Functional Olefin Copolymers: Uniform Architectures of Propene/7-Methyl-1,6-octadiene Copolymers by ATR-FTIR Spectroscopy Control of Monomer Composition

Martijn Hackmann and Bernhard Rieger*

Department of Inorganic Chemistry II/Material Science and Catalysis, University of Ulm, D-89069 Ulm, Germany

Received June 25, 1999; Revised Manuscript Received December 30, 1999

ABSTRACT: Propene and 7-methyl-1,6-octadiene (MOD) were copolymerized with the catalyst system *rac*-Et[Ind]$_2$ZrCl$_2$/MAO in semibatch reactions and under constant comonomer concentrations using an autoclave setup that is equipped with an ATR-FTIR sensor coupled with a dosage system for the liquid MOD comonomer. The concentration of the monomer propene is regulated precisely in both types of polymerization by a gas flow controller. This setup enables to monitor the MOD concentration on-line and in real-time during the reaction by following characteristic bands arising from the double bonds. Copolymers with poorly defined incorporation data and thermal properties were obtained without control of the MOD concentration in time. This is caused by a nonuniform distribution of the MOD units over the polymer chains due to a relatively large shift of the MOD concentration during the copolymerization reaction. By means of solvent extraction fractionation experiments, these copolymers could be fractionated into three fractions with different amounts of incorporated MOD, varying from 11.5 to 7.2 mol %. Functional copolymers with uniform architectures (up to 30.5 mol % incorporated MOD) were prepared by using the on-line ATR-FTIR data to control the MOD concentration during the copolymerization reactions.

Introduction

Chiral metallocene dichlorides allow for the first time a precise correlation between catalyst symmetry and microstructure of the polypropene chains, leading to new or at least improved material properties.[1−3] However, only a limited number of polar monomers bearing sterically hindered functionalities can be incorporated in lower molecular weight copolymers, due to the sensitivity of early transition metal complexes to electron-donating functional groups.[4] Controlled copolymerization of ethene or propene with polar olefins such as cheap acrylates, their derivatives, and vinyl ethers to linear copolymers is still a long-standing goal in polyolefin engineering, since copolymers of this type might endow a new generation of materials with remarkably high adhesive, dyeing, and moisture adsorption properties.[5]

Recently, we reported on an intriguing method to prepare copoly(α-olefin)s, of which the tacticity, molecular weight, polarity, and nature of the side functionalities could be easily adjusted.[6,7] In these studies, propene was successfully copolymerized with the linear nonsymmetrically substituted dienes *R*(+)-5,7-dimethyl-1,6-octadiene (isocitronellene) and 7-methyl-1,6-octadiene (MOD). The higher substituted (i.e., more sterically hindered) vinyl groups of these monomers remained untouched by the zirconocene/MAO catalysts in these reactions, excluding the possibility of cross-linking or cyclopolymerization as published for 1,5-hexadiene homo- and copolymerization reactions.[8−10] Derivatization of these untouched vinylene groups resulted in side-functional copoly(α-olefin)s with pendant hydroxy, amine, epoxy, bromine, or perfluorohexyl groups.[6] The polarity of the copoly(α-olefin) backbone could be easily adjusted by controlling the degree of incorporated diene.

In general, linear higher α-olefins copolymerize very well with propene.[11−15] Both the stereochemistry of the main chain and the comonomer content can be controlled by the metallocene structure.[11,13,14] However, attempts to compare the kinetic data of these studies fail, because in none of these so-called *semibatch* copolymerizations was the higher α-olefin concentration controlled. Such uncontrolled conditions led to totally different amounts of incorporated comonomer and thus to differences in the copolymerization parameters as the kinetic data were ruled by the degree of conversion. We recognized that it is of major importance to control both the higher α-olefin and the propene concentration in order to obtain a uniform distribution of the comonomer units over all polymer chains.[6] Large shifts up to 36 mol % of the comonomer feed concentration were namely observed at low overall conversions, causing already microstructural heterogeneity of the copoly(α-olefin) samples.

The present study deals with the regulation of the MOD comonomer in the copolymerization reaction with propene. Kolthammer et al. demonstrated nicely that the metallocene-catalyzed homopolymerization of 1-octene can be monitored on-line with ATR-FTIR spectroscopy by following characteristic bands arising from the 1-octene double bond.[16] Therefore, the control of the MOD comonomer is performed by an autoclave setup, which is equipped with an ATR-FTIR spectrometer coupled with a dosage system for the liquid comonomer and a gas flow controller for propene. This system is able to allow a precise control of the concentrations of the monomers applied, enabling the preparation of functional copoly(α-olefin)s with uniform architectures.

Experimental Section

Materials. Propene (purity ≥ 98.5 vol %) was generously provided by the BASF AG and purified by passing through columns packed with molecular sieve (3−4 Å) and BASF catalyst R3-11 (kindly supplied by BASF AG). 7-Methyl-1,6-

10.1021/ma991014w CCC: $19.00
Published on Web 02/18/2000

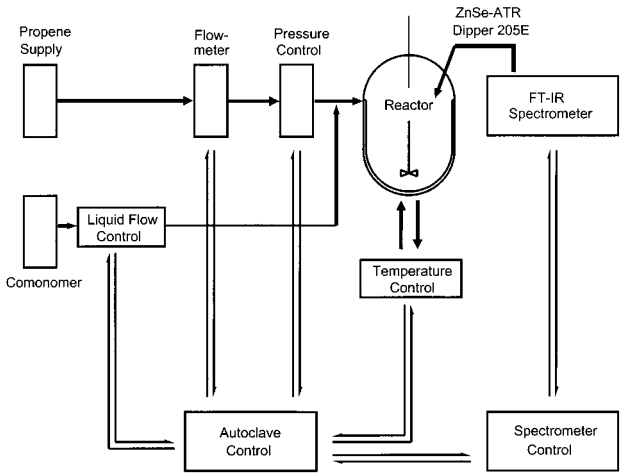

Figure 1. Schematic representation of the developed autoclave setup that is equipped with an ATR-FT-IR spectrometer coupled with a dosage system for the liquid comonomer to control the copolymerization kinetic. The propene concentration is regulated with a gas flow controller.

octadiene, abbreviated as MOD (Aldrich, 98%), was stirred over $LiAlH_4$ for 24 h and distilled under argon prior to use. *rac*-Et[Ind]$_2$ZrCl_2, abbreviated as EBI, was prepared according to published methods.[17] Toluene (Merck, p.A.) was purified by refluxing over $LiAlH_4$ and subsequent distillation under argon. Methanol (technical grade), 2,6-di-*tert*-butyl-4-methylphenol (Merck), and methylaluminoxane (MAO) (Witco GmbH, 10 wt % solution in toluene, 4.73 wt % Al) were used as received.

Polymerization Equipment. The polymerization reactions were performed in a specially developed autoclave setup depicted in Figure 1. A 1 L Büchi steel autoclave was equipped with a DPR-205E deep immersion probe (Axiom Analytical) that was connected to a Fourier transform-infrared (FTIR) spectrometer (Nicolet Impact 410T) in an inboard configuration via Axiot optical conduits and mirror assemblies (32 mm i.d.). A two-reflection conical ZnSe attenuated total reflectance (ATR) crystal (Axiom Analytical) was used at the DPR-205E sensing head tip. The FTIR spectra were recorded using a DTGS KBr detector. The instrumental parameters were a gain setting of 16 at 8 cm^{-1} resolution with a mirror velocity of 0.6329 and 256 scans for each spectrum. The propene concentration was measured by a calibrated gas flow meter (Bronkhorst F-111C-HA-33P), and the pressure was kept constant (±50 mbar) during the entire polymerization period (Bronkhorst pressure controller P-602C-EA-33P).[3,18] The concentration of the liquid comonomer MOD was measured with the described ATR-FTIR spectrometer system and regulated by a calibrated Liqui-Flow controller (Bronkhorst L1C2-FA-33-P), operating at 0.2 bar nitrogen 5.0 overpressure. The polymerization temperature was measured in the reaction solution with a thermocouple and kept constant (±0.2 °C) via a Julabo ATS2 thermostat. The propene pressure, propene consumption, amount of added MOD, and polymerization temperature were controlled by real-time monitoring, one data set taken every second. The EBI solution was injected via a pressure container mounted onto the autoclave and operating at 0.2 bar argon 5.0 overpressure.

A calibration curve with 15 MOD standards that varied from 0.0 to 1.212 mol L^{-1} in toluene was processed with the QuantIR 1.12 program (Nicolet) using the Partial Least Squares (PLS) method.

Method of Polymerization. Prior to every polymerization reaction, the ATR-FTIR crystal was purified with a 10% HCl solution and tested on its intensity with a 0.20 mol L^{-1} MOD solution in toluene. The reactor was purged with argon 5 times and rinsed with 15 mL of MAO at 80 °C for 2 h.

a. Copolymerizations with Control of the MOD Concentration. The autoclave was charged with 710 mL of toluene and 64.2 mL of MAO (0.10 mol of Al). After thermal equilibration of the autoclave system, the appropriate propene pressure was adjusted and a FTIR background spectrum recorded. A 27.3 mL (0.165 mol) aliquot of MOD was injected, and the polymerization was started by adding 10 μmol of EBI. This zirconocene complex was stabilized with the addition of a small amount of MAO (Al/Zr = 100). FTIR spectra were collected every 10 min. The propene and MOD concentrations were controlled as described above. During the polymerization, additional EBI (stabilized with MAO, Al/Zr = 100) was added, since the catalyst was slightly deactivated by the continuous addition of MOD. This resulted in a variation of the overall Al/Zr ratio from 10.000 at the beginning to ±2.000 at the end of each polymerization reaction. The propene consumption was kept below 50 mL min^{-1} in order to achieve optimal control over the MOD concentration, since the regulation of MOD was limited by the low capacity of the Liqui-Flow controller (50 mL/h). The reaction was terminated by carefully transferring the copolymer solution into a beaker containing 2 L of methanol acidified with 10 mL of 37 wt % HCl solution and containing 1 g of 2,6-di-*tert*-butyl-4-methylphenol. The precipitated copolymer was filtered, washed several times with acidified methanol and pure methanol, and dried in a vacuum at 40 °C for 2 days. The waxy or oil-like copolymers were isolated as follows: after decanting the methanol phase, the copolymers were dissolved in *n*-hexane and filtered, followed by rotary evaporation of the *n*-hexane. Finally, the copolymers were dried in a vacuum at 40 °C for 2 days.

b. Copolymerizations without Control of the MOD Concentration. These reactions were performed as described for the controlled copolymerizations with the following changes: EBI (stabilized with MAO, Al/Zr = 100) was injected only initially, and the amount was varied from run to run in order to keep the rate of polymerization below 100 mL min^{-1} propene consumption. The overall Al/Zr ratio was 2000.

NMR characterization[19] of the copolymers: ^{1}H NMR ($CDCl_3$): δ = 0.60−1.80 (m, CH, CH_2, CH_3, backbone and aliphatic H), 1.94 (m, 2H, $-CH_2-CH{=}C-$), 5.12 ppm (t, 1H, $-CH = C(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ = 17.69 + 25.69 (2C, $-CH{=}C(CH_3)_2$, 19.5−21.5 (m, 1C, $-CH_2-CH(CH_3)-$), 27.02−46.50 (7C, *C*H and *C*H_2 aliphatic), 125.08 (1C, $-CH{=}C(CH_3)_2$), 131.02 (1C, $-CH{=}C(CH_3)_2$).

Copolymer Characterization. Solution ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 323 K using a Bruker AMX-500 spectrometer with a dual probe operating at 500.1 and 125.8 MHz, respectively. Chemical shifts are referenced with respect to TMS. The amount of incorporated MOD (in mole percent) was calculated from ^{1}H NMR using the relative intensities of the peaks at 5.12 and 0.6−2.1 ppm. Molecular weights and molecular weight distributions were obtained from gel permeation chromatography (GPC) operating at room temperature. The setup consisted of Waters μ-Styragel columns with pore sizes of 10^5, 10^4, 10^3, and 500 Å and a guard column. Sample detection was performed by a Waters 410 differential refractometer and a parallel connected Viscotek H502B differential viscometer, allowing absolute molecular weight determination and universal calibration. THF was used as the eluent, and the setup was calibrated with monodisperse polystyrene standards. Glass and melt transition temperatures were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7. Heating and cooling rates typically were 10 and 5 °C/min, respectively, with samples weighting 5−10 mg. The data of the second heating curve are reported.

Results and Discussion

Polymerization Technique. The autoclave setup depicted in Figure 1 was developed to monitor and control the MOD concentration on-line during the copolymerization reactions. The progress of these reactions was followed by quantification of the CH_2 out-of-plane bend of MOD at 910 cm^{-1} as no other bands interfered in this region. The contribution of the CH_2 out-of-plane bend of propene at 910 cm^{-1} was included in the background spectrum. The peak was quantified

Table 1. Copolymerizations of Propene with 7-Methyl-1,6-octadiene (MOD) at 30 and 60 °C without Control of the MOD Concentration[a]

run no.	T_p[b] (°C)	EBI[c] (μmol)	propene (mol L^{-1})	MOD feed[d] (mol %)	MOD copolym[e] (mol %)	yield (g)	act[f] $\times 10^{-4}$
1	30	4	3.80	5.1	2.0	16.5	289.3
2	30	16	1.90	10.1	8.8	14.1	20.3
3	30	30	0.85	20.1	9.2	20.2	76.3
4	30	50	0.55	28.2	11.1	15.0	18.9
5	60	3	2.55	5.0	2.4	13.4	999.2
6	60	10	1.90	10.0	7.4	28.5	127.9
7	60	20	0.85	20.5	9.1	15.3	260.8
8	60	23	0.55	28.2	9.1	19.4	44.2

[a] Copolymerizations were carried out with a molar ratio Al/Zr of 2000 in toluene and with a concentration of MOD of 0.21 mol L^{-1}. [b] Polymerization temperature. [c] *rac*-Et[Ind]$_2$ZrCl$_2$. [d] Initial concentration of MOD (relative to the total concentration of both monomers) in the feed. [e] Amount of MOD incorporated in copolymer determined by ^{1}H NMR analysis. [f] Activity in {g of copolymer/(mol of EBI·h·[mol L^{-1} of total monomer concentration])}.

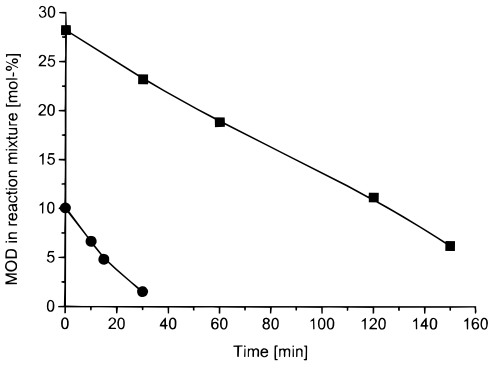

Figure 2. On-line monitoring of semibatch propene/MOD copolymerizations at 60 °C with 10.0 and 28.2 mol % MOD in the feed initially (runs 6 (●) and 8 (■), respectively).

from a baseline drawn between 928 and 891 cm^{-1} using a partial least-squares calibration method. All polymers stayed in solution during the reactions, which were performed until low to moderate yields to prevent changes in the monomer concentrations caused by diffusion c.q. viscosity problems. It turned out that the applied polymerization conditions did not influence the ATR-FTIR crystal's intensity, enabling direct quantification of the on-line recorded FTIR spectra. The ATR-FTIR measurements were correct by ±10% according to test experiments.

Copolymerizations without Control of the MOD Concentration. First, copolymerizations of propene and MOD were performed in a semibatch process, in which the propene concentration was kept constant during the reaction via a gas flow controller and that of the liquid comonomer MOD was adjusted only initially. The concentration of MOD was set at 0.21 mol L^{-1} in all copolymerization experiments, and the propene concentration was varied in different runs in order to change the propene to MOD ratio. The results of these semibatch copolymerizations are summarized in Table 1 and Figures 2 and 3. Figure 2 shows two curves that contain the on-line ATR-FTIR measurements of performed propene/MOD copolymerizations at 60 °C with 10.0 and 28.2 mol % MOD in the feed initially (runs 6 and 8, respectively). These measurements clearly show that the comonomer MOD is rapidly consumed during the copolymerization reactions. In the case of run 6, the concentration of MOD in the reaction

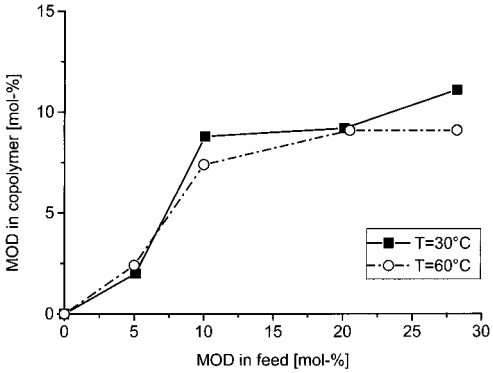

Figure 3. Amount of MOD in the feed versus the level of incorporated MOD in the copolymer at 30 °C (■) and 60 °C (○) without control of the MOD concentration during the propene/MOD copolymerizations.

mixture even dropped below the detection limit (~2 mol % MOD) of the ATR-FTIR spectrometer after 30 min. Similar curves were obtained with copolymerizations performed at 30 °C. The rate of MOD consumption is dependent on the rate of the copolymerization reaction. The combination of reaction temperature, amount of catalyst, and concentration of the monomers determines the slope of the curve. The rate of copolymerization, reflected by the activity (see Table 1), is governed by the MOD content in the reaction mixture. Higher MOD contents are believed to result in increased levels of formed metallacyclic complex structures that slow the rate of polymerization.[6,20] Therefore, higher amounts of catalyst were used at higher MOD contents to compensate for this effect. ^{1}H and ^{13}C NMR analysis proved that the vinylene end group of MOD remained untouched during copolymerization, excluding the possibility of cyclopolymerization or cross-linking.[6]

The copolymerization reactions were terminated after a certain degree of conversion, giving yields of approximately 15 g per run. This should lead to relatively comparable changes in the propene to MOD ratios during the reactions and therefore to proportional MOD incorporations in the copolymers. However, this is not depicted by Figure 3 (data from Table 1), wherein the amount of MOD in the feed is plotted against the level of incorporated MOD in the copolymers. Initially, the degree of incorporated MOD in the copolymers goes along with the amount of MOD in the reaction mixture but levels off at a feed mixture of 10 mol % MOD. This leveling off can only be explained in terms of the relatively large shifts of the MOD to propene ratios during the polymerization reactions (see Figure 2). This change becomes larger at higher MOD concentrations in the feed, resulting in the observed incorporation plateau.

Copolymerizations with Control of the MOD Concentration. To control the incorporation of MOD into the propene/MOD copolymer ultimately, the ATR-FTIR spectrometer system was coupled with a dosage system for the liquid MOD comonomer (Figure 1). This enabled continuous addition of MOD, the flow of which varied during the reaction depending on the actual MOD concentration in the reaction mixture. Table 2 summarizes the results on the controlled copolymerization reactions. The same monomer concentrations and polymerization conditions (see Experimental Part) were applied as the runs from Table 1, making the copolymerization data of both fully comparable. The data on the copolymerization activities have limited meaning,

Table 2. Controlled Copolymerizations of Propene with 7-Methyl-1,6-octadiene (MOD) at 30 and 60 °C[a]

run no.	T_p[b] (°C)	propene (mol L^{-1})	MOD feed[c] (mol %)	SD[d] (mol %)	MOD copolym[e] (mol %)	yield (g)	act[f] $\times 10^{-4}$
9	30	3.80	5.3	*g*	7.9	30.4	32.6
10	30	1.90	9.9	1.1	12.9	12.1	7.1
11	30	0.85	19.4	1.7	21.1	5.1	1.5
12	30	0.50	29.2	3.4	30.5	2.7	0.8
13	60	2.55	5.1	*g*	5.9	27.1	126.2
14	60	1.90	9.8	0.8	12.1	11.3	5.2
15	60	0.85	21.2	2.7	24.0	14.1	6.5
16	60	0.50	32.0	2.0	28.6	6.3	3.8

[a] Copolymerizations were carried out in toluene with a concentration of MOD of 0.21 mol L^{-1}. [b] Polymerization temperature. [c] Mean concentration of MOD (relative to the total concentration of both monomers) during polymerization as determined by linear regression of the data points obtained by ATR-FTIR spectroscopy. [d] Standard deviation of the concentration of MOD during the polymerization. [e] Amount of MOD incorporated in copolymer determined by ^{1}H NMR analysis. [f] Activity in {g of copolymer/(mol of EBI·h·[mol L^{-1} of total monomer concentration])}. [g] Could not be detected precisely by ATR-FTIR spectroscopy due to low concentration of MOD.

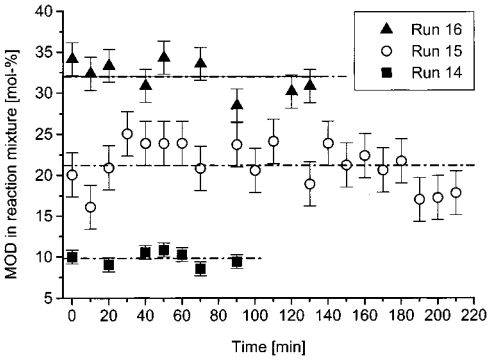

Figure 4. On-line control of the MOD concentration in time during the copolymerization with propene performed at 60 °C. The dotted lines are the mean values of each run, and the error bars represent the standard deviation of each data point, both of which were determined via linear regression of the ATR-FTIR data points.

as the amount of EBI, on which the activities are calculated, was added gradually over the whole polymerization period. In Figure 4, the ATR-FTIR data points of three runs (runs 14−16) are presented in which the MOD concentration was controlled during the reaction. The dotted lines drawn in Figure 4 are the mean values of each run, and the error bars represent the standard deviation of each data point. Both of them were determined via linear regression of the ATR-FTIR data points and are included in Table 2. These results show that the MOD concentration could be successfully controlled within ±12% accuracy or less by use of the developed autoclave setup. The data concerning the incorporated MOD contents in the copolymers are estimated to be correct by ±25%, considering cumulated errors in both the monomer concentrations and polymerization conditions and handling as well as in the ^{1}H NMR data. The dependence of the degree of incorporated MOD in the copolymer as a function of the concentration of MOD in the reaction mixture is plotted in Figure 5. The difference between control and no control of the MOD concentration in time is evident by comparing Figures 3 and 5. If the error limits in both plots are included, nothing changes to the difference between the incorporation proceedings between them. With control of the MOD concentration, the amount of

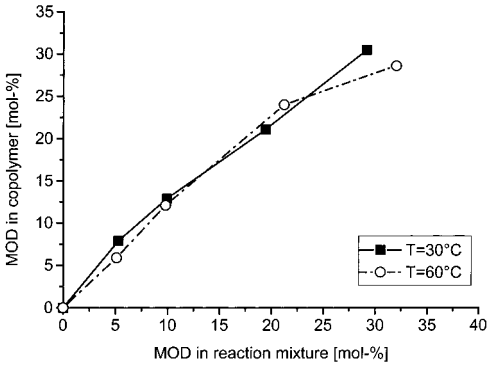

Figure 5. Amount of MOD in the feed versus the level of incorporated MOD in the copolymer at 30 °C (■) and 60 °C (○) with on-line control of the MOD concentration during the copolymerization reactions.

MOD in the feed equals approximately the degree of MOD incorporated in the copolymer. The leveling off at a feed mixture of 10 mol % MOD is not observed anymore. Further it appeared that the MOD incorporation is independent of the polymerization temperature.

The equal incorporation of MOD compared to the feed composition can be understood considering other investigations on copolymerization experiments with higher, liquid α-olefins. Recently, nearly equal incorporation data compared to the monomer feed ratio were reported for 1,5-hexadiene/propene and 1,7-octadiene/propene copolymerizations by Shiono et al. using specific metallocene catalysts.[10] Similar results were found in copolymerizations of propene and several higher α-olefins.[6,12] However, as no control of the comonomer concentrations during the copolymerization reactions was performed in these studies, the most equal incorporation values compared to the feedstock compositions were obtained at negligible overall conversions and at high comonomer-to-propene ratios, implicating almost equal comonomer concentrations during the copolymerization reactions. Thus, the equality between feed and copolymer compositions can be explained from the fact that in our study control of both monomer concentrations could be achieved during the copolymerization reactions for the first time.

The reactivity ratios were determined according to the method of Kelen−Tüdos,[21] delivering the following values: $r_1 = 0.71$ and $r_2 = 0.24$ (30 °C); $r_1 = 0.83$ and $r_2 = 0.39$ (60 °C). This means that propene is preferably inserted after a MOD unit and that the insertion after a propene unit is more or less of random nature. This is consistent with the ^{13}C NMR observations of mainly isolated MOD units in the copolymers.[22]

The properties of the copolymers prepared without control of the MOD concentrations are displayed in Table 3 and those of the controlled ones in Table 4. GPC analysis showed an increase of the weight-average molecular weights ($\bar{M}_w$) as the polymerization temperature decreased for both polymerization types, which was also found for propene/isocitronellene copolymers and propene homopolymers.[6,23] Considering the weight-average molecular weights ($\bar{M}_w$) determined by universal calibration of the tailor-made copolymers, there is a clear trend toward lower molecular weights as the incorporation of MOD in the copolymer increases. As in other α-olefin copolymerization studies, this tendency is distorted in the case of the copolymers prepared without control of the comonomer concentration.[10,12,15]

The microstructural heterogeneity of the copolymers prepared under uncontrolled conditions is clearly dem-

Table 3. Characterization of Copolymers Prepared without Control of the MOD Concentration

run no.	$\bar{M}_w \times 10^{-3}$ [a] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$ [a]	$\bar{M}_w \times 10^{-3}$ [b] (g mol^{-1})	T_g [c] (°C)	$T_{m,peak}$ [c] (°C)	ΔH_m [c] (J g^{-1})	phys app [d]
1	41.8	2.6	n.d.[e]	−14.8	119.9	58.9	powder
2	28.5	1.8	18.8	−21.5	71.2	16.1	powder
3	26.6	1.8	12.0	−25.2	71.6	18.5	powder
4	19.0	1.8	17.8	−31.3	60.3	16.2	fluffy
5	26.7	1.9	13.3	−13.7	106.9	46.1	powder
6	14.4	1.8	11.5	−27.9	67.4	15.7	powder
7	12.3	1.8	7.7	−32.7	59.8	13.3	wax
8	10.9	1.8	9.2	−32.9	51.7	6.0	wax

[a] Determined by GPC, polystyrene calibration. [b] Determined by GPC, universal calibration. [c] Measured by differential scanning calorimetry. [d] Physical appearance. [e] Not determined.

Table 4. Characterization of Tailor-Made Copolymers through ATR-FT-IR Spectroscopy

run no.	$\bar{M}_w \times 10^{-3}$ [a] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$ [a]	$\bar{M}_w \times 10^{-3}$ [b] (g mol^{-1})	T_g [c] (°C)	$T_{m,peak}$ [c] (°C)	ΔH_m [c] (J g^{-1})	phys app [d]
9	38.1	2.2	19.6	-18.9	91.4	25.8	powder
10	22.0	1.9	18.0	-29.1	59.6	9.7	fluffy
11	13.3	1.8	9.7	-44.7	n.o.[f]		wax
12	9.1	1.6	7.8	-47.4	n.o.[f]		oil/wax
13	16.1	1.9	n.d.[e]	-21.3	84.6	30.1	powder
14	10.7	1.8	9.1	-40.0	55.1	1.7	wax
15	7.8	1.8	6.7	-52.1	n.o.[f]		oil/wax
16	4.5	1.6	3.5	-54.0	n.o.[f]		oil

[a] Determined by GPC, polystyrene calibration. [b] Determined by GPC, universal calibration. [c] Measured by differential scanning calorimetry. [d] Physical appearance. [e] Not determined. [f] Not observed.

onstrated by their thermal properties. These show a negative response on the level of incorporated MOD. In general, both the glass transitions and the melt transition temperatures lower as more MOD is incorporated in the copolymer. This effect is also expressed by the melt transition enthalpy (ΔH_m), which is a measure for the degree of crystallinity of the copolymers. Furthermore, the second heating curves of the copolymers with more than 2.4 mol % MOD are characterized by a recrystallization exotherm below the melt transition, indicating microstructural heterogeneity. It must be noted that all the copolymers from Table 3 do possess a distinct melt transition and degree of crystallinity. The tailor-made copolymers on the other hand also display a negative dependence of the glass transition and melt transition temperatures on the MOD incorporation. However, they lack a melt endotherm above 12.9 mol % incorporated MOD. Furthermore, the degree of crystallinity (expressed by ΔH_m) at MOD contents of ±12 mol % (runs 10 and 14) is much lower than the ones prepared under uncontrolled conditions at comparable melt transition temperatures (runs 4, and 7 and 8, respectively). These differences in thermal behavior between copolymers prepared under controlled and uncontrolled reaction conditions can be explained from the differences in distribution of the 2-methyl-2-hexadiene side chains over the copolymer backbones. These side chains diminish the ability of the copolymers to crystallize, as was published before.[6] It is evident that a uniform distribution of the MOD units over the polymer chains prevents crystallization of the polymer in the end if the units are placed within the critical length of isotactic propene segments needed for crystallization.

Further proof of the microstructural heterogeneity of the copolymers prepared under uncontrolled conditions versus the homogeneous architecture of the tailor-made copolymers is provided by solvent extraction fractionation. For these experiments, two copolymers were selected, i.e., runs 7 and 15. Two reasons underlie the selection of these two copolymers in order to compare the fractionation results completely: (a) both had equal MOD concentrations in the feed, at least initially, and (b) both had similar isolated yields. The fractionation solvents were selected on their dielectric constants, going from relatively high (3-pentanone) to low (*n*-pentane) during the solvent extraction fractionation experiments. The results of these experiments are listed in Table 5. Whereas copolymer 15 turned out to be one fraction, copolymer 7 could be fractionated into three copolymer fractions. The average amount of incorporated MOD in the three fractions decreased from 11.5 mol % (3-pentanone) to 7.6 mol % (dichloromethane) to 7.2 mol % (*n*-pentane).

Table 5. Solvent Extraction Fractionation[a]

	3-pentanone fraction		dichloromethane fraction		*n*-pentane fraction	
run no.	yield (wt %)	MOD[b] (mol %)	yield (wt %)	MOD[b] (mol %)	yield (wt %)	MOD[b] (mol %)
7	50	11.5	37	7.6	13	7.2
15	100	24.0				

[a] Solvent extraction fractionation was carried out with 2 g of each copolymer during 4 h of extraction with 100 mL of each solvent at room temperature. [b] Amount of MOD incorporated in copolymer determined by ^{1}H NMR analysis.

Conclusions

The present study clearly demonstrates that the concentration of the comonomer 7-methyl-1,6-octadiene drops down rapidly in copolymerizations with propene. This leads to a nonuniform distribution of the MOD comonomer units over the polymer chains and to changes in the copolymerization kinetics during the reaction. As a result, the copolymers are characterized by microstructural heterogeneity, which was proved by thermal analysis and solvent extraction fractionation experiments. Control of the MOD concentration in time via ATR-FTIR spectroscopy leads to copolymers with uniform architectures. How far our findings on in-situ monomer control are relevant for the structure−property relationship of ethene/octene or other copoly-

mers will be a subject for further studies. It will be interesting to see whether differences in the polymer microstructures of such polymers influence their compatibilization behavior in polymer blends.

Acknowledgment. Generous financial support by the European Community for providing a scholarship under the TMR program and the DFG (SFB 239, project F10) is gratefully acknowledged. Furthermore, thanks are returned to BASF AG for supplying propene and the BASF catalyst R3-11.

References and Notes

(1) Hackmann, M.; Rieger, B. *Cattech* **1997**, *2*, 79−92.
(2) Voegele, J.; Dietrich, U.; Hackmann, M.; Rieger, B. In *Metallocene-Based Catalysts*; Scheirs, J., Kaminsky, W., Eds.; J. Wiley & Sons Ltd.: Berlin, 2000; Chapter 22, pp 485−512.
(3) Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelä, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348−4355.
(4) a) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679−9680. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (c) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455−1457.
(5) Recently, nickel- and palladium(II)-based catalysts were found to be capable of copolymerizing ethene with readily available acrylic monomers to branched, high molecular weight products. (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267−268. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888−899. (c) Schubbe, R.; Angermund, K.; Fink, G.; Goddard, R. *Macromol. Chem. Phys.* **1995**, *196*, 467−478. (d) Möhring, V. V. M.; Fink, G. *Angew. Chem.* **1985**, *97*, 982−984. However, up to now there are no suitable late transition metal complexes that would allow to tailor the properties of linear, functional poly(α-olefins) by a combination of stereoregularity and content of a polar comonomer.
(6) (a) Hackmann, M.; Repo, T.; Jany, G.; Rieger, B. *Macromol. Chem. Phys.* **1998**, *199*, 1511−1517. (b) Hackmann, M.; Feifel, T.; Rieger, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater.: Sci. Eng. Chem.)* **1999**, *80*, 143−144.
(7) Rieger, B.; Hackmann, M.; Dietrich, U. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater.: Sci. Eng. Chem.)* **1999**, *80*, 51−52.
(8) (a) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953−4954. (b) Coates, G.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91−98. (c) Cavallo, L.; Guerra, G.; Corradini, P.; Resconi, L.; Waymouth, R. M. *Macromolecules* **1993**, *26*, 260−267.
(9) Kaminsky, W.; Drögemüller, H. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 89−94.
(10) Naga, N.; Shiono, T.; Ikeda, T. *Macromolecules* **1999**, *32*, 1348−1355.
(11) Uozumi, T.; Soga, K. *Makromol. Chem.* **1992**, *193*, 823−831.
(12) Arnold, M.; Henschke, O.; Knorr, J. *Macromol. Chem. Phys.* **1996**, *197*, 563−573.
(13) Schneider, M. J.; Mülhaupt, R. *Macromol. Chem. Phys.* **1997**, *198*, 1121−1129.
(14) Forlini, F.; Fan, Z.-Q.; Tritti, I.; Locatelli, P.; Sacchi, M. C. *Macromol. Chem. Phys.* **1997**, *198*, 2397−2408.
(15) Kim, I.; Kim, Y. J. *Polym. Bull.* **1998**, *40*, 415−421.
(16) Kolthammer, B. W. S.; Mangold, D. J.; Gifford, D. R. *J. Polym. Sci., Polym. Chem.* **1992**, *A30*, 1017−1026.
(17) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63−67.
(18) For an appropriate equation of state for the system toluene/propene, see e.g.: Plöcker, U.; Knapp, H.; Pausnitz, J. *Ind. Eng. Chem. Process Des. Rev.* **1978**, *17* (3), 324.
(19) The signals in the NMR spectra were assigned according to the ^{1}H and ^{13}C NMR spectra of the propene−(*R*(+)-5,7-dimethyl-1,6-octadiene) copolymer published in ref 6a. The interpretation of the ^{13}C NMR spectra was supported by ^{13}C DEPT NMR spectra and theoretical calculations.
(20) Yu, Z.; Marques, M.; Rausch, M. D.; Chien, J. C. W. *J. Polym. Sci., Polym. Chem.* **1995**, *A33*, 979−987.
(21) Kelen, T.; Tüdos, F. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1−27.
(22) The intensity of the ^{13}C NMR signals of main chain CH_2 groups from 40 to 47 ppm was used for calculation of the diad sequence distribution according to published methods described in refs 11 and 13. The MOD−MOD diad was observed at 40.1−40.6 ppm, the propene−MOD or MOD−propene diad at 42.5−43.5 ppm, and the propene−propene diad at 45.2−46.5 ppm. The MOD−MOD diad was only observed if the level of incorporated MOD was higher than 13 mol %. The intensity of this MOD−MOD diad was lower by a factor of 4−6 compared to the propene−MOD or MOD−propene diads.
(23) Rieger, B.; Mu, X.; Mallin, D. T.; Rausch, M. D.; Chien, J. C. W. *Macromolecules* **1990**, *23*, 3559−3568.

MA991014W