Macromol. Symp. ***181,*** *5–16 (2002)*

Modified Polypropylenes by Copolymerization with Nonconjugated Dienes and Additional Chemical Reactions

Manfred Arnold, Steffen Bornemann, Thomas Schimmel, Thomas Heinze*

Martin-Luther-University Halle-Wittenberg, Department of Chemistry,
Institute of Technical Chemistry and Macromolecular Chemistry,
D-06099 Halle / Saale, Germany

Summary: Modified polypropylenes were synthesized by copolymerization of propene with several nonconjugated dienes using a constrained geometry catalyst in combination with methylaluminoxane. The incorporation of the dienes yields in polymer structures containing both cyclic units and linear branches, respectively. By variation of the polymerization conditions the cyclization tendency can be reduced. The resulting propene/diene copolymers are equipped with higher amounts of pendant double bonds which can be used for following chemical reactions. As an example, the epoxidation of the free double bonds was carried out using several epoxidation reagents. In a further modification step, the ring opening of the epoxy groups is presented demonstrating the simplicity of the chemical modification possibilities of such polypropylene materials.

Introduction

The demand of polypropylene (PP) was increasing continuously within the last years.[1] Nowadays, more than 25 million tons PP are consumed each year all over the world.[2] So, the search of new, broader application possibilities is very important – not only from the industrial point of view. A tailoring of the polymer structures seems a successful path to produce materials with well-defined material properties.[3]

An interesting catalyst class for the synthesis of such tailored polymers are the metallocenes.[4-6] Compared to conventional Ziegler-Natta catalysts more homogeneous polymers can be obtained. Furthermore, a better incorporation of comonomers is to observe.[7]

In the past we published some results of the copolymerization of propene with different α-olefins[8]: linear[9], branched[10] as well as cyclic α-olefins.[11,12] Polymeric materials with manifold properties can be prepared. The incorporation of linear side branches into the PP chain yields in more soft materials with lower glass transition temperatures.

CCC 1022-1360/00/$ 17.50+.50/0

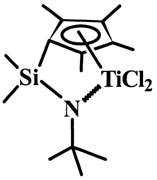
Contrary to this, the incorporation of rings results in brittle, fragile materials with high glass transition temperatures.

Functional propene copolymers can be obtained from the copolymerization of propene with functional olefins.[13-16] However, only a low amount of functional groups in the copolymer was obtained. So, another pathway to functional PP could be the copolymerization of propene with nonconjugated dienes.

In contrast to the propene/α-olefin copolymerization only a few number of publications dealing with the copolymerization of propene with nonconjugated dienes can be found. [17-21] Normally, the dienes are inserted into the growing polymer chain by cyclopolymerization. However, from the study of the literature data we concluded, that it should be possible to synthesize diene copolymers with reduced amounts of cyclic units. So, the aim of this work was to find out polymerization conditions for the synthesis of propene/diene copolymers with a desired degree of functionality. In the second part of this publication, we report on some first results of chemical modification reactions starting from the pendant C=C double bond.

Experimental

The titanium [*N*-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-η)-2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silanaminato (2-)-*N*]-dimethyl catalyst (CBT) as well as the methylaluminoxane (MAO) (10 wt.-% solution in toluene) were obtained by Crompton GmbH. Propene (Fluka) was dried by passing through a molecular sieve 3A column. The comonomers were commercially obtained from Fluka and purified by distillation over calcium hydride. Toluene (BSL GmbH Schkopau) was refluxed over sodium/benzophenone.



CBT catalyst

Polymerization reactions were carried out as described elsewhere.[22] To determine the solubility of propene in toluene, we used a calculation method.[23]

Epoxidation was carried out at room temperature using different epoxidation reagents. To open the epoxy ring, an epoxidized copolymer was dissolved and converted with acetic acid/pyridine or water/sulfuric acid.

Nuclear magnetic resonance (NMR) spectra of the copolymers were recorded on a Varian 500 spectrometer. The molecular weights of the polymers were determined by size exclusion chromatography (SEC) by using polystyrene standards in THF at room temperature. The thermal behavior of the copolymers was investigated using differential scanning calorimetry (DSC) with a heating rate of 10 K/min.

Results and discussion

Synthesis of propene/α,ω-diolefin copolymers

The copolymerization of propene with nonconjugated dienes gives access to polymeric structures containing free, pendant double bonds in the side branches of the copolymers. The problem preventing a commercial use of this copolymers is the so called cyclopolymerization. These kind of polymerization is known for several monomers[24]. In the field of the homopolymerization of nonconjugated dienes cyclopolymerization was found, too[25-27]. However, the synthesis of copolymers with reduced cyclization selectivity should be possible. The resulting copolymers should have both cyclic units and side branches in the chain. Possible structure segments of propene copolymers with nonconjugated dienes are drawn in Figure 1.

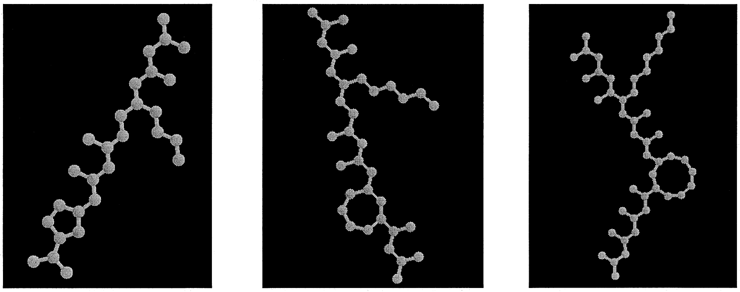


Figure 1. Structure variations of propene copolymers with 1,5-hexadiene (left), 1,7-octadiene (middle) and 1,9-decadiene (right), respectively.

The copolymerization of propene with 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene was carried out at 30°C in toluene using a so called constrained geometry catalyst[28] in combination with MAO. From the characterization of the copolymer composition by NMR spectroscopy a copolymerization diagram as well as a diagram for the cyclization selectivity can be created (Figure 2). It can be shown that a synthesis of copolymers with different amount of incorporated diene is practicable. Comparing the insertion rate of the several dienes we can conclude that 1,5-hexadiene as well as 1,7-octadiene are relatively good incorporated into the growing polymer chain. The insertion rate for the 1,9-decadiene is a little smaller.

As expected from literature data, most of the 1,5-hexadiene monomer units are incorporated by cyclopolymerization. The use of 1,7-octadiene yields again in such polymer structures. Certainly, if we use the longer 1,9-decadiene as a comonomer in propene copolymerization, a significantly lower degree of cyclization can be observed. There could be two reasons for the lower cyclization selectivity when 1,9-decadiene is used in copolymerization:

1) Due to the lower ring strain five- or seven-membered rings are more stable than nine-membered rings.
2) The movement of the second C=C double bond to the catalytic center takes more time than the insertion of a new monomer.

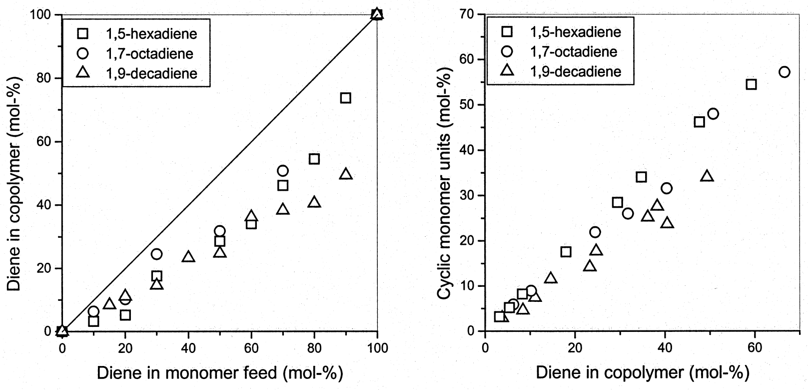


Figure 2. Copolymerization diagram (left) as well as cyclization selectivity (right) for the copolymerization of propene with 1,5-hexadiene (□), 1,7-octadiene (○) and 1,9-decadiene (Δ), respectively.

As known from the propene copolymerization with α-olefins,[9] the addition of higher amounts of the comonomer yields in copolymers with lower molecular weights. For propene/diene copolymers the same tendency we found (Figure 3, left). Furthermore, comparing the molecular weights of copolymers of propene with α-olefins and dienes, respectively, we observe a broadening of the molecular weight distribution when dienes were used. The reason is a simple one: It is well known, that the constrained geometry catalyst can be used for the synthesis of long chain branched polyolefins.[29] Terminated polymer chains containing double bonds can be inserted. Such an effect we can observe also in copolymerization of propene with nonconjugated dienes. If we compare the SEC chromatograms of propene copolymers with dienes and 1-olefins, usually a broader molecular weight distribution can be detected for propene/diene copolymers. We assume that there occur some branching reactions resulting in more inhomogeneous polymers. Of course, by variation of the polymerization conditions we can synthesize copolymers with only an insignificant degree of branching and narrow molecular weight distribution.[30]

All in all, the obtained copolymer should behave like a cycloolefin copolymer. The incorporation of cyclic units into the polymer chain results in a stiffening of the polymer. As an effect, we will get polymers with increasing glass transition temperature. In Figure 3 (right) the dependence of the diene content in the copolymer on the glass transition temperature is demonstrated. The value of the glass transition is distinctly influenced by quantity and size of the cyclic units. So, propene/1,9-decadiene consist of a relatively high number of noncyclic diene units. Such side branches are responsible for a reduced glass transition temperature. Nevertheless, we observe for propene/1,9-decadiene copolymers the highest values for the glass transition temperatures.

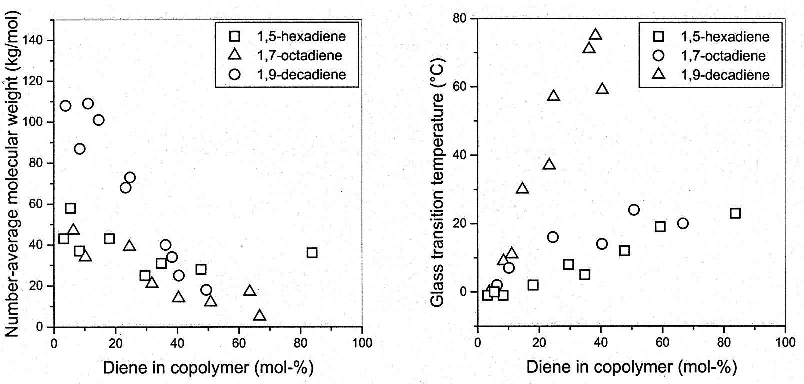


Figure 3. Properties of propene/diene copolymers. Molecular weight (left) and glass transition temperature (right) of propene copolymers with 1,5-hexadiene (□), 1,7-octadiene (**O**) and 1,9-decadiene (Δ).

As we reported above, the use of different dienes yields in different polymer structures. By using 1,9-decadiene as comonomer, a higher degree of unsaturation can be observed. Now, the question is: How can we reduce the cyclopolymerization in a manner that copolymers with a low number of cyclic units and high number of free double bonds are formed?

The physical parameters necessary are: monomer and catalyst concentration as well as temperature. In detail we will report these results later.[30] Now, we want to show the possibility of the synthesis of propene/1,9-decadiene copolymers with drastically reduced cyclopolymerization. In Figure 4 (left) the composition of propene/1,9-decadiene copolymers synthesized at 30°C is shown. A high degree of cyclization of the inserted diene comonomer was detected. Having a look at Figure 4 (right), a totally changed copolymerization behavior can be found. Under the polymerization conditions used here we synthesized propene/diene copolymers containing a relation between noncyclic diene units (n.c.u.) and cyclic units (c.u.) of approximately 3 : 1. So, copolymers containing a higher degree of unsaturation useful for modification reactions can be prepared with the constrained geometry catalyst at 50°C. We believe that it is possible to synthesize propene copolymers with nonconjugated dienes without cyclopolymerization (e.g. by using other catalysts).

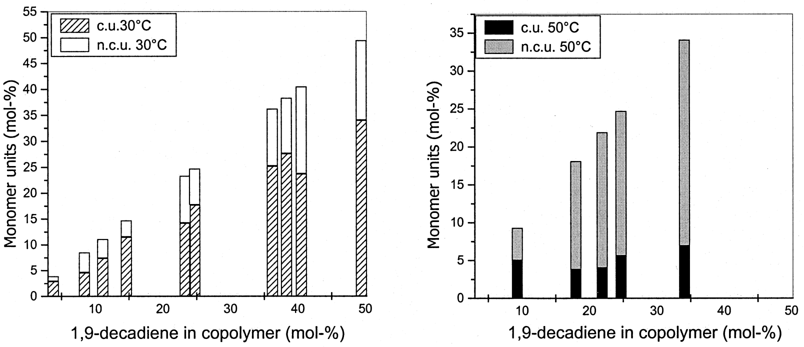
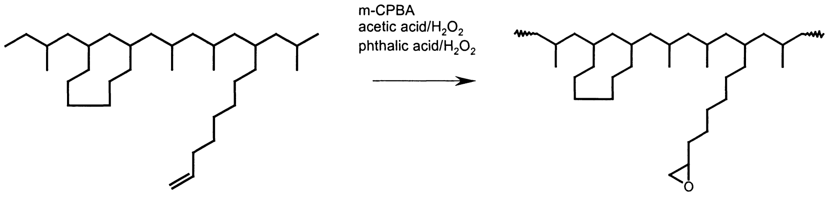


Figure 4. Propene/1,9-decadiene copolymers. Noncyclic (n.c.u.) and cyclic (c.u.) 1,9-decadiene units in the copolymers for polymerization reactions at 30°C (left) and 50°C (right).

Chemical modification reactions at propene/α,ω-diolefin copolymers

Epoxidation

Some years ago, we investigated the epoxidation of 1,4-cis-polybutadiene.[31] Now, the epoxidation of propene/diene copolymers with longer side branches is a focus of our research. In Scheme 1 the principal synthesis route for the epoxidation of a propene/1,9-decadiene copolymer is illustrated. For the epoxidation we used different reagents. Several copolymers with various content of pendant double bonds were selected.



Scheme 1. Epoxidation of propene/1,9-decadiene copolymers.

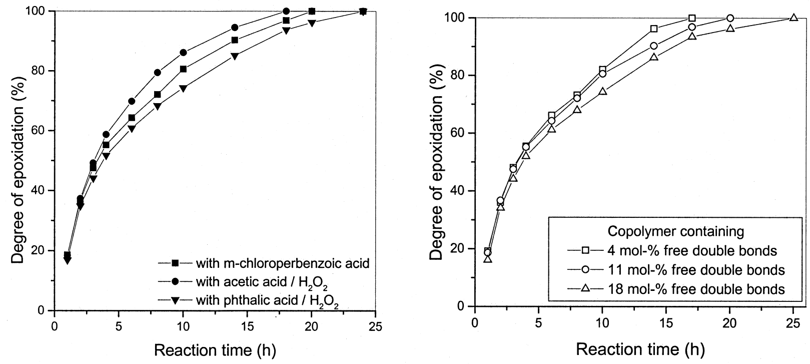


Figure 5. Epoxidation of propene/1,9-decadiene copolymers. Time versus degree of epoxidation for different epoxidation methods (left) and several propene/1,9-decadiene copolymers (right).

An important epoxidation reagent in organic chemistry is *m*-CPBA.[32] In contrast to this, peroxyacetic acid as well as peroxyphthalic acid are formed *in situ* by the reaction of hydrogen peroxide with the adequate acids.[32,33] All of the three discussed methods can be used for the epoxidation of propene/diene copolymers. In Figure 5 the time course for the epoxidations with various chemicals is demonstrated. After a reaction time of about 24 h a conversion of 100% was reached.

Epoxidation was investigated for propene/1,9-decadiene copolymers with different degree of unsaturation (Figure 5, right diagram). No clear lengthening of the needed reaction time was found in dependence of the content of free double bonds in the copolymer. A complete epoxidation can be obtained.

Unsaturated polymers are very sensitive materials in epoxidation. Crosslinking of the polymers can be obtained by changing the reaction parameters[34]. By characterizing the copolymers using SEC, occurring undesired side reactions can be discovered. In Figure 6 (right) the SEC curves of a propene/1,9-decadiene copolymer before and after epoxidation are shown. A blank test epoxidation using an atactic PP was also carried out (Figure 6, left). We observed no change of the SEC curves indicating possible side reactions after epoxidation for the propene/1,9-decadiene copolymer as well as for the atactic PP, respectively. We can conclude that we have at our disposal different, careful methods for the epoxidation of polymers.

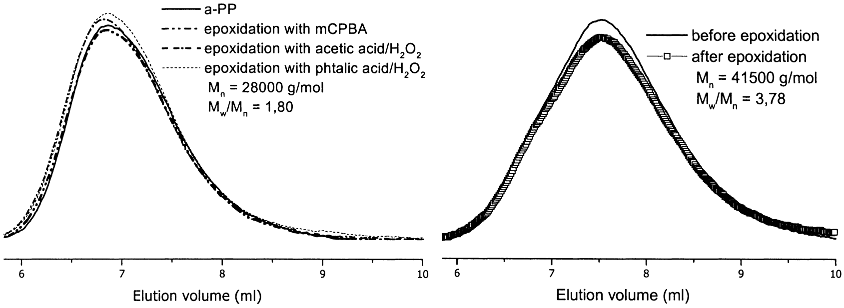


Figure 6. Epoxidation of polymers. SEC chromatographs of blank test epoxidation of an atactic PP using different epoxidation methods (left). Epoxidation on a propene/1,9-decadiene copolymer (right).

NMR spectroscopy is a powerful tool for the observation of the conversion of the epoxidation. In Figure 7 the ^{13}C-NMR spectra of a propene/1,9-decadiene copolymer in the unsaturated (top) and epoxidized form (bottom) are shown. From the comparison of the peaks for the C=C double bond and the epoxy group the degree of epoxidation can be determined.

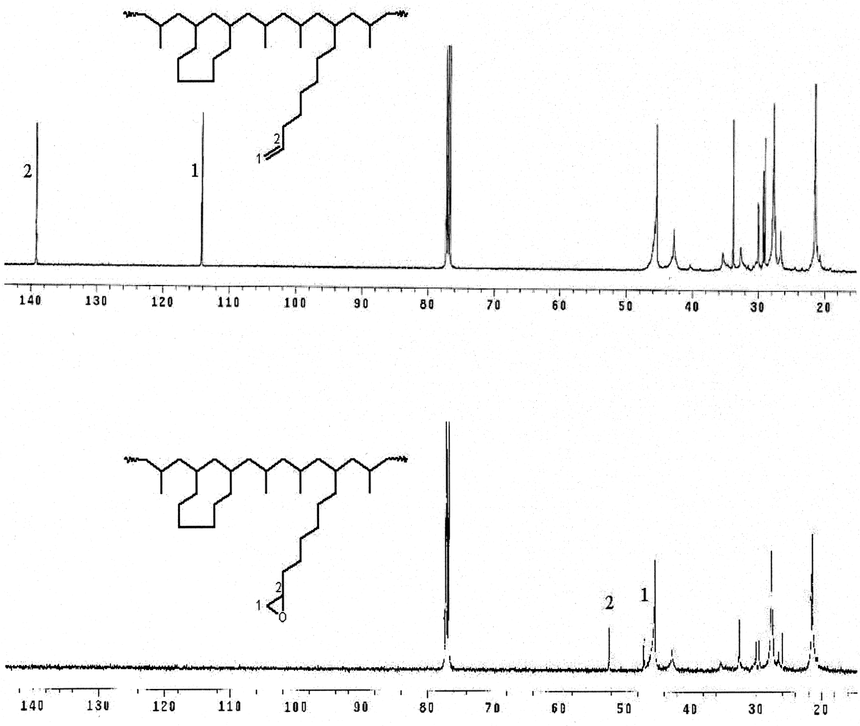
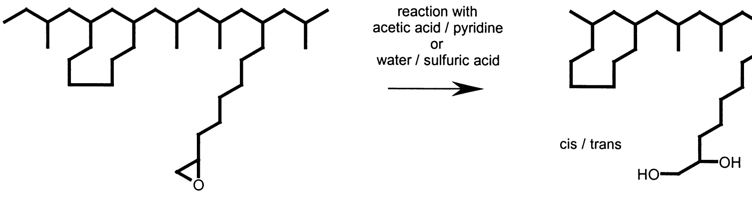


Fig. 7. ^{13}C-NMR spectra of a propene/1,9-decadiene copolymer before (top) and after epoxidation (bottom).

Ring opening

Ring opening of epoxides happens relatively easily. Both in acid and alkaline medium these reaction can be carried out.[35] For our investigations we used as ring opening reagent acetic acid/ pyridine and water/ sulfuric acid (Scheme 2). Both methods were successful. The composition of the reaction products can be detected by ^{1}H-NMR spectroscopy (Figure 8). After a reaction time of 4 h at a temperature of 50°C a conversion of 100% was detected. So, it is possible to synthesize polypropylene materials with a broad range of functionality.



Scheme 2. Ring opening of the epoxy group of epoxidized propene/1,9-decadiene copolymers.

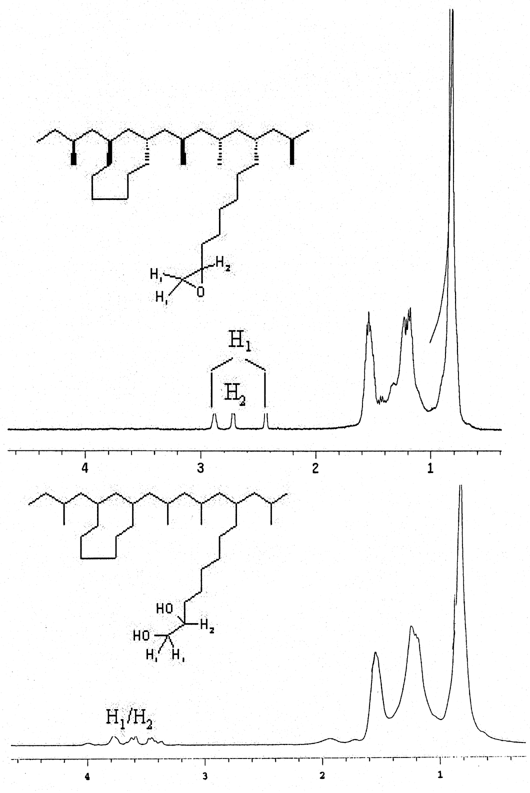


Figure 8. Determination of the ring opening by ^{1}H-NMR spectroscopy. Epoxidized propene/1,9-decadiene copolymer (top) and propene/1,9-decadiene copolymer containing hydroxy groups in the side chain (bottom).

Acknowledgement

We wish to express our appreciation to Crompton GmbH and BSL GmbH Schkopau for donating the homogeneous catalysts, the MAO and the toluene, respectively. Furthermore, we thank Dr. C. Wohlfarth for the calculations of propene solubility. This investigations were supported by the Deutsche Forschungsgemeinschaft.

[1] K.B. Sinclair, *Macromol. Symp.* **2001**, *173*, 237.
[2] P. Baum, J. Engelmann, *Nachr. Chem.* **2001**, 49, 368.
[3] A. Tuchbreiter, R. Mülhaupt, *Macromol. Symp.* **2001**, *173*, 1.
[4] G.W. Coates, *Chem. Rev.* **2000**, *100*, 1223.
[5] O. Olabisi, M. Atiqullah, W. Kaminsky, *J.M.S.- Rev. Macromol. Chem. Phys.* **1997**, *C37(3)*, 519.
[6] W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* **1997**, *127*, 143.
[7] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed. Eng.* **1995**, *107*, 1255.
[8] M. Arnold, J. Knorr, F. Köller, S. Bornemann, *J.M.S., Part A: Pure Appl. Chem.* **1999**, *A36(11)*, 1655.
[9] M. Arnold, O. Henschke, J. Knorr, *Macromol. Chem. Phys.* **1996**, *197*, 563.
[10] M. Arnold, S. Bornemann, F. Köller, T.J. Menke, J. Kressler, *Macromol. Chem. Phys.* **1998**, *199*, 2647.
[11] M. Arnold, O. Henschke, F. Köller, *Macromolecular Reports* **1996**, *A33(Suppls. 3&4)*, 219.
[12] O. Henschke, F. Köller, M. Arnold, *Macromol. Rapid Commun.* **1997**, *18,* 617.
[13] K. Hakala, T. Helaja, B. Löfgren, *Polym. Bull.* **2001**, *46*, 123.
[14] M.J. Schellekens, B. Klumperman, *J.M.S.- Rev. Macromol. Chem. Phys.* **2000,** *C40(2&3)*, 167.
[15] A. Kaya, L. Jakisch, H. Komber, G. Pompe, J. Pionteck, B. Voit, U. Schulze, *Macromol. Rapid Commun.* **2000**, *21*, 1267.
[16] K. Hakala, B. Löfgren, T. Helaja, *Eur. Polym. J.* **1998**, *34*, 1093.
[17] P. Walter, S. Trinkle, D. Lilge, C. Friedrich, R. Mülhaupt, *Macromol. Mater. Eng.* **2001**, *286*, 309.
[18] P. Pietikainen, P. Starck, I.V. Seppala, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2379.
[19] F.G. Sernetz, R. Mülhaupt, R.M. Waymouth, *Polym. Bull.* **1997**, *38*, 141.
[20] D.H. Lee, K.B. Yoon, J.R. Park, B.H. Lee, *Eur. Polym. J.* **1997**, *33*, 447.
[21] N. Naga, T. Shiono, T. Ikeda, *Macromolecules* **1999**, *32*, 1348.
[22] J. Knorr, S. Bornemann, T. Schimmel, M. Arnold, *Polym. Prepr.* **2000**, *41(1)*, 468.
[23] C. Wohlfarth, U. Finck, R. Schultz, T. Heuer, *Angew. Makromol. Chem.* **1992**, *198*, 91.
[24] G.B. Butler: “Cyclopolymerization and Cyclocopolymerization”, Marcel Dekker, Inc., New York, 1992, p. 239.
[25] C.S. Marvel, J.K. Stille, *J. Am. Chem. Soc.* **1958**, *80*, 1740.
[26] L. Resconi, G.W. Coates, A. Mogstad, R.M. Waymouth, *J.M.S., Part A: Pure Appl. Chem.* **1991**, *A28*,1225.
[27] N. Naga, T. Shiono, T. Ikeda, *Macromol. Chem. Phys.* **1999**, *200*, 1466.
[28] J.C. Stevens, *Stud. Surf. Sci. Catal.* **1996**, *101*, 11.
[29] A.E. Hamielec, J.B.P. Soares, *Prog. Polym. Sci.* **1996**, *21*, 651.
[30] S. Bornemann, T.Schimmel, T. Heinze, M. Arnold, in preparation (Polymer).
[31] M. Arnold, T. Langner, *Plaste u. Kautschuk* **1990**, *37*, 289.
[32] L.A. Paquette (Ed.) “Encyclopedia of Reagents for Organic Synthesis”, Vol. 2, John Wiley & Sons, Chichester, 1995, p. 1192.
[33] Y. Kurusu, *Polymers for Advanced Technologies* **1996**, *7*, 67.
[34] K. Udipi, *J. Appl. Polym. Sci.* **1979**, *23*, 3301.
[35] H. Kropf, J. Thiem, H. Nimz, in: “*Houben-Weyl: Methoden der org. Chemie*”, 4th ed., H. Kropf, Ed., Vol. 6/1, Thieme, Stuttgart 1979, p. 357.