Macromol. Symp. ***157**, 93–99 (2000)*

New Polymer Structures Based on Vinyl Ether Polymerization

Eric J. Goethals,[1] Wouter Reyntjens,[1] Xiaochun Zhang,[1] Beatrice Verdonck,[1] and Ton Loontjens,[2]

[1]University of Ghent, Department of Organic Chemistry, Polymer Division, Krijgslaan 281, 9000 Ghent, Belgium
[2]DSM Central Research Laboratories, P.O. Box 18, 6160MD Geleen, Netherlands

SUMMARY: Sequential living cationic polymerization of octadecyl vinyl ether (ODVE) and methyl vinyl ether (MVE) was used for the preparation of amphiphilic ABA-type block copolymers. The polymerization of ODVE was initiated with the trimethyl silyl iodide/1,1,3,3-tetramethoxy propane/ZnI_2 system at 0°C in toluene. The living bifunctional polyODVE thus obtained was used as initiator for the polymerization of MVE. Below the LCST of polyMVE (37°C), the copolymers are amphiphiles. Above the LCST of polyMVE, the polyMVE-blocks become hydrophobic and the amphiphilic nature of the block copolymer is lost. This was demonstrated by using the block copolymers as emulsifiers for water/decane mixtures. The emulsions were stable for several hours at room temperature, while the emulsion stability decreased to about 30 seconds at 40°C.

PolyMVE-α,ω-bis-methacrylates were obtained by end-capping of living bifunctional polyMVE with 2-hydroxyethyl methacrylate (HEMA). Copolymerization of these bis-macromers with HEMA leads to segmented networks. The networks showed a reversible swelling/deswelling behavior in water as a function of temperature. This is caused by a change of the hydrophilicity of the polyMVE segments in the networks.

Hexa(chloromethyl)melamine, combined with zinc chloride was found to be an efficient hexafunctional initiator for the living cationic polymerization of vinyl ethers. This simple initiating system opens new ways for the synthesis of endgroup-functionalized star-shaped poly(vinyl ethers).

Introduction

The possibility to polymerize vinyl ethers in a living manner has opened the way for the synthesis of a number of new, well-defined polymer structures with tailored properties[1,2)]. In this presentation, two examples will be given. First, the

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

synthesis of block-copolymers containing poly(methyl vinyl ether) (polyMVE) will be described. PolyMVE is a polymer that is water-soluble at low temperatures but becomes insoluble above a “lower critical solution temperature” (LCST), which is situated at appr. 37°C$^{3)}$. This property has been used to produce materials with temperature-controlled hydrophilicity.

In a second part, the synthesis of endgroup-functionalized, star-shaped polyVE’s with a new hexa-functional initiator system based on hexa(chloromethyl)melamine (HCMM), will be presented.

Results and discussion

Polymerization of MVE

MVE is a gaseous compound at room temperature. Therefore, a small-scale semi-continuous polymerization procedure leading to well-defined polymers has been elaborated. The system consisted of a reactor, which can be cooled to –40°C by means of an external cooling fluid, provided with a magnetic stirrer in which the solvent (toluene) can be distilled directly. Gaseous MVE, delivered by a pressure bottle, is introduced at a controlled rate by means of a gas flow controller. The initiation system was a combination of an acetal and trimethyl silyl iodide (TMSI) with zinc iodide as activator$^{4)}$. The sequence of introduction of the reagents was as follows : 1) solvent, 2) MVE to reach a starting monomer concentration of 0.4mol./l, 3) the acetal, 4) TMSI, 5) zinc iodide. Then, monomer addition is continued at a known flow rate until the desired ratio [VE]/[In] is reached. After the monomer addition has been stopped, the polymerization is continued until all monomer has been consumed and is terminated by addition of an alcohol and triethyl amine.

The reaction conditions leading to controlled polymerizations using this reaction system have been studied. It was found that a temperature of -5°C, an initiator to activator ratio of 10/1 and an addition rate of monomer corresponding to 1.16 mol/hr, leads to polymers with predictable molecular weights and narrow molecular weight distributions. Some typical results are shown in Table 1.

Table 1. Living cationic polymerization of MVE at –5°C with semi-continuous monomer addition[a)]

$[ZnI_2]$ (mmol/l)	$[I_0]$ (mmol/l)	$[M_{tot}]/[I_0]$	$\overline{M}_n$ (theo)[b)]	$\overline{M}_n$ (GPC)[c)]	$\overline{M}_w/\overline{M}_n$
2.08	8.41	201	11700	10800	1.15
2.74	10.9	153	8900	7800	1.14

a) solvent: toluene; initiator: TMP, $[I_0]$: initiator concentration, $[M]_{tot}$: total monomer concentration added

b) $\overline{M}_n$ (theo) = $73+58*[M_0]/[I_0]$

c) $\overline{M}_n$ (GPC) calibrated with polystyrene standards

It can be seen that, for molecular weights up to 10,000, the observed values are close to the ones calculated for living polymerization with quantitative initiation. The polydispersities are generally below 1.2.

Synthesis of amphiphilic block copolymers from ODVE and MVE

ODVE was polymerized at -5°C in toluene using the bifunctional initiator system 1,1,3,3-tetramethoxy propane (TMP)/TMSI/ZnI_2 system, as described earlier[5, 6)]. After completion of the polymerization, MVE was introduced at a controlled rate to produce an ABA block copolymer with the following characteristics:

$\overline{M}_n$ of the central ODVE block: 3500 ($\overline{M}_w/\overline{M}_n$=1.20)

$\overline{M}_n$ of the ABA copolymer: 7200 ($\overline{M}_w/\overline{M}_n$=1.20)

To study the emulsifying properties of the ABA copolymer an ASTM method was used[7)]. In this method, equal volumes of water and an organic solvent are mixed thoroughly with a blender and the thus formed emulsion is transferred to a graduated cylinder. The time necessary for 10% demixing is taken as a measure for the emulsion stability. In the present tests, decane was selected as the organic phase. It was already shown earlier, that polyODVE-MVE block copolymer behaves as an amphiphilic polymer, which has emulsifying properties at room temperature[8)]. Above the LCST of polyMVE (i.e. 37°C), the block copolymer is no longer amphiphilic and thus looses its emulsifying properties. This was indeed observed as shown in Fig.1 where the 10% demixing times of water – decane emulsions are plotted for different block copolymer concentrations at two temperatures. This figure demonstrates that the emulsifying properties have completely been lost at 40°C.

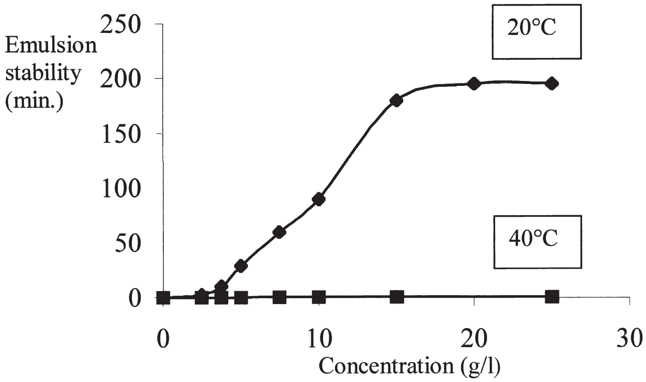
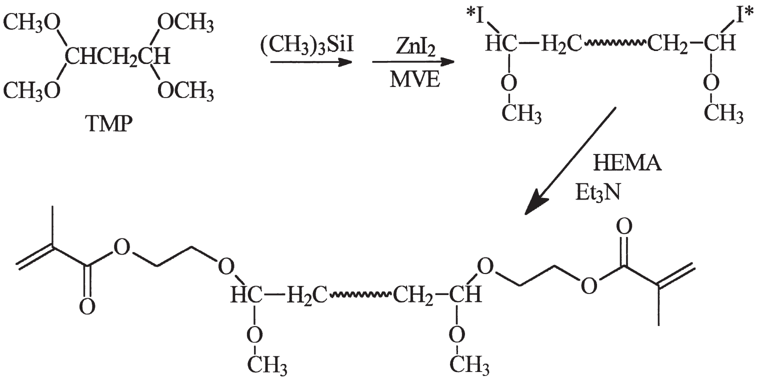


Fig. 1: Temperature dependence of emulsion stability of water-decane (50/50) mixtures as a function of block-copolymer concentration. Emulsion stability measured as the time necessary for 10% demixing.

Synthesis of segmented polymer networks containing polyMVE segments

When bifunctionally living polyMVE is terminated with 2-hydroxyethyl methacrylate (HEMA), the corresponding α,ω-bis-methacrylate is formed:



This bis-macromonomer has been copolymerized with HEMA. The resulting segmented polymer networks are hydrophilic and show considerable swelling in water at 20°C. Increase of the temperature above the LCST of polyMVE results in a drastic decrease in swelling. This is illustrated by Fig.2, in which repeated swelling – shrinking in water, of a copolymer network containing 40% of polyMVE, by repeated cooling – heating, is shown. PolyMVE networks have been prepared earlier by γ-ray induced cross-linking of linear polyMVE[9, 10)]. We believe that the use of the bis-macromonomer as starting material for the preparation of networks is more versatile and allows a control of properties by copolymerization with various comonomers.

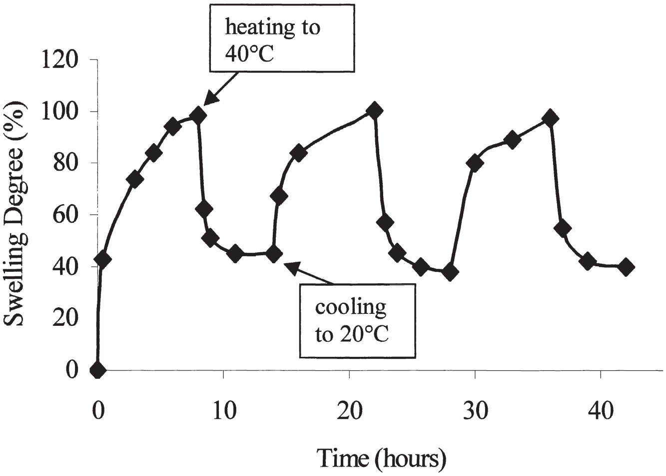
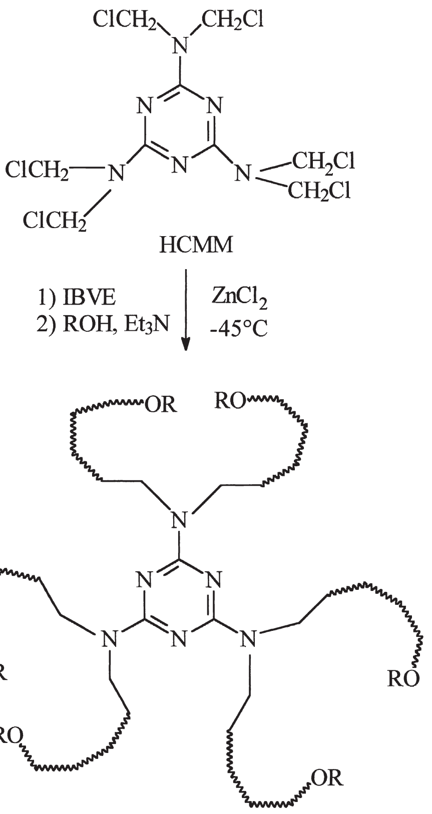


Fig. 2: Swelling-deswelling kinetics of polyMVE-polyHEMA segmented networks in water. Network composition: polyMVE/polyHEMA = 40/60 (mass).

Synthesis of star-shaped polyVE's using a new multifunctional initiator

Hexa(methoxymethyl)melamine (HMMM) reacts with boron trichloride to form hexa(chloromethyl)melamine (HCMM). It was found that HCMM, in combination with zinc chloride, was able to initiate the polymerization of VE's. The polymerizations were quantitative and were terminated with an alcohol in the presence of triethyl amine. The proposed reaction scheme is as follows:



The presence of the aromatic triazine ring in the polymer was evidenced by the observation that, in GPC analysis, a UV-absorption was detected at the elution volume of the polymer. The molecular weight distributions of the obtained polymers were relatively narrow (1.1 – 1.3) and the ratios [polymer protons]/[endgroup protons] in the H-NMR-spectrum, are in agreement with the formation of one endgroup for each chloromethyl unit in the initiator system, suggesting that a hexa-functional living polymerization has taken place. The molecular weights measured by GPC are appr. 30% lower than the values, calculated assuming the formation of a hexa-armed star-shaped polymer, which is in agreement with the fact that star-shaped polymers have a smaller hydrodynamic volume compared with that of their linear analogues of the same molecular weight.

Table 2 gives a survey of some characteristics of the polymerization and the end-products obtained with isobutyl vinyl ether (IBVE).

Table 2. Polymerization of IBVE with HCMM/$ZnCl_2$ at 0°C in toluene

$\overline{M}_n$*(calc.)*$^{a)}$	$\overline{M}_n$ *(NMR)*$^{b)}$	$\overline{M}_n$ *(GPC)*$^{c)}$	$\overline{M}_w/\overline{M}_n$
7200	6790	4530	1.28
14890	13410	9870	1.32
19900	16490	12910	1.31
31610	29220	22400	1.28

a) $\overline{M}_n$ (calc.)=([M]/[I_0])*100 + 390 (MW of HMMM)

b) $\overline{M}_n$ (NMR) from NMR peak ratio of CH_3 group of IBVE and acetal end group

c) $\overline{M}_n$ (GPC) based on polystyrene

When the polymerization was terminated by HEMA, a polymer with methacrylate endgroups was obtained. This multi-macromonomer was converted into an insoluble polymer network by exposure to air. This observation confirms that each polymer contains several endgroups.

References

1. M. Sawamoto, *Trends pol. Sci.*, **1**, 111 (1993)
2. "Cationic polymerization", K. Matyjaszewski, Ed., Marcel Dekker inc., New York (1996)
3. Moerkerke R., Mondelaers W., Schacht E., Dušek K., Šolc K., *Macromolecules*, **31**, 2223 (1998)
4. S.S. Lievens, E.J. Goethals, *Polym. Int.*, **41**, 277 (1996)
5. E.J. Goethals, W. G. Reyntjens, S.S. Lievens, *Macromol. Symp.*, **132**, 57 (1998)
6. V. Bennevault, F. Larrue, A. Deffieux, *Macromol. Chem. Phys.*, **196**, 3075 (1995)
7. ASTM-D 244 (1977): SAS-A 3742
8. S.S. Lievens, E.J. Goethals, *Polym. Int.*, **41**, 437 (1996)
9. B.G. Kabra, M.K. Akhtar, S.H. Gehrke, *Polym.*, **33**, 990 (1992)
10. R. Kishi, H. Ichijo, O. Hirasa, *J. Intel. Mat. Syst. Struct.*, **4**, 533 (1993)