

Synthesis of higher, *trans* configured oligomers of diisoalkyloxysubstituted divinylbenzenes (PV-oligomers) via metathesis telomerization of the corresponding lower oligomers

Emma Thorn-Csányi*, Oliver Herzog

Institute of Technical and Macromolecular Chemistry, University of Hamburg, Bundesstr. 45, D-20146 Hamburg, Germany

Abstract

In this contribution the preparation of higher, all *trans* configured oligomers of diisoalkyloxysubstituted divinylbenzenes (PV-oligomers) via metathesis polycondensation of the corresponding low oligomers (telomerization) is described. The main concern was with the selectivity of the telomerization process. In this context two highly active metathesis catalysts were investigated. Two 2,5-disubstituted divinylbenzene trimers (with isopentyloxy resp. isoctyloxy substituents) were used as feed component. The time dependent product distribution was determined by means of MALDI TOF mass spectrometry. Results reveal that the molybdenum complex $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoPh})[\text{OCMe}(\text{CF}_3)_2]_2$ is much better suitable than the ruthenium based catalyst $\text{Ru}(\text{=CHPh})(\text{PCy}_3)[1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-4,5-dihydroimidazol-2-ylidene}]\text{Cl}_2$. With the molybdenum alkylidene complex higher conversions and above all considerably higher average degrees of polymerization were obtained before “side reactions” (splitting of the internal double bonds) occur.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Schrock-type molybdenum alkylidene complex; Grubbs-type ruthenium catalyst; Olefin metathesis; Telomerization; PV oligomers

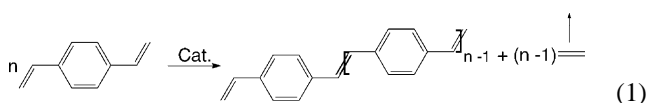
1. Introduction

Oligo- and poly(*p*-phenylene vinylene) (OPV & PPV) as well as their substituted derivatives belong to the polyconjugated substrates with valuable opto-electronic properties [1]. As a consequence, many research groups are working on the preparation of highly regular products.

Our interest is focussed on the direct synthesis of PPV based on olefin metathesis. In general, there exist two ways for metathesis chain growth process; ring opening metathesis polymerization of a cyclic olefin (ROMP) and metathesis polycondensation of an acyclic diene (ADMET). Results of our investigations reveal that regarding synthesis of all *trans* configured PPV products the metathesis polycondensation method is suitable only [2–5].

Using 2,5-disubstituted *p*-divinylbenzenes and the highly active Schrock-type molybdenum alkylidene complex $\text{Mo}(\text{NPh}^{\text{Me}_2})(\text{neoPh})[\text{OCMe}(\text{CF}_3)_2]_2$ [6,7] easily process-

able all-*trans* configured PV-oligomers (Eq. (1)) with defect-free structure were obtained [8–11].



They can serve as model-compounds for the corresponding polymers (esp. in the monodisperse form) [12,13] and as active materials in electronic devices, like organic light emitting diodes (OLEDs) [14].

In our former works, the monodisperse oligomers were isolated from the metathesis polycondensation mixtures. By varying the solvent we obtained products with different average degree of polymerization. The lower oligomers were isolated from these mixtures using conventional organic separation techniques [11,15]. This method fails if higher degrees of polymerization and higher amounts of monodisperse oligomers are desired, thus a new strategy was needed.

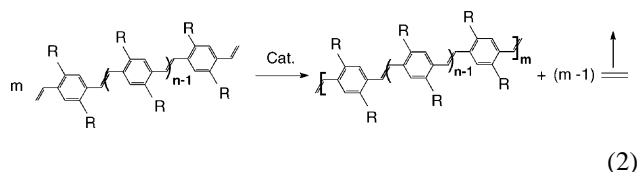
Our new method to obtain all *trans* configured monodisperse oligomers consists of two different synthesis stages:

- The step-wise formation of lower oligomers via organic coupling-reactions (incl. the double bond isomerization) [16–19] and

* Corresponding author. Tel.: +49-40-42838-3166; fax: +49-40-42838-6008.

E-mail address: thorn@uni-hamburg.de (E. Thorn-Csányi).

- their metathesis polycondensation (telomerization) to higher oligomers (Eq. (2)) [16–18] (in [16] 1-propenyl instead of vinyl end groups).



Starting from an oligomer the telomerization leads to products, which differ from each other by several repeat units and can be more easily separated than homologous product mixtures obtained by monomer polycondensation. Using a trimer for example ($n = 2s$, Eq. (2)) only oligomers with a degree of polymerization which is a multiple of three will be present, like hexamer, nonamer, dodecamer etc.

If the telomerization is highly selective, only the terminal double bonds may be splitted. Consequently, a catalyst is required whose activity is several orders of magnitude higher towards terminal vs. internal double bonds.

In this contribution we present results obtained employing two highly active catalysts, a Schrock-type molybdenum complex (with the 2,6-dimethyl phenylimido ligand) [6,7] and the Grubbs-ruthenium-catalyst of the second generation [20]. Two 2,5-diisalkoxyxysubstituted PV trimers were chosen as metathesis substrates.

2. Results

The structure of the 2,5-disubstituted PV trimers investigated is demonstrated in Scheme 1.

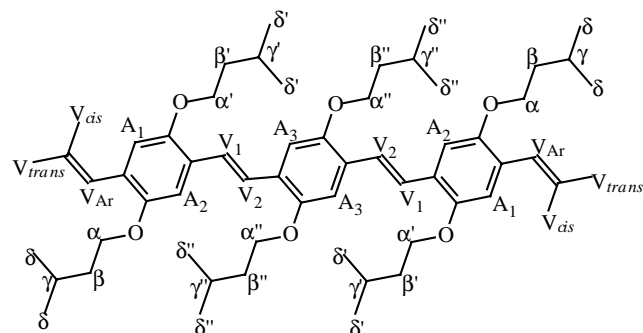
The substituents were 2-ethylhexyl-oxy (2-AHO) or 3-methylbutyl-oxy (3-MBO) chains, respectively.

In Figs. 1 and 2 the ^1H NMR spectra and in Tables 1 and 2 the assignment of the ^1H NMR-signals are presented (the method of synthesis, based on Wittig-route, will be published elsewhere). The results of product characterization (additionally, ^{13}C NMR, IR and MALDI TOF MS investigations were carried out [17]) prove the monodispersity, the defect-free structure and the all-*trans* configuration.

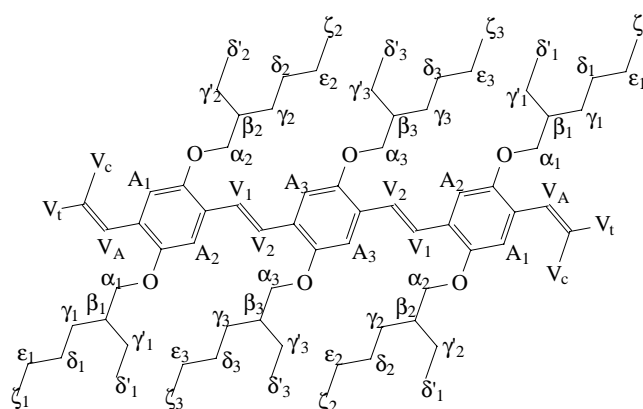
Table 1

^1H NMR chemical shifts for *trans*, *trans* configured 2,5-bis[(3-methylbutyl)oxy]-PV trimer in CDCl_3

Proton	δ [ppm] and J (Hz)
δ -Methyl	0.991, 1.001 and 1.009, each d , $^3J(6.6)$
β -Methylene	1.70–1.80 m
γ -Methine	1.82–2.00 m
α -Methylene	4.042, 4.049 and 4.082, each t , $^3J(6.6)$
Vinyl V_{trans}	5.255 dd, $^3J(11.1)$, $^2J(1.4)$
Vinyl V_{cis}	5.746 dd, $^3J(17.7)$, $^2J(1.4)$
Vinyl V_{Ar}	7.059 dd, $^3J(11.1)$, $^3J(17.7)$
Aromatic A	7.029 s, 7.145 s, 7.167 s
Vinylene	7.477 s



2,5-Di-[(3-methylbutyl)-oxy]-PV trimer;
Structural formula with protons labelled



2,5-Di-[(2-ethylhexyl)-oxy]-PV trimer;
Structural formula with protons labelled

Scheme 1.

2.1. Telomerization of 2,5-di[(2-ethylhexyl)-oxy] substituted PV-trimer

The telomerization was investigated kinetically. The time dependent product distributions were determined by means

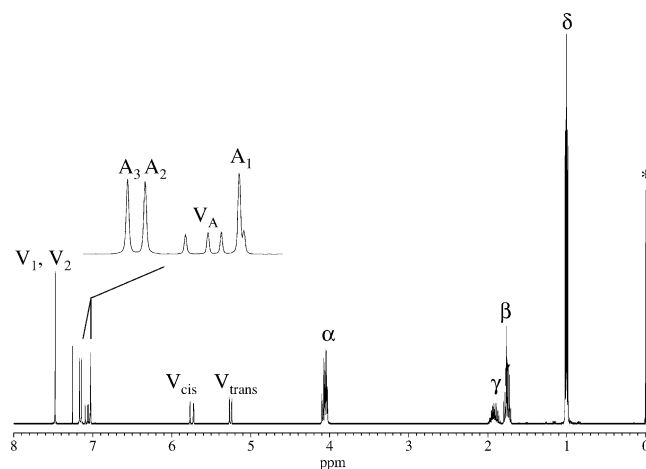


Fig. 1. ^1H NMR spectrum of 2,5-bis[(3-methylbutyl)oxy]-*p*-PV trimer.

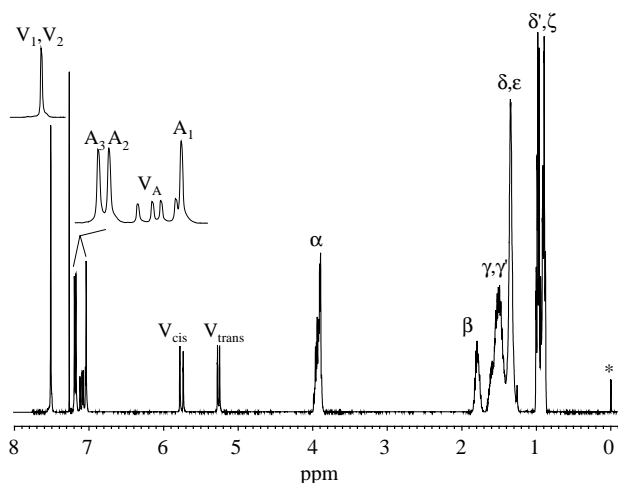


Fig. 2. ^1H NMR spectrum of 2,5-bis[(2-ethylhexyl)oxy]-*p*-PV trimer.

of MALDI TOF mass spectrometry (s. Figs. 3 and 4). In the course of the telomerization samples were taken from the reaction mixture and dissolved in chloroform prior to analysis. It should be mentioned that the reaction mixtures were completely chloroform soluble, thus the samples investigated by MALDI TOF MS were representative.

Results obtained after short reaction times using the Mo- as well as the Ru-complex as metathesis catalyst

Table 2

^1H NMR chemical shifts for trans, trans configured 2,5-bis[(2-ethylhexyl)oxy]-PV trimer in CDCl_3

Proton	δ (ppm) and J (Hz)
Methyl	ζ_3 0.884 t, ζ_2 0.891 t, ζ_1 0.916 t, each 3J (7.0) δ'_1 0.958 t, δ'_2 0.978 t, δ'_3 0.985 t, each 3J (7.5)
Methylene-H	1.27–1.68 m
β -Methine	1.72–1.85 m
α -Methylene	3.86–3.99 m
Vinyl V_{trans}	5.254 dd, 3J (11.1), 2J (1.3)
Vinyl V_{cis}	5.750 dd, 3J (17.8), 2J (1.3)
Vinyl V_{Ar}	7.074 dd, 3J (11.2), 3J (17.8)
Aromatic A	7.028 s, 7.165 s, 7.185 s
Vinylene	7.503 s

(s. Scheme 2) show, that a highly selective telomerization takes place in both cases. The reason is that the conversion of the internal in comparison to terminal double bonds is sterically hampered. In course of the reaction the average chain length grows, thus the amount of inner double bonds increases (relatively versus terminal double bonds as well as absolutely). Consequently, the probability of inner double bond splitting rises. Results obtained after longer reaction times confirm this expectation (s. Figs. 3 and 4).

For telomerization the molybdenum complex is much better suited than the ruthenium-based catalyst. With the

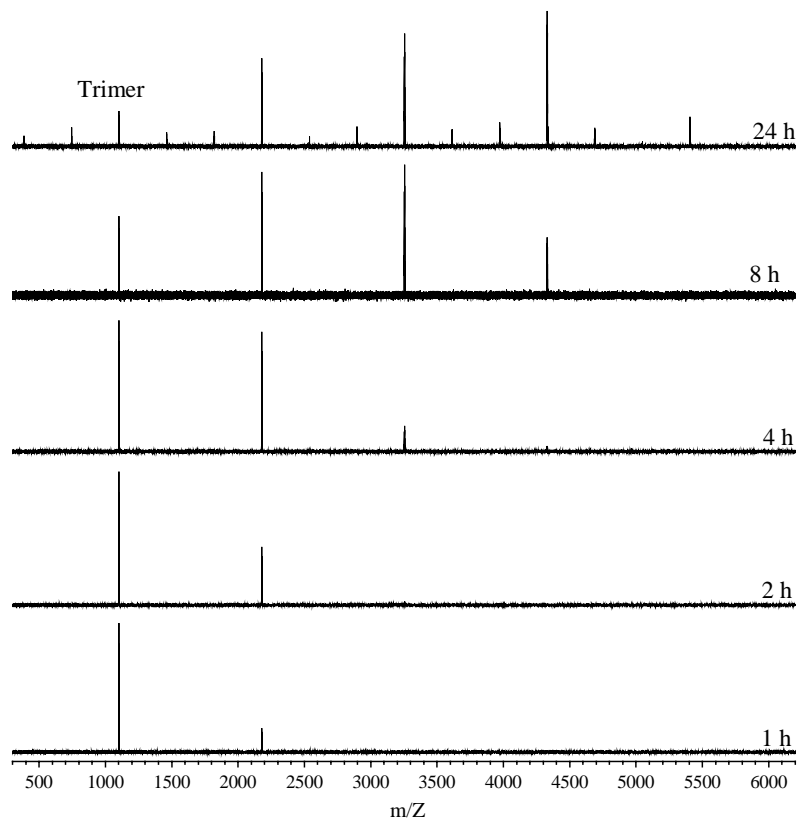


Fig. 3. MALDI TOF mass spectra of the time dependent product distribution of 2,5-bis[(2-ethylhexyl)oxy]-*p*-PV trimer telomerization (Mo catalyst) ($c_{\text{Cat}} = 10 \text{ mmol/l}$, 50°C , hexane).

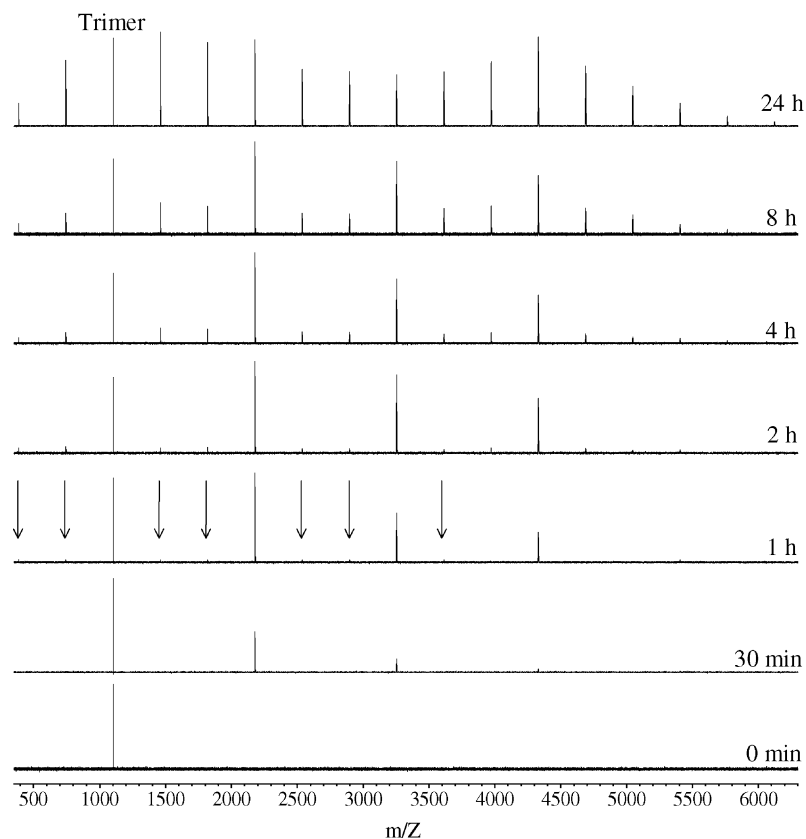


Fig. 4. MALDI TOF mass spectra of the time dependent product distribution of 2,5-bis[(2-ethylhexyl)oxy]-*p*-PV trimer telomerization (Ru catalyst) ($c_{\text{Cat}} = 10 \text{ mmol/l}$, 50°C , hexane).

molybdenum complex, nonamer, most likely even dodecamer (conclusion from the spectrum obtained after 24 h) is formed as main product, before side reactions occur.

In contrary, with the ruthenium-based catalyst by-products (arisen as consequence of splitting of inner double bonds) appear at earlier stages of the telomerization, at lower conversion and above all at much lower average degree of polymerization.

The lower selectivity of the Ru-catalyst can be explained by its smaller sterical demand, it is more accessible for sterically hindered inner double bonds than the Mo-complex. Our results concerning metathesis degradation of polyisoprenes

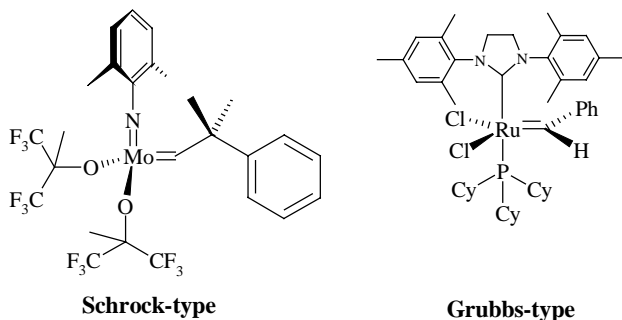
prove that the conversion of sterically hindered methyl substituted double bonds proceeds easier with the Ru- than with the highly active Mo-based catalyst [21].

For the splitting of the inner double bonds the highly active methyldene species $[\text{Mo}]=\text{CH}_2$ and $[\text{Ru}]=\text{CH}_2$ are responsible.

2.2. Telomerization of 2,5-di-[(3-methylbutyl)-oxy] substituted PV trimer

Taking into account the fact that the metathesis step growth process proceeds as precipitation polycondensation [4,22,23] it may be expected, that by varying the solvent the degree of the telomerization likewise can be tuned. In this context 2,5-di-[(3-methylbutyl)-oxy] PV-trimer was chosen as substrate. It is less soluble than the 2,5-di-[(2-ethylhexyl)-oxy] PV-trimer, already the hexamer is insoluble in hexane, even at 50°C . As catalyst the molybdenum complex with dimethyl substituted phenylimido ligand was used.

The time dependent MALDI-TOF mass spectra (Fig. 5 and Table 3) prove as expected that it is possible to quench the reaction at the dimerization stage. Only hexamer was obtained. Neither higher telomers nor products of inner double bond splitting are observed. The separation of



Scheme 2.

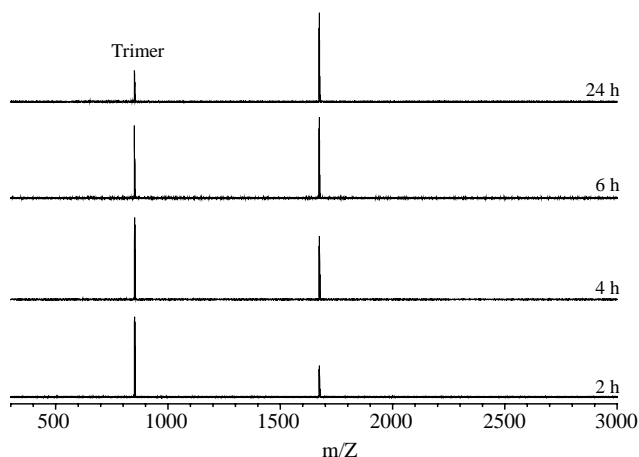


Fig. 5. MALDI TOF mass spectra of the time dependent product distribution of 2,5-bis[(3-methylbutyl)oxy]-*p*-PV trimer-telomerization (Mo catalyst) ($c_{\text{Cat}} = 10 \text{ mmol/l}$, 50°C , hexane).

Table 3
Time dependent product distribution of telomerization of Di-3MBO-PV trimer

Time (h)	Trimer (wt.%)	Hexamer (wt.%)
2	59.0	41.0
4	43.4	56.6
6	34.3	65.7
24	17.4	82.6

trimer and hexamer is very simple due to the fact, that their solubilities differ strongly. Therefore this way provides an elegant method for the preparation of hexamer. Taking into account the results of the telomerization of 2,5-di[(2-ethylhexyl)-oxy] PV-trimer (presented in Fig. 3) we are confident that working with the highly active and selective molybdenum complex the dimerization route is a suitable way also for the selective conversion of higher oligomers (e.g. from hexamer upwards).

3. Experimental

All metathesis reactions were carried out using argon and standard Schlenk technique under exclusion of water and oxygen (Oxysorb, Fa. Messer Griesheim). Hexane was predried over lithium aluminum hydride and distilled under an atmosphere of argon, then degassed and condensed from butyllithium. The molybdenum alkylidene complex (Scheme 2) was prepared [18] according to literature [6,7]. The ruthenium complex used was a commercially available product (Strem Chemicals Inc.).

The PV-trimers were prepared via Wittig-reaction with subsequent I_2 -catalyzed isomerization. Their identity was proven by ^1H and ^{13}C NMR spectroscopy as well as by MALDI-TOF MS.

The polycondensation reaction (telomerization) was started by addition of the catalyst solution ($c = 10 \text{ mmol l}^{-1}$)

in hexane to the trimer (trimer: catalyst = 50 : 1). As catalyst served the Schrock-type alkylidene complex $\text{Mo}(\text{NAr}^{\text{Me}_2})(\text{CHCMe}_2\text{Ph})[\text{OCMe}(\text{CF}_3)_2]_2$ or the Grubbs-type catalyst $\text{Ru}(\text{=CHPh})(\text{PCy}_3)[1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-4,5-dihydroimidazol-2-ylidene}]\text{Cl}_2$. The reactions were performed at 50°C . After a given time a small sample was taken and the reaction was subsequently quenched with methanol in the case of the Mo-complex or with ethyl vinyl ether in the case of the Ru-catalyst.

The resulting product mixture was purified by dissolution in chloroform and subsequent filtration over an analytical column packed with silica using chloroform as eluent (for separation of the catalyst residues).

The molecular mass of products obtained were measured with a Bruker Biflex III MALDI-TOF MS spectrometer using 2,5-dihydroxy benzoic acid as matrix.

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, as solutions in CDCl_3 with TMS as internal standard.

4. Conclusion

It is possible to synthesize higher, trans configured PV oligomers with vinyl end groups by kinetically controlled metathesis telomerization of a lower analogon. The highly active Ru-catalyst seems to be of practical use only for the dimerization (in particular for lower oligomers) while the highly active Mo-based complex is also well suited for telomerization, yielding higher PV oligomers. Especially the highly selective dimerization of higher oligomers opens a valuable way to obtain a monodisperse long chain oligomer quantitatively or at least in an easily isolable form.

Acknowledgements

This work was supported by Fonds der chemischen Industrie, BMBF, to whom we express our appreciation.

References

- [1] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Brédas, M. Lögdlund, W.R. Salaneck, *Nature* 397 (1999) 121.
- [2] E. Thorn-Csányi, H.-D. Höhnk, *ISOM* 9, 21–26.7.91, Collegeville, PA, *J. Mol. Catal.* 76 (1992) 101.
- [3] E. Thorn-Csányi, K.-P. Pflug, *Makromol. Chem.* 194 (1993) 2287.
- [4] E. Thorn-Csányi, K.-P. Pflug, *J. Mol. Catal.* 90 (1994) 69.
- [5] E. Thorn-Csányi, P. Kraxner, in: J.S. Salomon (Ed.), *The Polymeric Materials Encyclopedia*, CRC Press, Florida, Sess. 67 (1996) 219.
- [6] J.H. Oskam, H.H. Fox, K.B. Yap, D.H. McConville, R. O'Dell, B.J. Lichtenstein, R.R. Schrock, *J. Org. Chem.* 459 (1993) 185.
- [7] E. Thorn-Csányi, P. Kraxner, *J. Mol. Catal. A.: Chem.* 115 (1997) 21.
- [8] E. Thorn-Csányi, P. Kraxner, *Makromol. Chemie, Rapid Commun.* 16 (1995) 147.
- [9] E. Thorn-Csányi, P. Kraxner, *Macromol. Chem. Phys.* 198 (1997) 3827.

- [10] E. Thorn-Csányi, P. Kraxner, A. Strachota, *Macromol. Rapid Commun.* 19 (1998) 223.
- [11] R. Peetz, A. Strachota, E. Thorn-Csányi, *Macromol. Chem. Phys.* 204 (2003) 1439.
- [12] O. Narwark, S.C.J. Meskers, R. Peetz, E. Thorn-Csányi, H. Bäßler, *Chem. Phys.* 294 (2003) 1.
- [13] O. Narwark, A. Gerhard, S.C.J. Meskers, S. Brocke, E. Thorn-Csányi, H. Bäßler, *Chem. Phys.* 294 (2003) 17.
- [14] US 6,395,410, *invs.*: R. Wehrmann, A. Elschner, E. Thorn-Csányi, *Chem. Abstr.* 132 (2002) 42599.
- [15] O. Klockmann, Doctoral Thesis 2000, University of Hamburg.
- [16] A. Strachota, Doctoral Thesis 2000, University of Hamburg.
- [17] O. Herzog, Doctoral Thesis 2003, University of Hamburg.
- [18] S. Brocke, Doctoral Thesis in work, University of Hamburg.
- [19] F. Scheliga, Doctoral Thesis in work, University of Hamburg.
- [20] M. Scholl, Sh. Ding, Ch.W. Lee, R.H. Grubbs, *Org. Lett.* 1 (1999) 953.
- [21] K. Ruhland, O. Herzog, E. Thorn-Csányi, unpublished results.
- [22] E. Thorn-Csányi, P. Kraxner, *Macromol. Symp.* 122 (1997) 77.
- [23] E. Thorn-Csányi, *Nato Sci. Ser.* 56 (2002) 295.