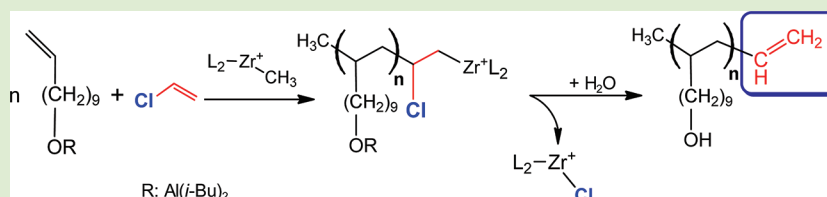


Synthesis of Allyl-Terminated Polar Macromonomers by Metallocene-Catalyzed Polymerizations of 10-Undecene-1-ol

Matthias Johannsen, Ulrich Schulze,* Karin Sahre, Hartmut Komber, and Brigitte Voit

Leibniz-Institut für Polymerforschung Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

S Supporting Information



ABSTRACT: Poly(10-undecene-1-ol) macromonomers were synthesized by metallocene-catalyzed polymerization using vinyl chloride as a chain transfer agent. Using this technique, predominantly allyl terminated polymers could be obtained, which was verified by NMR spectroscopy and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS). By means of the mass spectra, a detailed interpretation of the nature of the head and end groups of these polymers was possible.

Macromonomers are excellent precursors for the direct synthesis of graft copolymers. The strength of the macromonomer technique holds the possibility to synthesize such graft polymers with very well-defined side chains in contrast to grafting from or onto polymer chains. By variation of the molar masses of the macromonomers and the copolymerization conditions, the number and length of the side chains and the length of the backbone may be adjusted.^{1–4} The method also enables the preparation of comb polymers by the homopolymerization of the macromonomers.^{5,6} A widespread overview of this topic is given by Ito^{7,8} and Hadjichristidis et al.⁹

Our special interest is focused on the synthesis of macromonomers with polar groups. Recently, we reported on the synthesis of poly(10-undecene-1-ol) (P(Uol)) as a potential polar macromonomer.¹⁰ However, the achieved double bonds as result of the chain termination reaction were either internal double bonds or terminal vinylidene groups. Here, we first report on the successful synthesis of allyl-terminated P(Uol) macromonomers by controlled chain transfer.

Several research groups have investigated the polymerization behavior of vinyl chloride (VCl) in the insertion polymerization.^{11–16} However, these efforts have been largely unsuccessful due to very fast β -chloride elimination that occurs after 1,2-insertion of the VCl into the metal–polymer bond. Particularly, using metallocene catalysts the chain termination after an 1,2-insertion of VCl is described as inevitable.¹¹

The current paper reports the utilization of this effect for the synthesis of P(Uol)s bearing terminal allyl groups. The copolymerizations of Uol with VCl were conducted using the catalysts *rac*-Et[Ind]₂ZrCl₂ (Et-Ind₂) and *rac*-Me₂Si[2-Me-4,5-Benz Ind]₂ZrCl₂ (MBI) both activated by methylaluminoxane

(MAO). The results of the syntheses are summarized in Table 1.

Table 1. P(Uol)s Synthesized by Copolymerization of Uol and VCl in Dependence on T_{pol}^a

sample	catalyst	p_{VCl} (bar)	T_{pol} (°C)	relative yield ^b (%)	\bar{M}_n^c (g/mol)	allyl ^c (%)
P(Uol)1	Et-Ind ₂	0	30	20.4	9300	0
P(Uol)2	Et-Ind ₂	0.3	20	4.3	4900	67
P(Uol)3	Et-Ind ₂	0.3	30	3.3	2650	76
P(Uol)4	Et-Ind ₂	0.3	50	1.6	2150	64
P(Uol)5	Et-Ind ₂	0.6	30	2.2	3250	77
P(Uol)6	MBI	0	30	4.8	8700 ^d	0
P(Uol)7	MBI	0.3	20	4.5	1070	94
P(Uol)8	MBI	0.3	30	5.4	1100	96
P(Uol)9	MBI	0.3	50	5.9	1400	91
P(Uol)10	MBI	0.3	70	11.5	1600	74

^aMonomer concentration (c_{mon}) = 483 mmol/L; $c_{\text{mon}}/c_{\text{catalyst}}$ = 4000; t_{pol} = 120 min; Al_{MAO}/Zr = 1300. ^bRelative yield: calculated in relation to the content of Uol in the feed. ^cEstimated by ¹H NMR spectroscopy. ^dEstimated by SEC.

In the copolymerizations using VCl as a comonomer and Et-Ind₂ as the catalyst, the relative polymer yields are reduced compared to the polymerizations without VCl. It is probably that the reduction of the yield is caused by a loss of catalyst activity due to the formation of the metal chloride catalyst species formed by the β -chloride eliminations and its

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subsequent reactivation by aluminum alkyls as discussed by Gaynor¹⁴ for the copolymerization of ethylene with VCl. On the contrary, in the copolymerization with VCl using MBI as a catalyst, a reduction of the relative polymer yield compared to the reference sample was not observed. It is assumed that when using MBI the catalyst deactivation by β -chloride elimination is less pronounced compared to that in the case of Et[Ind]₂ZrCl₂.

As shown in Table 1, the relative polymer yields obtained with the MBI/VCl and Et-Ind₂/VCl are in a comparable range. However, depending on the catalyst, the content of allyl end groups in the polymers is different, about 90% with MBI/VCl but only 60–70% with Et-Ind₂/VCl. From the propene polymerization it is known that the catalyst Et-Ind₂ produces polymers with molar masses, which are about 1 order of magnitude lower than the molar masses of polymers synthesized using MBI due to a higher ratio of chain terminations to chain propagation reactions for Et-Ind₂ than for MBI. In this context, the catalyst activity of MBI is nearly twice as high compared to that of Et-Ind₂.^{17,18} The results of the homopolymerization of Uol without VCl show also that higher molar masses are achieved with MBI than with Et-Ind₂ (see Table 1). In contrast, the catalytic activity of Et-Ind₂ is increased compared to that of MBI affording higher polymer yields. This effect is attributed to a dissimilar steric hindrance of the coordination and insertion of VCl and Uol due to the different sizes of both monomers in interaction with the bulky ligands of MBI. Therefore, it is concluded that a steric hindrance at MBI in comparison to Et-Ind₂ favors the coordination of VCl in contrast to both coordination and insertion of Uol. This results in a higher allyl end group content in MBI catalyzed polymerization. This assumption is supported by the significant lower molar masses of the polymers synthesized with MBI/VCl in comparison to those obtained with Et-Ind₂/VCl.

For the polymerizations of Uol with the catalyst Et-Ind₂, decreasing molar masses and nearly constant relative yields are observed with increasing polymerization temperature (Table 1 and Supporting Information, Figure S1a). The decreasing molar masses are explained by an increasing ratio of chain transfer reactions to chain propagation steps as known from other olefin polymerizations.^{19,20} This polymerization behavior indicates that catalyst Et-Ind₂ preferentially coordinates Uol rather than VCl since a temperature-induced lower solubility of VCl (chain transfer agent) should lead to higher molar masses. This assumption is also confirmed by the virtually constant content of allyl end groups over the temperature range used. Similar observations are made for the coordination behavior of propylene and VCl by Stockland and Jordan.¹¹

Using MBI, increasing polymerization temperatures cause a substantial rise of the relative yields and a moderate reduction of the content of allyl end group as shown in Table 1 (see also the Supporting Information, Figure S1b). The polymer yields and the contents of allyl end groups run into opposite directions. As well-known from the polymerization of propene, the increase of the relative yield in dependence on the temperature could be explained by an increase of the catalytic activity.^{21–24} However, in this context it is more probable that a reduction of the solubility of VCl in dependence on the temperature is the dominant reason since the content of allyl end groups is also decreased. Furthermore, with rising temperatures an increase of the molar masses is observed.

The end groups of the polymers have been characterized by ¹H NMR spectroscopy. Figure 1 depicts the ¹H NMR spectra

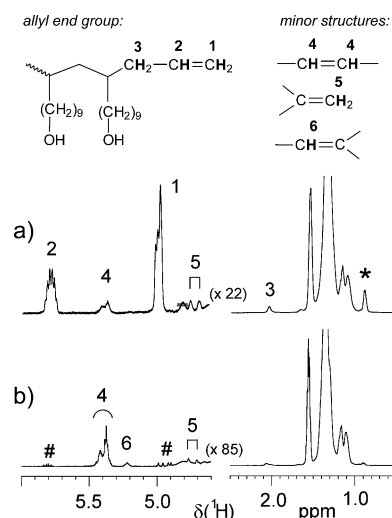


Figure 1. ¹H NMR spectra (solvent: CD₃OD) of two P(Uol) samples synthesized using Et-Ind₂ as a catalyst: (a) terminated with VCl (P(Uol)2) and (b) without VCl (P(Uol)1). Symbol * marks a methyl headgroup signal CH₃–CH(C₉H₁₈OH)–CH₂– (see ref 25). Signals of monomer traces are indicated by #.

of two P(Uol)s polymerized (a) with addition of VCl [P(Uol)2] and (b) without VCl [P(Uol)1].

The ¹H NMR spectra show that the copolymerization with VCl results in two new signals in the olefinic protons' region (H₁, H₂) and one related signal at 2.05 ppm (H₃), which can be surely assigned to an allyl end group (structure III in Scheme 1). The assignment is also confirmed by ¹³C NMR spectroscopy (Figure S2, Supporting Information). This allyl group results from the expected β -chloride elimination as the termination reaction as shown in Scheme 1. A significant percentage of internal vinylene double bonds (signals at 5.3 to 5.5 ppm) is the result of β -hydride elimination after 2,1-insertion of the Uol. Furthermore, traces of vinylidene end groups are observed indicated by the weak signals at about 4.70 and 4.77 ppm (structure IV in Scheme 1). They are caused by the well-known β -hydride elimination after 1,2-insertion of the Uol. The spectra indicate that P(Uol) macromonomers with allyl end groups could be synthesized.

To confirm the results from NMR spectroscopy selected samples were also analyzed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS; for conditions of measurements see the Supporting Information). In the mass spectrum of P(Uol)5 at least six distributions of molar masses are proved. In Figure 2a this mass spectrum is shown in the region from 2050 to 2500 Da, and additionally a more expanded region is given in Figure 2b. The complete mass spectrum of P(Uol)5 is represented in the Supporting Information as Figure S3 and the mass spectra of P(Uol)2 as Figure S4. The peak positions correspond to the multiples of the monomer repeating unit of 170.29 g/mol \times *n* (*n* polymerization degree) with methyl, isobutyl, or hydrogen head groups (see ref 25 for information about the formation of the isobutyl groups) and allyl (All) and vinylidene (Vd) end groups. In Table 2 the corresponding assignments of the molar masses to the chemical structures at polymerization degrees *n* = 11 and 12 are summarized and compared with the calculated molar masses. Furthermore, the determined peak distances shown in Table 3 confirm the several combinations of the head and end groups.

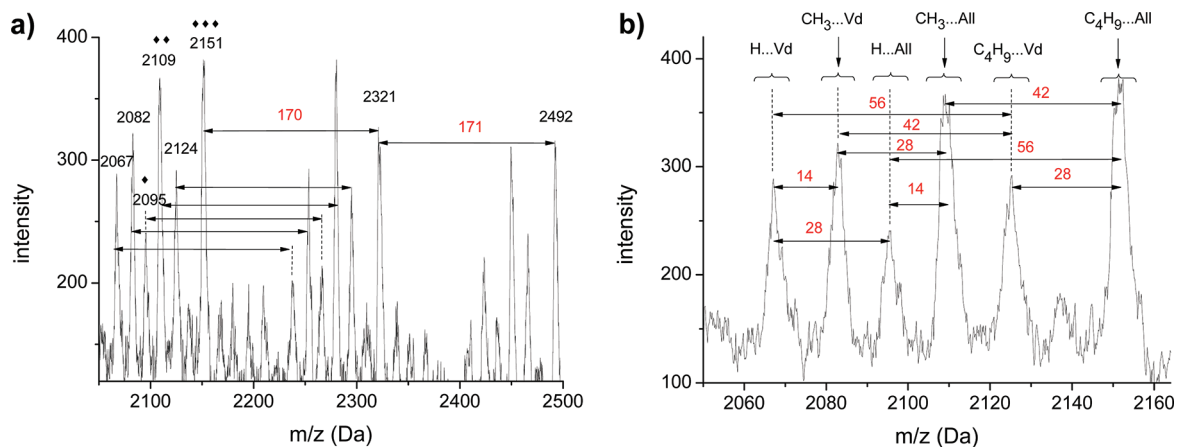
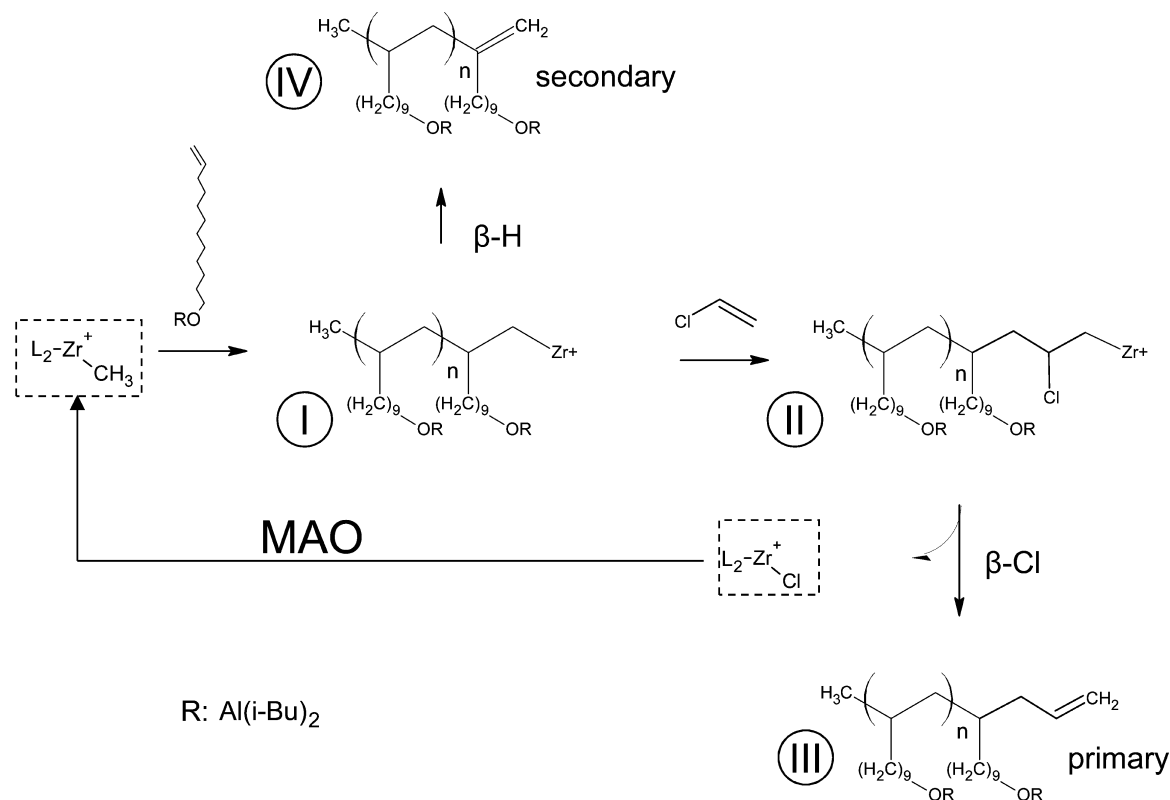
Scheme 1. Proposed Reaction Scheme of the Copolymerization of Uol with VCl Based on the Model of Stockland et al.¹²

Figure 2. Mass spectra of P(Uol)S (a) in the region from 2050 to 2500 Da and (b) expanded spectrum of P(Uol)S with the assignment of the head and end group combinations (see also Table 2); ♦, ♦♦, ♦♦♦ assignments of the peaks see Table 2.

In the mass spectra the shift in peak positions between the calculated and the measured molar masses of the chemical structure amounts not more than 1.5 Da (see Table 2). The ratios of the intensities of the mass peaks could provide information on the proportion of the different head groups. For example, it seems that in both samples the polymer chains with allyl end groups and isobutyl head groups and as well with methyl head groups are preferably formed. As expected, no poly(vinyl chloride) was detected for all samples due to the inevitable β -chloride elimination.

Arisen from the results of NMR spectroscopy and MALDI-TOF-MS, a pathway shown in Scheme 1 is postulated based on Stockland et al.¹² After the start of the polymerization, the chain propagation (I) by the insertion of Uol units proceeds. Coordinating with the central atom of the catalyst, VCl is also

inserted into the chain. The insertion results in a transition metal-alkyl complex (II) with a chloride group in the β -position. Such metal complexes are unstable and susceptible to β -chloride elimination. For this reason, a chain transfer reaction is inevitable, and an allyl-terminated polymer chain is generated (III). This pathway is the primary one. As secondary one, the β -hydride elimination after 1,2-insertions of the Uol takes place and causes the termination of the growing P(Uol) chain before the insertion of a VCl unit resulting in vinylidene end groups (IV).

It is proposed that the catalyst species resulting from the β -Cl elimination can be reactivated by MAO. This assumption is confirmed by the MALDI results showing that approximately half of the allyl terminated chains have methyl head groups. This is due to polymer chains that have been started after the

Table 2. Assignments of the Measured and the Calculated Molar Masses of the Sample P(Uol)S at Polymerization Degrees $n = 11, 12$

peak calculated (Da)	peak measured (Da)	assignment ^a
2094.48	2095, ◆	$n(12) \times 170.29 + \text{All} (27) + \text{H} (1) + \text{Na}^+ (23)$
2108.48	2109, ◆◆	$n(12) \times 170.29 + \text{All} (27) + \text{CH}_3 (15) + \text{Na}^+ (23)$
2150.48	2151, ◆◆◆	$n(12) \times 170.29 + \text{All} (27) + \text{C}_4\text{H}_9 (57) + \text{Na}^+ (23)$
2066.48	2067	$n(11) \times 170.29 + \text{Vd} (169.29) + \text{H} (1) + \text{Na}^+ (23)$
2080.48	2082	$n(11) \times 170.29 + \text{Vd} (169.29) + \text{CH}_3 (15) + \text{Na}^+ (23)$
2122.48	2124	$n(11) \times 170.29 + \text{Vd} (169.29) + \text{C}_4\text{H}_9 (57) + \text{Na}^+ (23)$

^aBold font indicates head and end group combinations.

Table 3. Determined Peak Distances of the Several Combinations of Head and End Groups

assignment head...end group	peak distance (Da)	assignment head...end group
(H...Vd)	14	(CH ₃ ...Vd)
(H...All)		(CH ₃ ...All)
(H...Vd)	28	(H...All)
(CH ₃ ...Vd)		(CH ₃ ...All)
(C ₄ H ₉ ...Vd)		(C ₄ H ₉ ...All)
(CH ₃ ...All)	42	(C ₄ H ₉ ...All)
(CH ₃ ...Vd)		(C ₄ H ₉ ...Vd)
(H...Vd)	56	(C ₄ H ₉ ...Vd)
(H...All)		(C ₄ H ₉ ...All)

MAO reactivation of the catalyst. Furthermore, the ¹H NMR spectra shown in Figure 1 indicate the reactivation of the catalyst by MAO. In the case of P(Uol)₂, the signal of the methyl groups at about 0.9 ppm is significantly more pronounced in comparison to a polymer synthesized without VCl (P(Uol)₁).

The polymerization of Uol in the presence of VCl is a suitable method for the synthesis of allyl-terminated P(Uol)_s. The molar masses of the synthesized polymers are acceptable for the use as macromonomers. Extended studies to the optimization of the polymerization process to increase the polymer yields are currently under investigation.

■ ASSOCIATED CONTENT

Supporting Information

Supplemental figures and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +49 351 4658 391. Fax: +49 351 4658 565. E-mail address: uschulze@ipfdd.de.

Notes

The authors declare no competing financial interest.

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