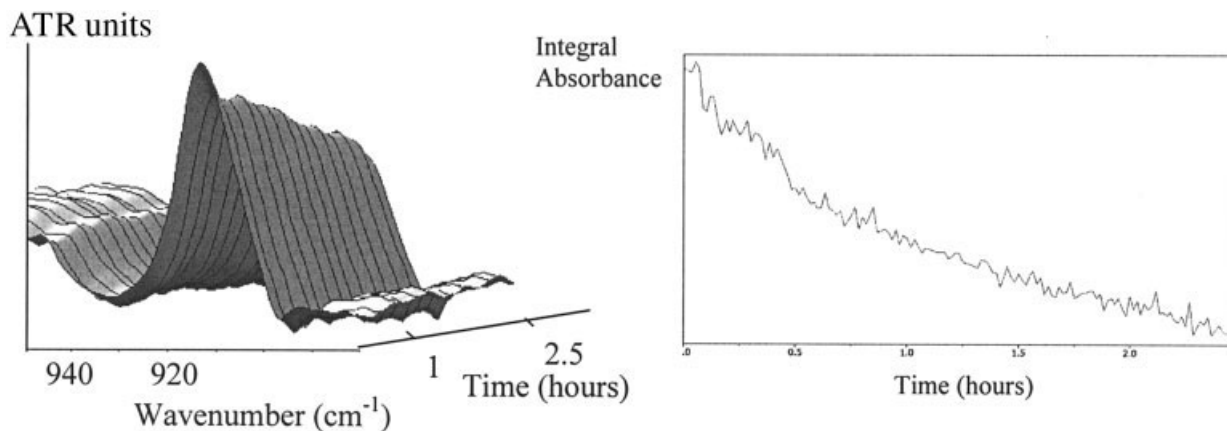
**Figure 3** (a) Waterfall plot of the $\delta_{oop}CH_2$ band and (b) Intensity progress of the $\delta_{oop}CH_2$ band.

until recently, it was not possible to get information about the decrease of the comonomer concentration during the copolymerization. Therefore, to obtain samples of well controlled comonomer composition, the monomers should be copolymerized only to small conversions so as to minimize the error caused by conversion dependent changing comonomer/propene ratios. Using *in situ* ATR–FTIR spectroscopy, the decrease of the comonomer concentration becomes detectable and thus, changes in the comonomer ratio can be identified.

This was done by analyzing the intensity profiles of characteristic bands of double bonds in the monomer 10-undecene-1-ol. Thus, the integral absorbance of the stretching vibrations $\nu$ C=C at 1641 cm$^{-1}$ (integration from 1650 to 1629 cm$^{-1}$) and the terminal out-of-plane vinyl deformation vibrations $\delta_{oop}$=CH$_2$ at 910 cm$^{-1}$ (933–896 cm$^{-1}$) was calculated. Figures 3(a) and 4(a) demonstrate the real-time waterfall plots of the $\delta_{oop}CH_2$= band and of the $\nu$ C=C band. Figures 3(b) and 4(b) show the corresponding intensity gradient derived from integral absorbances.

The polymerization progress is indicated by a decrease in band intensities of characteristic double bonds of the 10-undecene-1-ol component. However, it is clearly seen that the conversion is not complete after 2.5 h. The residue of double bonds points to non-reacted comonomer. However, $^1$H NMR spectroscopic results confirm the incorporation of this comonomer into the polypropene backbone chain. The average comonomer content in the copolymer amounts to 6.9 mol % (= 23.2 wt %) 10-undecene-1-ol. The resulting propene copolymer is also characterized by a melting temperature (second heating) of $T_m$ = 86°C, a polypropene crystallinity of $\alpha$ = 14%, and a glass transition temperature of $T_g$ = −13°C.

Figure 5 shows a first-order kinetic plot of the 10-undecene-1-ol conversion. Although the values are very scattered, the rate of comonomer incorporation can be estimated to be only dependent on the concentration of the comonomer, indicating a reaction of first-order rate law. The values of the 10-undecene-1-ol concentrations are based on the absorbance of the $\delta_{oop}CH_2$ band.
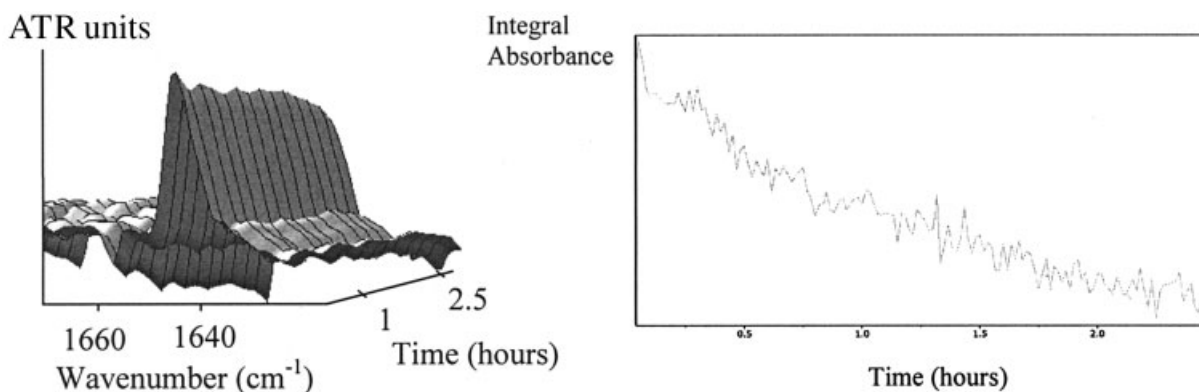


**Figure 4** (a) Waterfall plot of the $\nu$ C=C band and (b) Intensity progress of the $\nu$ C=C band.
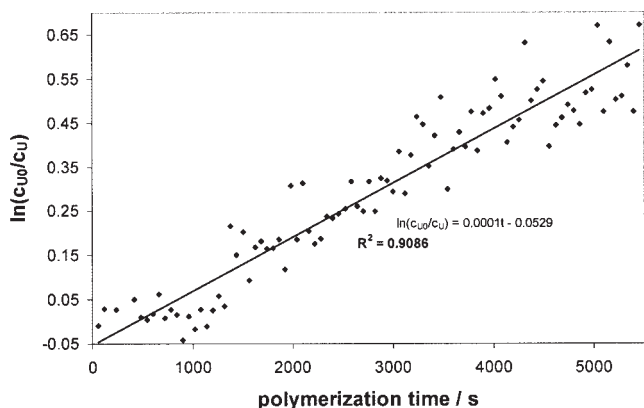
**Figure 5** First-order kinetic plot for the conversion of 10-undecene-1-ol in the copolymerization with propene ($c_{Ll}$, $c_{Ll0}$ comonomer concentration or initial comonomer concentration in the feed).

### Polycondensation of bisphenol A and 4,4′-dichlorodiphenylsulfone to polysulfone

The *in situ* monitoring of PSU polycondensation was performed to get a dynamic picture, both of structural changes and reaction kinetics under the slightly varying complex reaction conditions, which can often be found during the long reaction time which is necessary. Figure 6 shows the overall chemical reaction.

The real-time plot of the IR spectroscopic measurement shows the changes in the chemical structures based on the analyzed characteristic bands of disappearing monomers as well as growing polymer chains. Figure 7 illustrates this behavior in two important fingerprint spectral regions of 1550–1100 and 1100–650 cm$^{-1}$. Thus, characteristic bands of monomers are decreasing$_{(\downarrow)}$ during the reaction, e.g., the C—Cl stretching vibration and CH$_{oop}$ deformation vibration band of 4,4′-dichlorodiphenyl sulfone (DC-DPS) at 1089. Furthermore, the synthesis of polysulfone is also very well detectable, e.g., by means of formation of the C—O—C band at 1241 of the ether structure in the polymer. The IR spectra also show that the C—O—C linkage already arises during the formation$^{(\uparrow)}$ of the phenoxide ion of bisphenol A. This

result is very important for the interpretation of the total process of synthesis.

The disappearance of toluene in the second reaction step is also identified because of the disappearance$_{(\downarrow)}$ of the corresponding bands after 4.5 h at 1030, 729, and 694 cm$^{-1}$.

The obtained PSU is characterized by a weight average molecular weight $M_W = 27{,}600$ g mol$^{-1}$, the number average molecular weight $M_n = 7400$ g mol$^{-1}$ (SEC), $M_n = 7100$ g mol$^{-1}$ ($^1$H NMR), and a $T_g = 182°C$ (DSC).

### Modification by addition reaction of OH end groups of hyperbranched poly(urea-urethane)s

The modification of the OH end groups of hyperbranched poly(urea-urethane)s is shown in Figure 8. The chemical structure of the modified polyurethane is also proved by $^1$H NMR spectroscopy.[21] The end group reaction is followed, e.g., by disappearing of chemical shifts of OH end groups in the range of 5.4–5.04 ppm. The $M_n$ and the polydispersity index PDI of the modified HBP amounts to 13,800 g mol$^{-1}$ and 8.26. The PDI of the unmodified HBP amounts to 17.19 with $M_n = 14{,}900$ (SEC analysis),[16] indicating some fractionation during modification and subsequent workup but no major degradation. The molar masses of the modified and unmodifed samples as measured by SEC can not be fully compared due to changes in the solubility behavior.

The plot of the spectral region for the reaction monitoring is shown in Figure 9. The analysis of three IR bands is of particular interest to interpret the chemical reaction: the decrease of the intensities of the NCO isocyanate bands at 2281 and 2261 cm$^{-1}$ indicates the complete consumption of the phenyl isocyanate after about 2 h reaction time; simultaneously, the formation of a C=O urethane band at 1709 cm$^{-1}$ is noticed and assigned to the new urethane end group which differs in its vibrational properties a little bit from the numerous urethane backbone groups. The new urethane band appears only as shoulder. Thus, it is difficult to integrate the band area accurately for making a com-
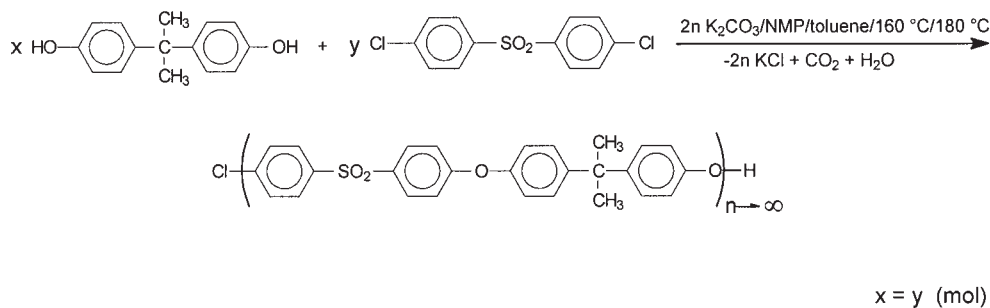


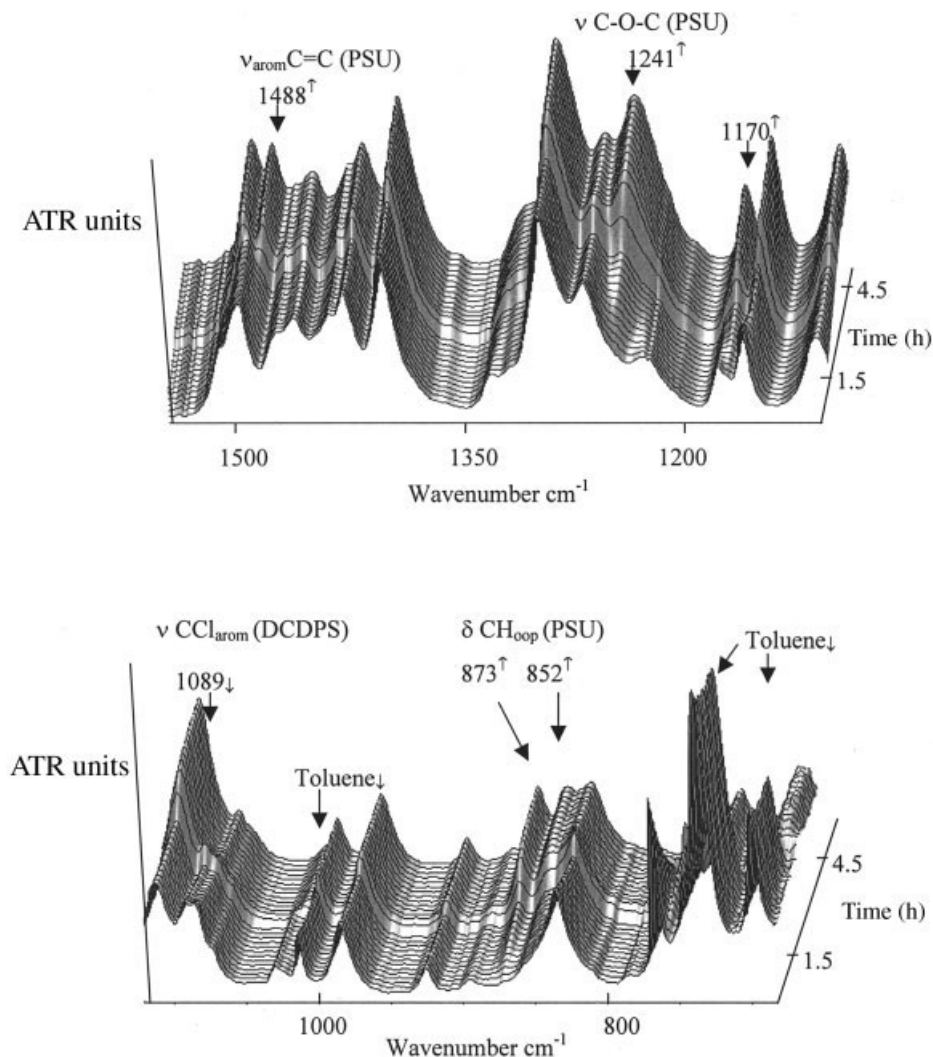**Figure 6** Scheme of the overall chemical reaction of PSU polycondensation.

**Figure 7** Waterfall plot of typical bands in spectral regions 1550–1100 (top) and 1100–650 cm$^{-1}$ (bottom) during the polysulfone polycondensation.

plete quantitative investigation. Nevertheless, the intensity of the new urethane band remains unchanged after about 1 h, and so, the spectra point to the end of the reaction at the time. Additional NMR investigation, however, has shown that part of the phenyl isocyanate is consumed in a side reaction involving partial premature hydrolysis and urea formation, and therefore, the extent of the end group formation might not correlate with the decrease in the isocyanate band.

The application of Fourier self deconvolution of bands as curve fitting procedure to estimate quantitatively urethane end group formation will be checked in the future.

The intensity of the stretching vibration band of OH end groups of poly(urea-urethane)s is too weak for a reasonable interpretation of the corresponding chemical reactions. Moreover, the OH bands are overlapped with the NH-bands of HBP.
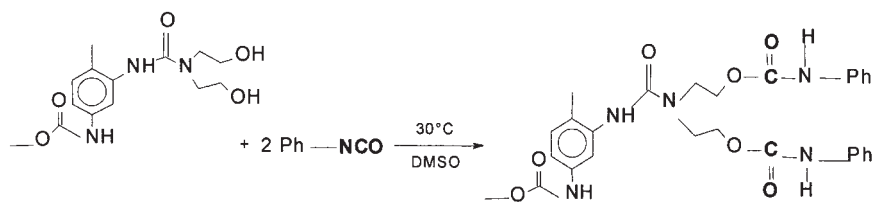


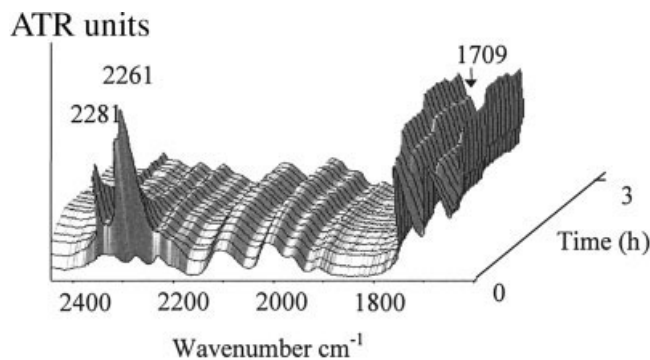**Figure 8** Reaction scheme of the modification of the hyperbranched polymer (HBP).

**Figure 9** Real-time IR spectra during HBP modification (reaction time 3 h).

## CONCLUSIONS

The present study demonstrates representatively that the *in situ* ATR–FTIR spectroscopic measurements allow to deliver insight in the process of polymerization, polycondensation, and polymer modification reactions in different organic solvents even at high monomer and polymer concentrations. The actual state of the investigated polymeric reactions can be described in real time under the particular reaction conditions. So, the monitoring of PSU polycondensation reaction was performed successfully for the study of the process of synthesis by this real-time monitoring technique. As a result, it was possible to get a reference for the formation of the polyether chain by the growth of the C—O—C linkage. It could be proved that during the formation of the phenoxide ion of bisphenol A the C—O—C linkage already arises.

The real-time monitoring of the kinetics of the metallocene catalyzed copolymerization of propene with a comonomer provides information on the decreasing comonomer concentration during the whole copolymerization process. This establishes the possibility to control the monomer/comonomer ratio on a constant level, and consequently get a copolymer with homogeneous composition even at higher comonomer conversion.

The modification of the OH end groups of hyperbranched poly(urea-urethane)s with phenyl isocyanate was followed effectively by real-time IR monitoring, being able to detect the newly formed urethane band of the end group in the presence of a large variety of urea and urethane bands within the complex highly branched polymer backbone.

The results of the qualitative investigations of the *metallocene catalyzed copolymerization, polycondensation, and polyaddition reactions* have promise to the current quantitative measurements using calibration models.

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