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Eric J. Goethals^a; Ronny R. De Clercq^a; Saskia R. Walraedt^a

^a Polymer Division Institute of Organic Chemistry, University of Ghent, Ghent, Belgium

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SYNTHESIS AND DEGRADATION OF POLYMERS CONTAINING POLYACETAL SEGMENTS

ERIC J. GOETHALS, RONNY R. DE CLERCQ,
and SASKIA R. WALRAEDT

Polymer Division
Institute of Organic Chemistry
University of Ghent
Ghent, Belgium

INTRODUCTION

Polymerizations which have relatively low polymerization enthalpy are characterized by a correspondingly low ceiling temperature. The ceiling temperature (T_c) is the temperature at which the rate of polymerization is equal to the rate of depolymerization. Since the former is proportional to the monomer concentration whereas the latter is not, the ceiling temperature is monomer-concentration-dependent. Inversely, an equilibrium monomer concentration, M_e , at different temperatures can be calculated from the thermodynamic parameters. The mathematical expression for M_e is

$$[M]_e = \exp(\Delta G^\circ/RT_c)$$

where ΔG is the free energy of polymerization.

For cyclic monomers, the enthalpy of polymerization is determined by the ring-strain of the cycles. Therefore, a number of polymerizations of low strain cyclic monomers are characterized by low T_c s or high M_e s. The corresponding pure polymers are thermodynamically unstable and tend to depolymerize until the M_e , corresponding to the temperature used, is reached. This depolymerization, however, will occur only if the active species necessary for the establishment of the equilibrium are introduced in the polymer. This means that the polymer can be used in normal atmospheric conditions and may even show a relatively high thermal stability as long as the active species remain absent.

Typical cyclic monomers that show low T_c s are the five-, six-, and seven-

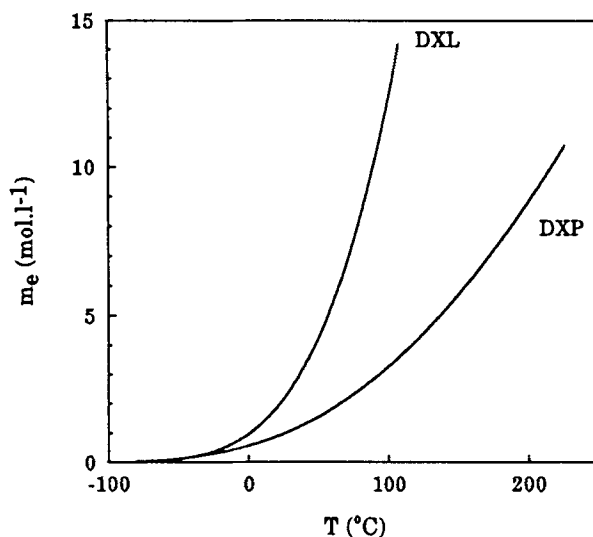
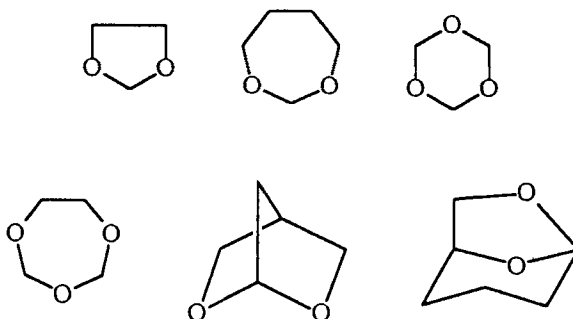


FIG. 1. Equilibrium monomer concentrations of DXL and DXP as functions of the temperature.

membered heterocycles which typically have enthalpies of polymerization in the order of 20–30 kJ/mol. Well-known examples are 1,3-dioxolane (DXL) and 1,3-dioxepane (DXP). In Fig. 1 the $[M]_e$ s of these polymerizations, calculated from thermodynamic data taken from the literature, have been plotted as a function of temperature. The curves stop at the points corresponding to the bulk monomer concentrations. If polymer degradations are carried out at temperatures higher than the T_c s corresponding to these concentrations, the depolymerizations will be complete.

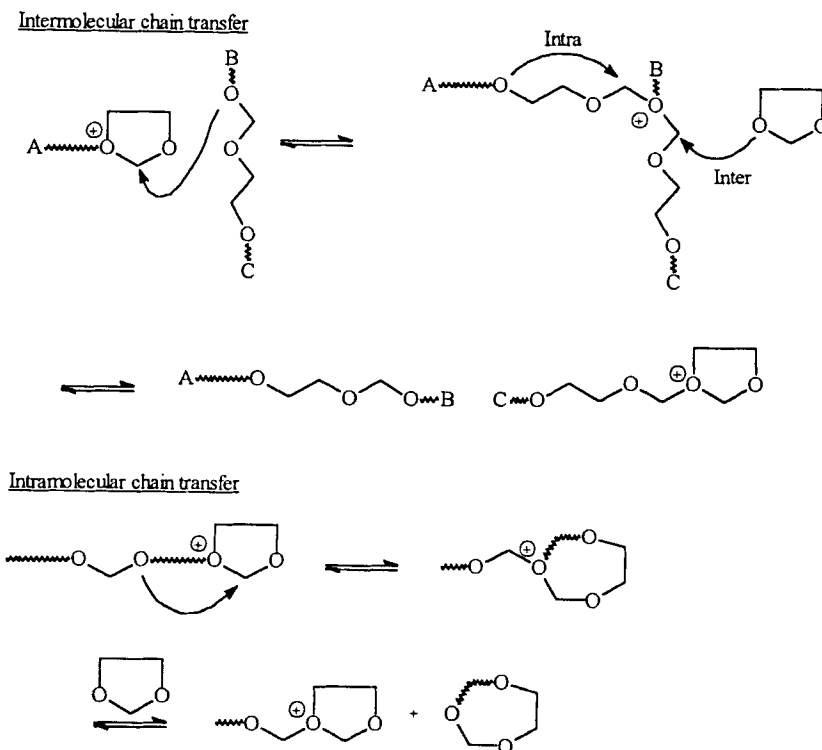
In the last few years we have been interested in the synthesis of polymers containing polyacetal segments because of the easy degradation of these polymers. The physical properties of these polymers can be varied by copolymerization of the various cyclic acetals available. The polymerization of cyclic acetals is initiated by typical cationic initiators such as strong alkylating or acylating agents, proton acids, and Lewis acids. A large number of monomers have been studied, the most important one being trioxane which leads to the well-known commercially produced polyoxymethylene. Examples of cyclic acetal monomers which have been reported to polymerize are shown below:



In the present paper we report on our investigations on the synthesis of well-defined polyacetals containing functional end groups, their use to prepare more sophisticated segmented copolymer structures, and their ability to be degraded under controlled conditions. The key monomers used for this study were 1,3-dioxolane (DXL) and 1,3-dioxepane (DXP).

MECHANISM OF CYCLIC ACETAL POLYMERIZATIONS

The mechanism of polymerization of cyclic acetals has long been a matter of dispute, but now the mechanism proposed by Penczek et al. [1] is generally accepted. The active species of the polymerization are assumed to be oxonium ions which exist in different forms due to an equilibrium between several cyclic and noncyclic oxonium ions, each of them having a different reactivity. This is a consequence of the fact that the active species is attacked not only by monomer but also by any oxygen atom of any polymer chain formed. The result of these reactions is a continuous "transacetalization" occurring between different polymer chains or within one polymer chain. In the latter case the transacetalization reaction leads to a macrocyclic oligomer.



The occurrence of the transacetalization reaction has two important consequences. First, the molecular weight distribution is broadened to a value of 2 (at

equilibrium) and second, the polymer contains a fraction of cyclic oligomers. According to the theory of Jacobson and Stockmeyer, the concentration of the cyclic oligomers is given by

$$[M_c]_n = An^{-5/2}$$

where $[M_c]_n$ is the concentration of the cyclic oligomer containing n monomer units and A is a constant typical for the polymer structure. From this equation it follows that the total concentration of all cyclic oligomers is independent of the monomer concentration and, for each polymer, a constant. The *fraction* of the cyclic oligomers in the final product will therefore decrease if the initial monomer concentration is increased. Taking this into account, and considering the equilibrium monomer concentration at the polymerization temperature, the molecular weight of the polymer formed is, in the case of a quantitative initiation, given by

$$\bar{M}_n = m \frac{[M]_0 - [M]_e - [M]_c}{[In]}$$

where $[M]_c$ corresponds to the concentration of the monomer which has formed cyclic oligomers, $[In]$ is the initiator concentration, and m is the molecular weight of the monomer.

SYNTHESIS OF TELECHELIC POLYACETALS

Telechelic polymers are polymers which contain functional end groups. Telechelics are used to prepare segmented copolymers or polymer networks by coupling reactions of their end groups. A frequently used method for the synthesis of telechelics is end-capping of living polymers. This method has also been applied to polyacetals [2].

However, for polyacetals the nature of the end groups is also important from another point of view: the termination of the polymerization, i.e., the deactivation of the oxonium ions, must lead to stable end groups in order to get stable polymers. The normal termination agents used in cationic polymerizations are nucleophiles. In the polymerization of cyclic acetals, they form the corresponding α -alkoxy end groups, some of which, such as hemiacetals or imino-acetals, are hydrolytically unstable. In fact, the thermal stability of the polyacetals very much depends on the nature of the polymer end groups and hence on the way the polymerization was terminated. This is illustrated by Fig. 2 where the thermal stabilities of polyDXLs terminated by the addition of a dialkyl sulfide, a tertiary amine, a trialkyl phosphine, or an acetate salt (leading to the corresponding sulfonium, ammonium, phosphonium, or acetate ester end groups) are compared.

The synthesis of well-defined telechelic polyacetals by end-capping is complicated by the occurrence of transacetalization reactions. If a monofunctional initiator is used, the polymerizing mixture will contain not only monofunctionally growing, but also bifunctionally growing and dead polymer chains. End-capping will therefore inevitably lead to the corresponding mixture of mono-, di-, and zero-functional polyacetals. This problem has also recently been recognized in attempts to prepare polyacetal macromonomers by end-capping of the polymerization of 1,3,6-trioxocane [3]. However, if the polymerization is initiated by a bifunctional

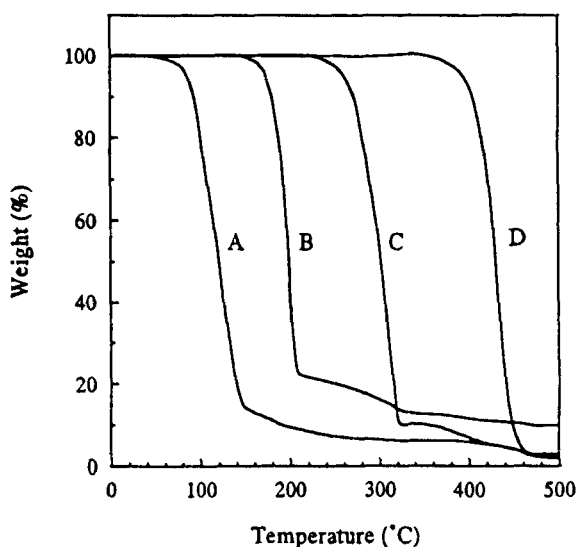
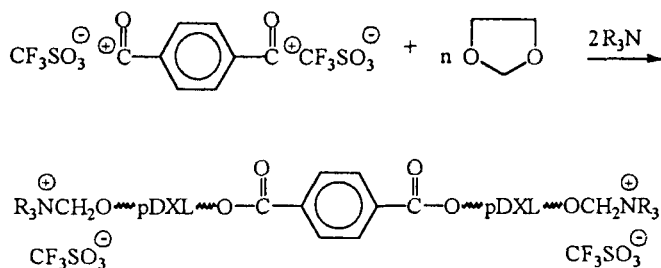


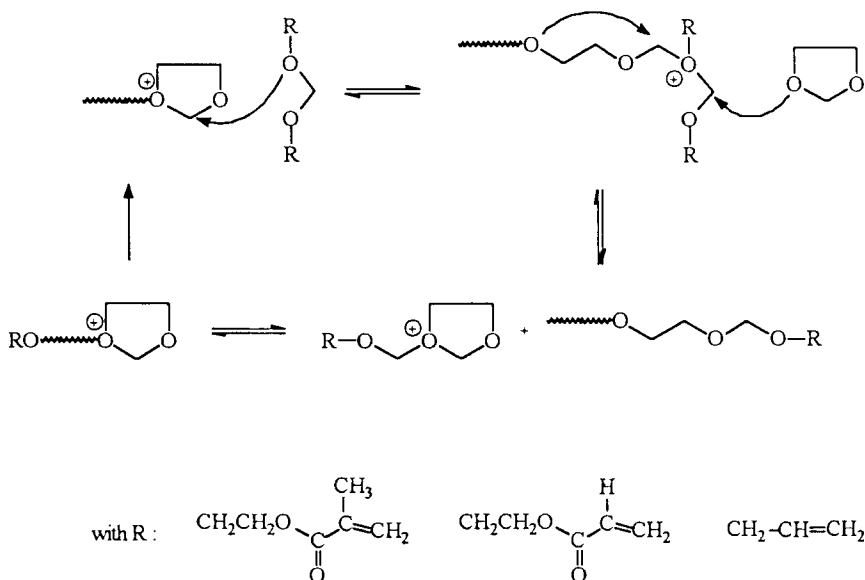
FIG. 2. Thermogravimetric analyses of telechelic polyDXL with sulfonium (A), ammonium (B), phosphonium (C), and acetic ester (D) end groups.

initiator system, all the polymers produced will be bifunctionally growing and the transacetalization reactions will not change this bifunctionality. End-capping of these polymers then leads to the di-telechelic polymers.

An excellent initiator for the production of di-telechelic polyacetals was found to be terephthaloyl bis triflate which is obtained from terephthaloyl chloride and silver triflate. End-capping with tertiary amines was found to lead to fairly stable end groups which behave as moderately reactive electrophiles in apolar medium [4].



End groups can also be introduced by carrying out the polymerization in the presence of a transfer agent. A low molecular weight formal can be used as a transfer agent. The transfer reaction is similar to the transacetalization reactions described above. If a functionalized formal is used, and if the concentration of initiator is small compared with that of the transfer agent, a polymer containing the same functional groups at each polymer chain end is obtained:



The molecular weight of the telechelic polymer thus obtained is given by

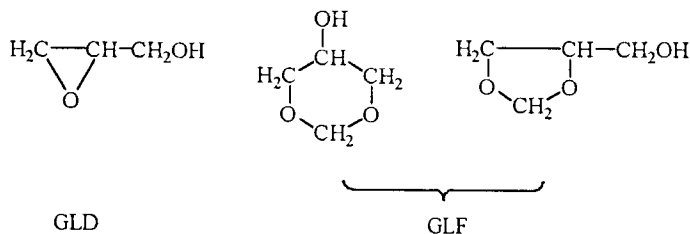
$$\bar{M}_n = m \frac{[\text{M}]_0 - [\text{M}]_e - [\text{M}]_c}{[\text{In}] + [\text{T}]}$$

where $[\text{T}]$ is the concentration of the transfer agent.

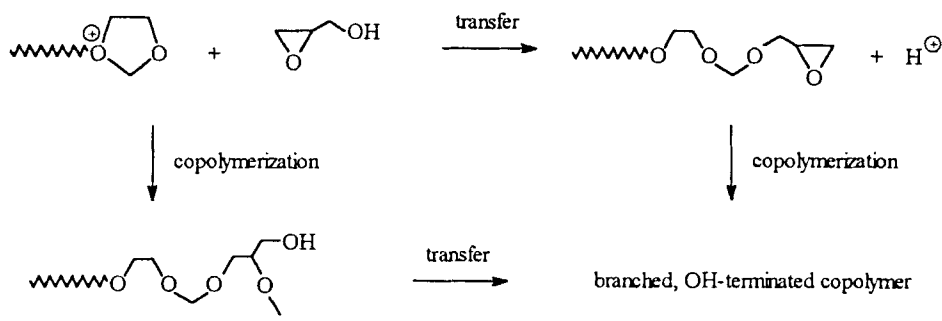
By using this principle, telechelic polyDXLs containing chloride, allylic, and (meth)acrylic end groups have been prepared [5].

Linear polyDXLs with primary alcohol end groups have been described by Franta et al. [6]. Their synthesis was based on the use of a diol as the transfer agent during polymerization. It was shown that the end groups were alcohol functions and not hemiacetal functions.

The synthesis of branched polyDXL structures having an alcohol function at each chain extremity is possible by copolymerization of DXL with a "monofer" [7]. Monofers are defined as monomers which carry on the same molecule a functional group that acts as a transfer agent in the polymerization. Monofers for the polymerization of DXL are glycidol (GLD) and glycerol formal (GLF), which is in fact a mixture of two isomers, a six- and a five-membered ring.

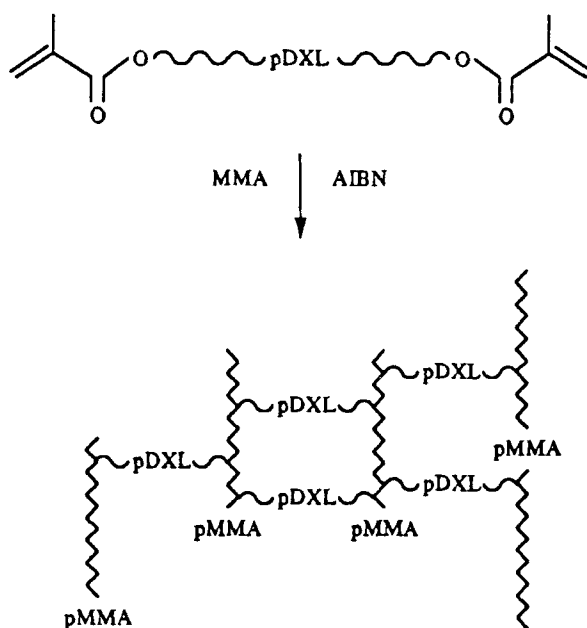


The mechanism of formation of branched polyacetal copolymers is as follows:



SYNTHESIS OF SEGMENTED COPOLYMERS AND NETWORKS CONTAINING POLYACETAL SEGMENTS

Block copolymers containing polyDXL segments have been prepared by coupling quaternary ammonium-terminated prepolymers with carboxylate-terminated prepolymers [8]. Polymer networks containing polyacetal segments have been prepared by free radical copolymerization of the α,ω -bis acrylate-terminated polyDXL with monomers such as (meth)acrylates and styrene [9]. The copolymers thus obtained consist of polymer chains of the vinyl monomer connected to each other by polyacetal segments:



The resulting materials possess a wide array of physical properties depending on the nature of the vinyl monomer, the length of the polyacetal segment, and the ratio of the two constituents. If the vinyl polymer segment has a T_g higher than the melting point of the polyDXL, and if the polyDXL is the minor compound (i.e.,

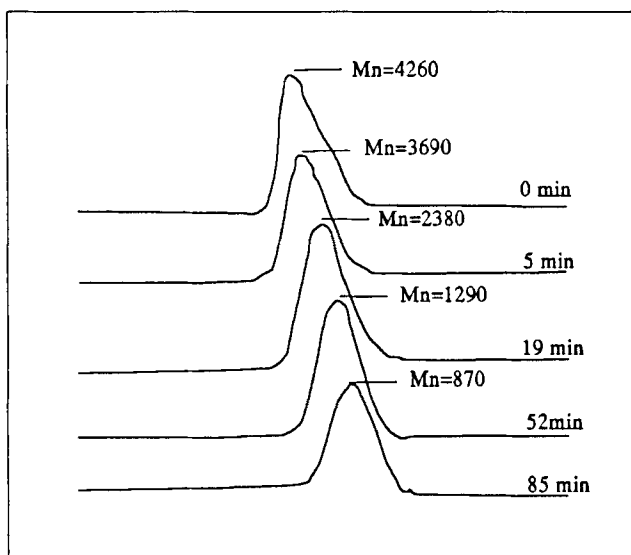


FIG. 3. GPC analyses of degrading polyDXL at 25°C in CHCl_3 , $[\text{TfOH}] = 0.02 \text{ mol} \cdot \text{L}^{-1}$.

DXL fraction lower than 0.5), the latter cannot crystallize and the resulting copolymer is a clear, transparent, and strong material. This is the case for copolymers obtained from polyDXL bis-macromonomer and styrene or MMA. If the T_g of the vinyl polymer is lower than the melting point of the polyDXL, the latter does crystallize and the polymer is a tough, opaque elastomer.

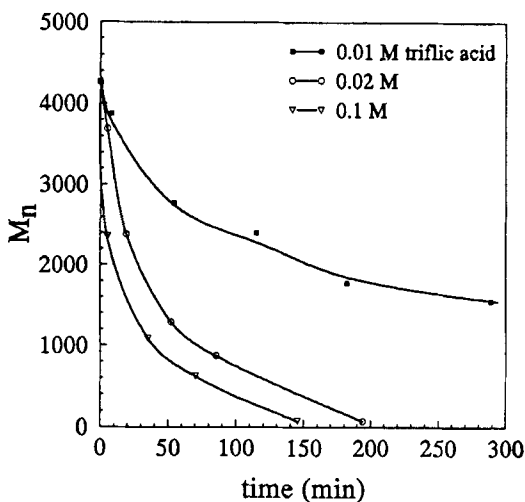


FIG. 4. Degradation of polyDXL by triflic acid in CHCl_3 at 25°C.

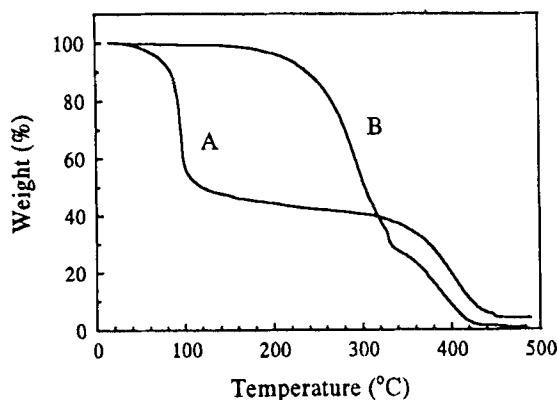


FIG. 5. Thermogravimetric analysis of a poly(MMA-*b*-DXL) network ([polyMMA]/[polyDXL] (w/w) = 1 and $M_n(\text{polyDXL}) = 3000 \text{ g} \cdot \text{mol}^{-1}$). A = acid-treated material, B = untreated material.

DEGRADATION OF POLYACETALS AND OF POLYACETAL COPOLYMERS

When a solution of a polyacetal is treated with a strong acid, degradation starts immediately and continues until the equilibrium monomer concentration corresponding to the reaction temperature is attained. This is visually observable by the change in viscosity of the solution. Analysis of the reaction mixture by means of gel permeation chromatography shows that the molecular weight distribution of the polymers remains approximately constant at a value of 2. This is due to the continuous transfer to polymer as described above. Examples of GPC analyses are shown in Fig. 3. The most powerful initiator for degradation was found to be triflic acid. Figure 4 shows how the molecular weight decreases as a function of time at room temperature. Boron trifluoride etherate in the presence of a proton donor, such as water, is also an efficient initiator. With a $\text{BF}_3/\text{H}_2\text{O}$ ratio of 0.5, the activity is the same as that of triflic acid.

Analysis of the reaction mixture at the end of degradation shows that the only detectable degradation product is monomer, provided the concentration is lower than the equilibrium monomer concentration. PolyDXL can also be degraded in bulk if the temperature is raised above the melting point and if the monomer formed is continuously removed by vacuum.

Degradation of the polyacetal segments of the block-copolymer networks described above leads to decrosslinking of the network with the formation of a linear vinyl polymer containing a small fraction of HEMA originating from the polyacetal macromonomer [9]. Thus, if a poly(DXL-*b*-MMA) network was suspended in methylene chloride containing triflic acid, the material became soluble within 20 minutes at room temperature. Surprisingly, the degradation was retarded by the addition of an alcohol to the solvent. If the material was suspended in aqueous acid, no degradation could be observed after several months. However, the thermal stability of a network that had been treated with acid was markedly lower than that of a non-treated one [9]. This is shown in Fig. 5 where it is clearly seen that the polyacetal

fraction of the acid-treated network is degraded at 90°C whereas the nontreated material starts to degrade at 210°C.

REFERENCES

- [1] R. Szymanski, P. Kubisa, and S. Penczek, *Macromolecules*, **16**, 1000–1008 (1983).
- [2] W. Chwialkowska, P. Kubisa, and S. Penczek, *Makromol. Chem.*, **183**, 753–769 (1982).
- [3] H. Kruger, H. Pasch, H. Much, V. Gancheva, and R. Velichkova, *Ibid.*, **193**, 1975–1986 (1992).
- [4] D. Van Meirvenne and E. J. Goethals, *Makromol. Chem., Suppl.*, **15**, 61–70 (1989).
- [5] E. J. Goethals, R. R. De Clercq, H. C. De Clercq, and P. J. Hartmann, *Makromol. Chem., Macromol. Symp.*, **47**, 151–162 (1991).
- [6] E. Franta, E. Gérard, Y. Gnanou, L. Reibel, and P. Rempp, *Makromol. Chem.*, **191**, 1689 (1990).
- [7] E. J. Goethals, G. G. Trossaert, P. J. Hartmann, and K. Engelen, IUPAC Symposium on Ring-Opening Polymerization, Warsaw, 1992; *Makromol. Chem., Macromol. Symp.*, In Press.
- [8] D. Van Meirvenne and E. J. Goethals, *New Polym. Mater.*, **1**(4), 281–288 (1990).
- [9] R. R. De Clercq and E. J. Goethals, *Macromolecules*, **25**(3), 1109–1113 (1992).