DOI: 10.1002/masy.201000055

Activity Monitoring for a Polymerization Catalyst System

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Summary: Catalyst systems for polymerization often exhibit variable and poorly controllable activity because of strong influences of trace components and catalyst preparation conditions. In cationic polymerizations in particular, determining catalytic activity and hence the amount of catalyst to be used is challenging. The assessment of a given initiator system typically requires testing it in polymerization reactions. Determining catalytic activity before using the initiator in a polymerization reaction is a desirable approach. This contribution describes the development of such an activity monitoring tool. In the first part, results from a fundamental characterization of the system diethylaluminum chloride/ethylaluminum dichloride/water by different NMR measurements and elemental analysis are reported. Structures characteristic of catalytically active systems are presented. The second part describes the application of transmission IR to the characterization of this system and the correlation of IR results to catalytic activity in dimerization and polymerization reactions. Implementation of the IR analysis as an on-line measurement is demonstrated.

Keywords: alkylaluminum halides; catalysis; infrared spectroscopy; monitoring; polymerization

Introduction

The control of catalyzed polymerization processes faces many difficulties. In cationic polymerizations in particular, determining catalytic activity and hence the amount of catalyst to be used is challenging. Extremely low concentrations of active centers and a strong influence of preparation conditions and trace components often cause variable catalyst quality. The assessment of a given cationic polymerization initiator system typically requires testing it in polymerization reactions because established analytic methods suitable for on-line monitoring of catalytic activity are not available. Real-time monitoring of monomer consumption and polymer formation, e.g. via ATR-IR[1] or calorimetric measurements,[2] does not directly separate the contribution of initiator activity from other factors that influence polymerization kinetics. Conductivity measurements have been employed to determine ion concentrations and degree of dissociation in initiator solutions, e.g.[3,4] Very few examples of linking initiator characteristics to catalytic activity can be found.[5,6]

Typical catalyst systems for cationic polymerizations consist of a Lewis acid and a proton or carbocation donor. Alkyl aluminum halide based initiating systems have been used for a variety of monomers,[7] e.g. styrene,[8] isobutyl vinyl ether,[9] or isobutene,[10–12] yet fundamental understanding of the formation reaction of catalytically active species and of corresponding molecular structures is still limited. Extensive studies of alkyl aluminum compound hydrolysis have been reported but without linking product structures to polymerization activity, e.g.[13,14]

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The objective of the work presented here is neither the elucidation nor the direct detection of active sites but to determine some indirect measure of catalyst quality and to implement a suitable measurement as an on-line tool for supporting polymerization process control. The development of such an activity monitoring technique is described for the initiator system diethyl aluminum chloride/ethyl aluminum dichloride/H_2O.

Experimental Part

Materials

All organoaluminum compounds were handled in a glovebox under an atmosphere of dry nitrogen. Solutions of alkyl aluminum chlorides were used as received (diethyl aluminum chloride, DEAC, 1N solution in hexanes, i.e. 18.3 wt%, Acros Organics; ethyl aluminum dichloride, EADC, 1N solution in hexanes, i.e. 19.3 wt%, Sigma-Aldrich). Hexane (Sigma Aldrich) was dried to <0.01% water. 1,1-diphenyl ethene (DPE) >97.5% (Acros Organics) and $H_2^{17}O$ with 78.2 atom% ^{17}O (Isotec) were used as received.

Sample preparation and transfer to sealed tubes or vials for analysis (e.g. NMR, elemental analysis, ESCA) was performed in the drybox. For other analytical techniques (e.g. IR), samples were transferred to glass vials closed with a septum so that they could be handled outside the glovebox. Aliquots were transferred to measurement cells or reactors via syringe. In this case, all equipment at ambient was dried and flushed with argon before bringing it into contact with alkyl aluminum halide solutions.

Methods

The mid- to far-infrared spectral range at wavenumbers below 900 cm^{-1} is particularly useful for the analysis of Al-Cl, Al-CH_2-, and Al-OX vibrations (skeletal modes). All IR spectra were measured at room temperature on a Biorad FTS 40 PRO spectrometer with DTGS detector using a transmission cell with polyethylene windows. The cell spacing was adjusted to solution concentrations. A typical transmission pathlength is 1mm. Either a standard transmission cell was used and filled via syringe, or a flow cell was used for implementing IR spectroscopy as an on-line method.

^{1}H-NMR spectroscopy was applied to the analysis of the nature and concentration of ethyl-groups. Methylene signals of ethyl groups bound to aluminum are sufficiently removed from all solvent proton signals to be analyzed quantitatively.^{27}Al-NMR was employed to determine aluminum coordination numbers and ligand types. Oxygen coordination in activated initiator solutions was inferred from ^{17}O-NMR spectroscopy. All NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature.

Total chlorine was determined by coulometric detection after combustion for samples diluted to between 1 ppm and 0.1% total chlorine. Total aluminum was determined via ICP-OES.

Additional information about elemental composition and binding states of individual elements was obtained via photoelectron spectroscopy (ESCA) with a ESCALAB220 instrument (Thermo VG Scientific) using Al Kα x-ray excitation.

Initiator Preparation

Precursor solutions were mixed in the desired ratio and diluted with hexane according to target concentration and reaction volumes. Water was added to the diluted mixture under vigorous mixing.

Dimerization and Polymerization Reactions

1,1-diphenylethene (DPE) dimerizations were studied in hexane solutions at a concentration of 0.1 mol/l DPE at −8 °C in a nitrogen purged reactor. Under these conditions only a limited conversion was reached at initiator concentrations up to 0.08 Al per monomer. Therefore it was possible to add a first small portion of initiator solution to the reactor for scavenging impurities without significantly changing the monomer concentration. The standard initiator to monomer ratio for the subsequent initiator addition was set to 0.01 Al per DPE. The reaction was monitored by on-line UV-VIS spectroscopy, scanning the range from 290 nm to 600 nm at a resolution of one spectrum every 0.1 minutes. Spectra were recorded with a Varian Cary 50 spectrometer using a Hellma fiber optic quartz probe with 5mm transmission pathlength.

Isobutene was polymerized in a continuous process in order to exclude batch to batch variability, e.g. varying impurity levels. Reactions were run in hexane at between −80°C and −60°C. Polymer yield was determined gravimetrically.

Characterization of Initiator Solutions

The hydrolysis of alkylaluminum chlorides is reported to form oxygen bridged structures $[(R_2Al)_2O]_n$ or $[RAlO]_n$ via loss of alkyl groups.[13–15] The first step at less than equimolar water concentrations is described as water complexation.[13] Ionization is the prerequisite for cationic polymerization, and different ion pairs are postulated to form in the presence of monomer.[8,16] The exact structures produced in the reaction with water depend on the chlorine content of the starting materials, the water to aluminum ratio, and on solvent polarity.[13,17]

Our development of an activity monitoring technique started by verifying the structures reported to be present in active initiator solutions for the system DEAC/EADC/H_2O and the chosen activation conditions. The composition of active initiator solutions was studied by NMR measurements and elemental analysis. ^{1}H-NMR is the method of choice to differentiate and quantify aluminum-bound ethyl groups. The methylene signal of ethyl groups in a EADC-type Cl_3AlEt-fragment (ca. 0.59 ppm) can be clearly distinguished from the one of a DEAC-type fragment containing two ethyl groups on the same Al-atom, Cl_2AlEt_2 (ca. 0.33 ppm) in accordance with the literature.[18] Figure 1 depicts the methylene range for the individual precursors, precursor mixture and activated solution. The fact that two signals are resolved in the DEAC-EADC-mixture indicates that ethyl group exchange is slow on the applicable NMR-timescale (400 MHz measurements). Taking into account the literature report of a 100 MHz spectrum that shows the fast exchange limit,[18] equilibration can be estimated to be complete on the timescale of seconds. Since preparation of the precursor mixtures always includes some mixing time before the addition of water, no influence of precursor equilibration on the hydrolysis studies reported here is expected.

Both types of ethyl groups are present in the precursor mixture and the reaction product with water. The ratio of the two

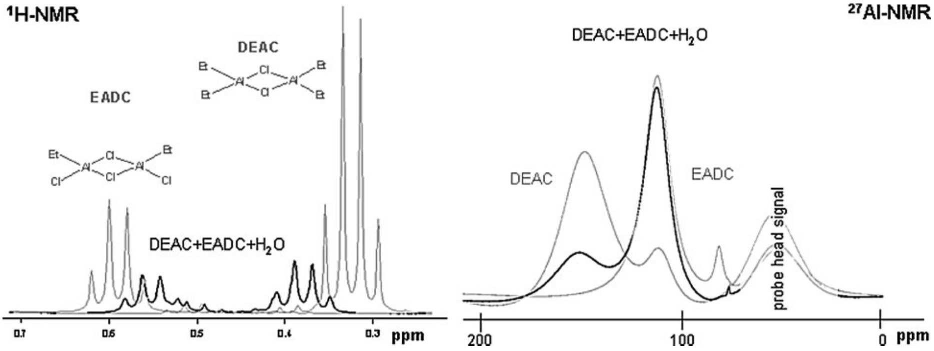

Figure 1.

NMR spectra (left: ^{1}H, right: ^{27}Al) of precursors and activated initiator mixture.

signals is changed by water addition, i.e. the fraction of Al atoms with two ethyl-groups is reduced in the hydrolysis product. In the case of a 1:1 mixture of DEAC and EADC and for molar water to aluminum ratios of ca. 0.5, the reduction corresponds to a loss of ca. 25% of the ethyl groups. A solvent signal is used as reference for quantification and the actual Al concentration in solution as measured by elemental analysis is taken into account. Elemental analysis of the hydrolyzed samples also shows a significantly reduced chlorine content. In contrast to the hydrolysis products proposed e.g. in [13] which form without any loss of chlorine, a reduction from 1.5 chlorine per Al in the starting 1:1 mixture of DEAC and EADC to 0.5 in the hydrolysis product formed at ca. 0.5 H_2O:Al is observed.

^{27}Al-NMR of the precursor mixture DEAC/EADC as well as of the catalytically active products from the reaction with water shows signals only in the chemical shift range typical of four-coordinate Al halides, or oxides, or four coordinate alkyl aluminum compounds,[19] see Figure 1. Two types of Al can be distinguished in the precursor mixture as well as in the hydrolysis product. As in the case of the ethyl-groups the difference is attributed to the presence of terminal chlorine. According to ^{17}O-NMR results (signal at 55–75 ppm) oxygen is three-coordinate and OH-groups are absent. In summary, the active initiator solution is shown to contain soluble structures which are oligomeric or higher aggregates, with composition $AlEt_zCl_xO_y$, z ca. 1.1–1.2 and x, y ca. 0.5.

Regardless of the mode of water addition, the activation procedures always resulted in an insoluble fraction containing up to 20% of the total Al. The composition as determined by ESCA is similar to that of the soluble fraction except for lower ethyl-group contents. Two different oxygen binding energies are detected corresponding to bridging Al−O−Al and bridging or non-bridging Al(OH). Only ca. 2 coordinated atoms or groups (Cl, Et, O) per aluminum are detected which indicates that high molecular or cage structures are formed, corresponding to $[(Cl,Et)Al(O,OH)]_n$.

IR spectroscopy was identified as a method suitable to detect structural elements of the activated initiator solution. Experimental and theoretical IR spectra of organoaluminum oxides and organoaluminum halides are discussed e.g. in. [13,14,20–23] Typical spectra are shown in Figure 2. In accordance with the literature, characteristic absorbances are assigned to Al-Cl (non-bridging Cl, ca. 483 cm^{-1}), to Al-Et (ca. 622 cm^{-1}) and to Al−O− modes with oxygen in unassigned structures, denoted Al−OX (e.g. at ca. 604 or 588 cm^{-1}). Different Al−OX bands are detected for different preparation conditions. The intensity of at least one characteristic Al−OX

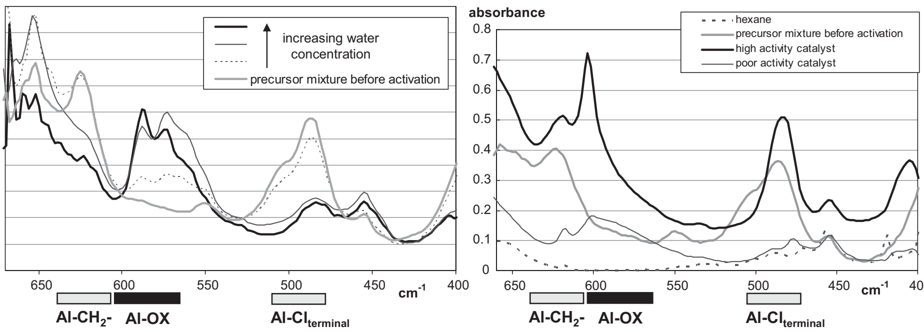

Figure 2.

Transmission IR spectra for samples prepared with from two different water addition procedures. Left: same initiator solution with increasing water addition, right: solvent, precursor mixture, and separately prepared initiator solutions from the polymerization tests.

band always increases with increasing water addition to the precursor mixture. The relation between the intensity distribution in the IR spectra and catalytic activity is discussed in the following paragraph.

Correlation of Spectroscopic Measurements to Catalytic Activity

The cationic dimerization of 1,1-diphenylethene to 1-methyl-1,3,3-triphenylindane was studied as a first simple example to check for a correlation between catalytic activity and IR-spectroscopic patterns. Since intermediate cations exhibit characteristic UV-VIS absorbances,[24] the course of this reaction can be easily followed via on-line UV-VIS measurements, compare Figure 3. The maximum intermediate cation concentration (absorbance around 380 nm) was always reached within the first minute after initiator addition under the reaction conditions studied here. This maximum concentration was defined as measure of activity for a first assessment of the information content of the initiator solution IR spectra. For a series of initiator solutions prepared with different water addition protocols, the activity parameter in relation to IR intensities was analyzed. Figure 4 shows that the selected Al-OX band tracks the catalytic activity reasonably well. The considerable scatter is attributed to the limited temporal resolution of the UV measurements in combination with the fast reaction that may prohibit exact detection of the maximum absorbance. Since this result corroborated the potential applicability of IR spectroscopy to the task of initiator quality monitoring, the DPE dimerization reaction was not pursued any further but instead isobutene polymerization was selected as the decisive test reaction.

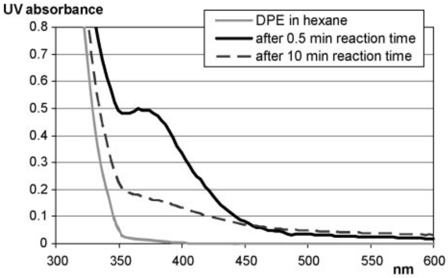

Figure 3.
UV-VIS spectra of diphenylethene in hexane before and after initiator addition. The absorption at about 380 nm is attributed to intermediate cations.

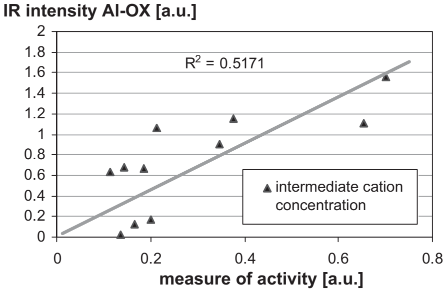

Figure 4.
Intensity of a selected IR band for initiator solutions that produced different cation concentrations under identical reaction conditions.

During a stationary isobutene polymerization with constant feeds and reaction conditions, initiator solutions prepared with different water concentrations were used. Activity in this case was measured by polymer yield relative to amount of initiator used for a fixed reaction time. As in the dimerization example the dominating AlOX band was selected for a first analysis of the relation between IR intensities and activity of the different initiator solutions. The analysis is presented in Figure 5.

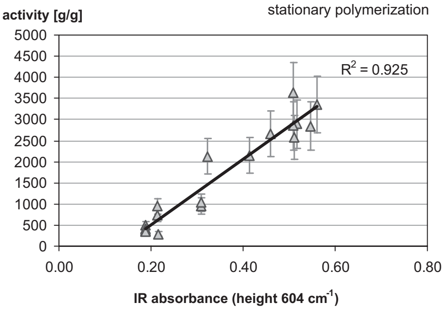

Figure 5.
Isobutene polymerization activity measured as polymer per gram catalyst from a stable continuous polymerization run using a series of initiator solutions prepared with different water concentrations in comparison to the intensity of a selected IR band.

Under these highly controlled reaction conditions, a very good direct correlation of activity with a single IR band (assigned to Al-OX) is obtained. A drawback of this simple correlation is that it neglects information about the concentration of AlCl and AlEt fragments. Initiator solutions may have different total concentrations of soluble species, i.e. different AlCl and AlEt IR signals, at the same Al–OX concentration and such samples are not necessarily expected to have identical catalytic activity.

A comprehensive analysis of the validity of the simple correlation and assessment of alternative IR parameters was based on stationary phases of individual polymerization runs with a larger variety of initiator preparation conditions. On-line IR measurements were used to gather representative data.

On-Line Activity Monitoring

The IR measurement was installed in the initiator solution feed to the polymerization, see Figure 6, using a transmission flow cell. Spectra were acquired every 1 to 5 minutes.

A series of independent polymerization runs with varying initiator solutions was performed in order to determine the relation between IR spectra and polymerization activity. Figure 7 shows that the simple analysis of a single IR band does not correlate well with activity for this extended dataset. The experiments with a larger variety of initiator preparation conditions show a much larger variation in catalytic activity for a given Al–OX IR intensity. In particular, many experiments with acceptable activity have a low Al–OX band whereas other experiments with identical activity fall in the range of highest Al–OX signals. This is a disadvantage for any process control concept based on the IR results because unnecessary measures might be taken because of low signal intensities.

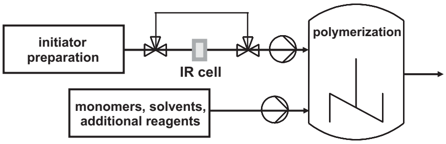

Figure 6.
Schematic of the on-line IR-installation.

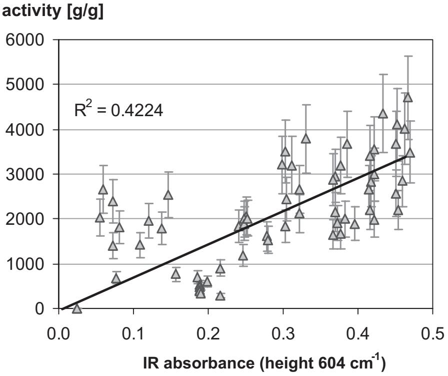

Figure 7.
Analysis of polymerization activity from runs with initiator solutions showing different IR intensities for the selected Al-OX signal.

In order to check the hypothesis that relevant information is contained in the AlCl and AlEt IR spectral ranges, different types of multivariate analysis were tested for the same set of experiments. An improved correlation based on the three selected IR ranges instead of a single band is presented in Figure 8. The optimized, multivariate analysis of the IR spectra takes into account the intensities of AlCl and AlEt bands as well as the selected Al–OX signal. The underlying nature of the improved IR indicator is also illustrated in Figure 8: spectra with identical Al–OX intensities are divided into two groups by taking into account the overall IR intensity thus better differentiating low and high activity experiments. As a confirmation of the correlation between the optimized IR indicator and polymerization activity an experiment with constant polymerization conditions and on-line IR measurements was performed. When a steady state was reached, initiator preparation was changed by increasing the water content in the initiator solution. Conversion calculated based on the IR indicator and on feed rates is compared to the measured conversion. The results presented in Figure 9 show

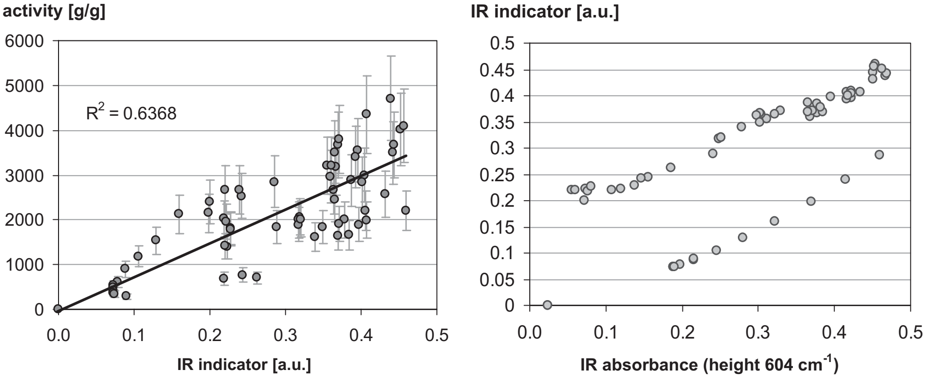

Figure 8.
IR indicator taking into account Al-Et, Al-Cl and Al-OX bands as a function of Al-OX intensity (left) and correlation with polymerization activity (right).

that the calculation tracks the measured data well. Deviations are within the range of scatter also seen in the correlation, Figure 8. The substantial scatter is attributed to poorly controllable parameters like impurities that also significantly influence polymerization activity. Even though variations in the process that are not related to the initiator solution may limit the achievable correlation between IR results and catalytic activity, the results presented so far demonstrate that even without knowing the structure of the active cationic species IR spectroscopy can be employed to differentiate between initiators with different catalytic activities and can thereby contribute to process control. The IR measurement serve as a qualitative tool for troubleshooting to decide whether problems in the polymerization process are related to initiator quality or not. Another implementation is the definition of upper and lower thresholds for the IR indicator and of measures to be taken when the indicator falls below these values, e.g. increase the initiator feed relative to the target feed rate when the indicator goes below the upper threshold and check the initiator preparation process when it goes below the lower threshold. In the case of IR indicator values below the lower threshold a second IR parameter like the Al−OX band intensity or total intensity may be used to decide whether the degree of hydrolysis is above or below the optimum and which changes to the activation procedure to make.

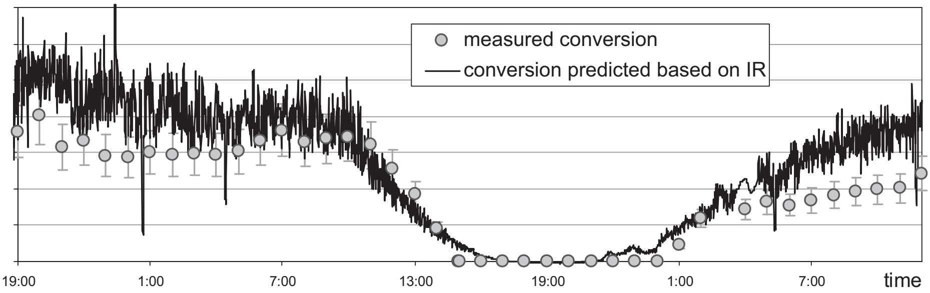

Figure 9.
Comparison of calculated conversion based on IR results for the initiator solution to measured conversion data for a polymerization run with variable initiator composition.

Conclusion

It has been shown that aluminum bound ethyl groups, chlorine and bridging oxygen atoms are essential structures in catalytically active products from the reaction of mixtures of diethyl aluminium chloride and ethyl aluminium dichloride in hexane with water. These structures can be detected via IR in the range from 400 to 700 cm^{-1}. IR spectroscopy can be used to determine a characteristic parameter that links initiator characteristics to catalytic activity. The implementation of this technique as an on-line activity monitoring tool has been demonstrated. Application of the technique for process control is exemplified.

Acknowledgements: Financial funding under BMBF projects #02PO2200 and #02PO2204 is gratefully acknowledged.

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