

Bromine as an initiator for the oligomerization of vinylformamide (VFA)

Alexander Madl¹, Stefan Spange^{1,*}, Norbert Mahr²

¹ Department of Polymer Chemistry, Institute of Chemistry,
TU Chemnitz, Strasse der Nationen 62, 09111 Chemnitz, Germany

² BASF Aktiengesellschaft, Farbenlaboratorium, 67056 Ludwigshafen, Germany

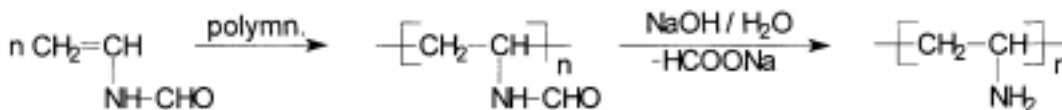
Received: 1 Juni 1999/Revised version: 2 November 1999/Accepted: 3 December 1999

Summary

Bromine was found to be an effective initiator for the cationically induced oligomerization of vinylformamide (VFA). Oligomeric products with molecular weights between 200 and 1500 g/mol were obtained. The structures of the oligo(vinylformamides) (OVFA) were investigated by means of NMR spectroscopy, GPC, and MALDI-TOF-MS. The influence of the reaction temperature on yield, DP, and head group functionality of the obtained OVFA was investigated. When the 1: 1 adduct of bromine with VFA was used as initiator at 253 K, also oligomeric products are obtained.

Introduction

Vinylformamide (VFA) is a suitable monomer for the synthesis of poly(vinylamine) (PVAm) (Scheme 1) and various other novel macromolecular architectures as recently reported(1).



Scheme 1: Polymerization of VFA and base hydrolysis of the obtained PVFA to PVAm

These macromolecules are important precursors for synthesising novel polyelectrolytes (1), (2). Oligo(vinylamines) with molecular weights between DP (degree of polymerization) = 3 to DP = 15 are of interest as cationically multifunctional polyelectrolyte building blocks for hybrid materials and block-copolymers. Oligomeric products of VFA can be obtained by cationic initiation of VFA by several initiators (3), (4). An acid or base hydrolysis of these oligomeric products leads to oligo(vinylamine) (OVAm) (4).

Recently, we reported on the cationically induced initiation of oligomerization of VFA by iodine and arylmethylchloride/silica (4). In the previous paper we reported a systematic study of the influence of the reaction temperature and the monomer/initiator

* Corresponding author

ratio on the structure and yield of the OVFA (5). Iodine, trifluoromethanesulfonic acid (HOTf), and trifluoromethanesulfonic acid trimethylsilylester (trimethylsilyl triflate, TMST) were used as initiators. Below 193 K, bromine adds upon VFA to N-(1,2-dibromomethyl)-formamide (4). Commonly, the adduct of bromine upon vinyl monomers is stable. But we found, that bromine serves as initiator for the oligomerization of VFA at higher temperatures than 193 K.

There are only few articles describing the use of bromine as initiator for cationic polymerization. A Japanese group reported that the vapour of halogenes (activity: iodine > bromine > chlorine) initiates the cationic polymerization of N-vinylcarbazole (NVC) (6). Together with diethylchloroaluminium (7) or trimethylaluminium (8) compounds, bromine acts as initiator for the cationic polymerisation of isobutene and styrene, but its own initiating activity is negligible for this purpose. More recently the use of bromine as initiator for the cationic ring-opening polymerization of cyclopropanone ketals was also reported (9).

The motivation for this study was the detailed investigation of the bromine induced initiation and oligomerization of VFA at different reaction temperatures, because bromine functions in oligomers are suitable for a lot of derivatization reactions.

Experimental

All experiments were carried out under purified argon atmosphere to exclude the effects of oxygen and moisture.

Reagents

Solvents were dried and purified by standard methods. They have been distilled freshly over CaH₂ or sodium before use. Vinylformamide (VFA) was provided by BASF Aktiengesellschaft, Ludwigshafen and distilled under vacuum over a Vigreux column before use. Bromine was used without further purification.

Measurements

¹H and ¹³C NMR spectra were recorded on a Varian Gemini 300 FT-NMR spectrometer using D₂O or CD₂Cl₂ as solvent. GPC was conducted with a UV-detector Gilson Typ 116 (212 nm) at 23 °C with a TSK PW-XL 3000 and TSK PW-XL 4000 column series using water / acetonitrile (90:10) as eluent (flow rate 0.5 ml/min). The molecular weight measured by GPC was calculated from the calibration curve for poly(vinylpyrrolidone) (PVP). MALDI mass spectra were recorded on a „Biflex“ instrument (Bruker Franzen Analytik GmbH, Bremen) equipped with a nitrogen laser and a linear mass analyzer. Acceleration voltage was 30 kV. As matrix IAA (indole acrylic acid; 50 mg/ml in methanol) was used, the concentration of the analyt was 10 mg/ml in water. In the spectra of the OVFA cationization by sodium and potassium is observed.

Oligomerization procedure according to Ref. (5)

14.3 µl (0.28 µmol) bromine were added by a syringe to a thermostated solution of 2.0 ml (2.024 g, 0.028 mol) VFA ([M]/[I] = 100) in 25.0 ml Toluene ([VFA] = 1.12 mol/l) in a polymerization tube equipped with a septum. The reddish-orange colour of the bromine disappeared immediately. After 0.5 to 2 hours the oligomer precipitated. The polymerization tube was stored for further 22 hours. After removing the solvent the

crude oligomer was dissolved in dry methanol, reprecipitated in dry acetone, filtrated and washed several times with acetone and dried under vacuum at 60 °C.

IR (solid, DRIFT): 3300 cm^{-1} (br, $-\text{NH}-\text{C}=\text{O}$), 3050 cm^{-1} (s, $-\text{C}=\text{C}-$), 2870 cm^{-1} (s, $-\text{CH}-$), and 1712 cm^{-1} (s, $-\text{NH}-\text{C}=\text{O}$).

^1H NMR (D_2O): $\delta = 1.0 - 1.3$ ppm ($-\text{CH}_3$ head group), 1.5 - 2.3 ppm ($-\text{CH}_2-$ chain), 3.2 - 4.1 ppm ($-\text{CH}-$ _{cis and trans} chain and $\text{Br}-\text{CH}_2-$ head group), 4.4 - 4.6 ppm ($-\text{OCH}_3$ terminal group), 5.3 - 5.6 ppm ($-\text{CH}=\text{}$ terminal group), 6.7 - 6.9 ppm ($=\text{CH}-$ terminal group), and 7.6 - 8.3 ppm ($-\text{CHO}$ side groups).

^{13}C NMR (D_2O vs benzene as external standard): $\delta = 17.0 - 18.5$ ppm ($-\text{CH}_3$ and $\text{Br}-\text{CH}_2-$ head groups), 38.5 - 42.0 ppm ($-\text{CH}_2-$ chain), 42.5 - 45.0 ppm ($-\text{CH}-$ chain), and 162.5 - 169.0 ppm ($-\text{CHO}$ side groups).

Calculation of the degree of polymerization from the NMR data

The average degree of polymerization (DP) was determined from the ratio of the normalized integral (NI) of the $-\text{CHO}$ side group to the NI of the $-\text{CH}_3$ and $-\text{CH}_2-\text{Br}$ head groups:

$$\text{DP} = \text{NI}[-\text{CHO}]/(\text{NI}[-\text{CH}_3] + \text{NI}[-\text{CH}_2-\text{Br}]) \quad (1)$$

The mole fraction of the bromomethylene head group of oligomers was determined from the ratio of the NI of the $-\text{CH}_2-\text{Br}$ head group to the sum of the NI of both ($-\text{CH}_3$ and $-\text{CH}_2-\text{Br}$) head groups:

$$-\text{CH}_2-\text{Br} (\%) = 100 \cdot \text{NI}[-\text{CH}_2-\text{Br}]/(\text{NI}[-\text{CH}_3] + \text{NI}[-\text{CH}_2-\text{Br}]) \quad (2)$$

The ratio of the NI of the $-\text{CH}_2-\text{Br}$ head groups was taken from difference between the NI of the $-\text{CH}_2-$ chain protons and the whole integral of the overlaid signals of the $-\text{CH}-$ chain protons and the $-\text{CH}_2-\text{Br}$ head groups.

The results reported in this paper are the average values from six runs of each examined reaction temperature.

Characterization of 1,2-dibromoethyl formamide

39.5 μl (40.0 mg, 0.571 mmol) VFA in 0.8 ml CD_2Cl_2 were placed in a NMR tube and cooled to 193 K. Then the spectrum of the monomer was recorded. 30.0 μl (91.0 mg, 0.571 mmol) bromine was added at 193 K and a new spectrum was recorded. 1,2-dibromo ethyl formamide is obtained in quantitative (100 %) yield. An isolation of the product was not possible due to decomposition at higher temperature.



^1H NMR (CD_2Cl_2): $\delta = 3.97$ ppm (d, 2H, $\text{Br}-\text{CH}_2-$), $\delta = 6.36$ ppm (m, 1H, $-\text{CHBr}-$), $\delta = 7.40 - 7.80$ ppm (br, $-\text{NH}-$), $\delta = 8.30$ ppm (s, 1H, $-\text{CHO}$)

^{13}C NMR (CD_2Cl_2): $\delta = 34.1$ ppm (t, $\text{Br}-\text{CH}_2-$), $\delta = 52.7$ ppm (d, $-\text{CHBr}-$), $\delta = 160.8$ ppm (s, $-\text{CHO}$)

Oligomerization procedure with 1,2-dibromoethyl formamide as initiator

In a polymerization tube, 14.3 μ l bromine were dissolved in 25.0 ml dichloromethane and cooled to 193 K. Then, 2.0 ml (2.024 g, 0.028 mol) VFA ($[M]/[I] = 100$) were added slowly with stirring. The reddish-orange colour of the bromine disappeared immediately, but no oligomer was precipitated. The temperature was allowed to increase slowly to 253 K in the next 4 hours, and the tube was stored for additional 20 hours. After storing the tube 0.5 to 2 hours at 253 K the oligomer precipitated. The working up procedure is the same as described.

Results and discussion

The bromine initiated oligomerization of VFA was performed analogously to the oligomerization procedures with the other initiators (iodine, HOTf, and TMST) (5). The temperature range for the oligomerization reaction was between 253 K and 313 K. Temperatures below 253 K are not suitable for the cationic oligomerization of VFA, because the yields of OVFA are too low. At 193 K, bromine addition upon the VFA exclusively occurs. The oligomerization process is observed when the reaction temperature is allowed to increase upon 253 K. Above 313 K, VFA tends to self-reactions and a thermally induced polymerization is observed. Then a controlled polymerization is not possible.

The NMR spectra of the OVFA products, obtained by initiation with bromine, show the same signals than do the spectra obtained by them with iodine as initiator since the same reaction procedure is used [Fig. 1 (II)]. A rather intense signal at 1.0 - 1.3 ppm indicates methyl head groups. These groups and the olefinic terminal groups are caused by the strong proton transfer reaction among the oligomerization process (4, 5).

The determination of the degree of polymerization and the head group functionality of the OVFA from the NMR spectra was difficult to achieve, because the signals of the Br-CH₂-head groups are shifted downfield compared to the I-CH₂-head groups. Therefore, the signals of the Br-CH₂-head group are overlaid with the signals of the methine protons of the polymer chain. For this reason, the normalised integral of the Br-CH₂-head groups was taken from the difference between the normalised integrals of the methylene chain protons and the whole integral set between 3.2 and 4.1 ppm, for both methine chain protons and head groups.

Since the oligomerization of VFA is started from the in situ produced 1,2-dibromoethyl-formamide, a oligomeric product is obtained, too. The NMR spectra of this product shows the signals of the chain protons and of the head and terminal groups [Fig. 1 (I)]. Among these signals, some not assignable signals are detected at 1.3 - 1.5 ppm, 2.0 - 2.4 ppm (shoulder), 3.7 - 3.8 ppm (shoulder), and 8.2 ppm (arrows in Fig. 1).

A GPC-analysis and MALDI-TOF-MS was performed for some representative samples. The collected results of the NMR- and GPC-analysis of the samples obtained at different reaction temperatures are shown in Tab. 1.

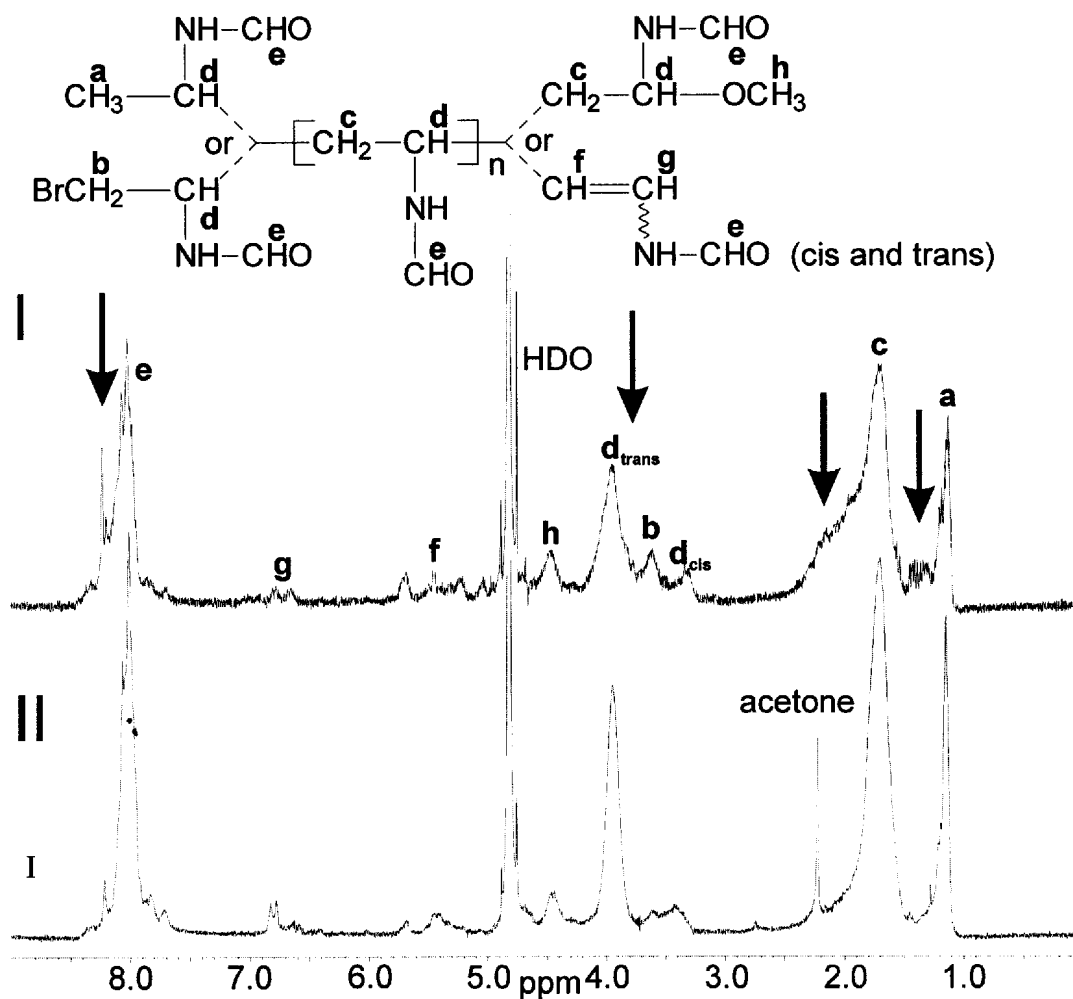


Fig. 1: ^1H NMR spectra (300 MHz, D_2O) of OVFA and assignment of the signals to the structure of OVFA I) obtained from in situ at 193 K prepared 1,2-Dibromoethylformamide at 253 K polymerization temperature, II) obtained by initiation with bromine ($[\text{VFA}] = 1.12 \text{ mol/l}$, $[\text{M}]/[\text{I}] = 100$, solvent: toluene) at 313 K reaction temperature, samples were reprecipitated from methanol in acetone

Molecular weights of the OVFA can either be calculated from the DPs, obtained from the head group analyses of the NMR spectra, or taken from the GPC analysis. The comparison between the values from the head group analysis and the detected values from the GPC, shows distinctly higher molecular weights for the GPC analysis. The molecular weight determined by GPC was calculated from the calibration curve of PVP standards. PVFA standards are still not available. Therefore, it is impossible to calculate absolute molecular weights from the GPC plots. It is obvious, that the highly polar polymer OVFA or PVFA interact with the columns of the GPC and not only size exclusion occurs. The MWDs of the analyzed oligomers are between 1.2 and 1.3. The same result was obtained for the oligomers, produced by iodine initiation of VFA. The rather small MWD shows the uniformity of the samples.

Tab. 1: Results of the oligomerization of VFA with bromine as initiator ($[VFA] = 1.12$ mol/l, initiator: bromine, $[M]/[I] = 100$, solvent: toluene) shown by the NMR- and GPC-analysis of the obtained products in dependence on the reaction temperature

T [K]	Yield [%]	DP (NMR) ¹	M _n [g/mol] (NMR) ²	Br-CH ₂ - [%] (NMR) ¹	Br [%] ³	M _n [g/mol] (GPC)	M _w [g/mol] (GPC)	M _w /M _n (GPC)
195/253	20.3	10.0	710	-	24.6	940	1090	1.2
253	10.7	9.2	653	35.4	10.8	1440	1770	1.2
273	34.1	9.0	639	20.1	4.8	1580	2045	1.3
293	47.7	6.9	490	10.9	3.4	1350	1700	1.3
313	42.2	5.3	376	4.0	3.9	1050	1300	1.3

1 calculated from the NMR-data

2 calculated from DP (NMR) with $M = 71$ g/mol, head groups were not considered

3 from quantitative elemental analysis

The MALDI-TOF-MS of two OVFA samples, obtained by bromine initiation at 253 K and 293 K reaction temperature, are shown in Fig. 2. According to the NMR-spectra, the MALDI-TOF-MS also agree with those obtained from the OVFA samples, obtained by iodine initiation (5). The MALDI-TOF-MS of the two samples, obtained at different reaction temperature, show quite different structures. In spite to the uniformity of the OVFA, as shown by GPC analysis, a multimodal distribution is observed in both MALDI-TOF-MS. Each of the single distributions has a repetition unit of 71 Dalton (Da) that corresponds to a monomeric unit. For the sample obtained at 293 K, the main distribution represents OVFA with a methyl-head group and an olefinic terminal group. A minor distribution represents OVFA with a methyl-head group and a methoxy terminal group. The detected structures corresponds to the ¹H NMR spectra of the samples.

The -CH(-NH-CHO)-OCH₃ end group results from the methanolysis of a -CH(-NH-CHO)-Br group after pretreatment with methanol during the purification step. The -CH(-NH-CHO)-Br terminal group is obtained by a counter ion termination of the growing cationic chain. The occurrence and the methanolysis of such terminal groups was also observed for the cationic polymerization of other vinyl monomers (10).

A third important distribution contributes also to both MALDI-TOF-MS. For this distribution, the m/z of the terminal group can be calculated with 44 Da. It is the main distribution for the sample obtained at 253 K. No chemical structure could be assigned to this group. According to the arguments mentioned for the iodo-methylene head group, it is assumed that the Br-CH₂- bonds were cleaved under MALDI conditions. Control experiments show that halogen carbon bonds remain not stable under the conditions used (11). Therefore, the oligomers with these head and end groups may be the result of the decay of the bromo functionalized oligomers.

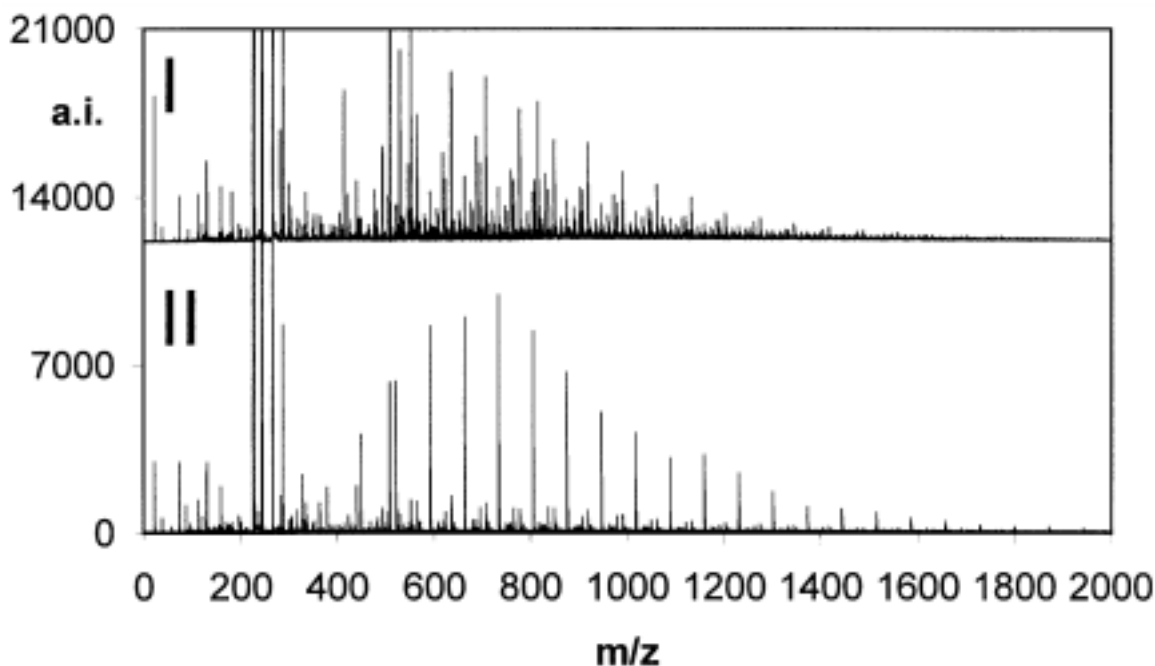


Fig. 2: MALDI-TOF-MS of OVFA, obtained with bromine initiation ($[VFA] = 1.12$ mol/l, $[M]/[I] = 100$, solvent: toluene) at I) 253 K and II) 293 K

The structure characterisation of the obtained OVFA samples by NMR spectroscopy and MALDI-TOF-MS clearly shows that initiation with bromine leads to carbon-carbon linked polymer chains. It is also shown that the results of the NMR spectroscopy and the MALDI-TOF-MS provide the same molecular weights in contrast to the results of the GPC. The molecular masses found with the MALDI-TOF-MS are between 200 and 1500 g/mol, with a maximum at 500 g/mol. From the NMR spectra average molecular masses of about 400 - 700 g/mol are calculated. The GPC provides considerably higher molecular weights. This result supports our interpretation that beside the size exclusion a specific effect influences the GPC separation of VFA.

The dependence of the results of the oligomerization on the reaction temperature is in accordance to those for iodine, HOTf, and TMST as initiators (5). The yield increases with increasing reaction temperature. The DP decreases slightly with increasing temperature. The comparison of the obtained DPs of the OVFA of about 5 - 10 with the monomer/initiator-ratio of $[M]/[I] = 100$ shows, that the bromine induced oligomerization of VFA is dominated by transfer reactions. After each 5th to 10th propagation step (in dependence of the reaction temperature) a transfer step occurs. Both the degreasing head group functionality and bromine content with increasing reaction temperature show the dominance of proton transfer reactions.

Surprisingly, at a certain reaction temperature the yield, the DP, and the head group functionality are the same for bromine as for the other initiators (5). That means, the cationically induced oligomerization of VFA occurs independent of the counter ion. For a cationic growing the initiator activity should increase with decreasing nucleophilicity of the counter ion ($Br^- \gg I^- > Otf^-$). The obtained results are a strong hint at contributions of non-ionic propagation steps for the cationically induced oligomerization of VFA. This subject is still under investigation (12).

Nevertheless, bromine is suitable as an efficient initiator for the oligomerization of VFA. OVFA is also obtained when the in situ generated 1:1 adduct from bromine and VFA is used as the initiator, as shown by NMR- and GPC analyses. Using the dibromide adduct as the initiator, an increase of the yield and the bromine content of OVFA is detected. A further investigation on the real structure of this oligomeric product by means of MALDI-TOF-MS is still under performing.

Since bromine is suitable as initiator for the cationically induced oligomerization of VFA rather than for vinyl ethers or other vinyl monomers, excluding the highly reactive NVC, it is assumed that the nucleophilicity of VFA is placed between those of vinyl ethers and NVC (13).

Acknowledgement

Financial support by the DFG „Schwerpunktprogramm Polyelektrolyte“, the Fonds der Chemischen Industrie, and BASF Aktiengesellschaft Ludwigshafen, Germany, is gratefully acknowledged.

References

1. a) Pinschmidt, Jr. RK, Renz WL; Carroll WE, Yacoub K, Drescher J, Nordquist AF, Chen N (1997) *J. Macromol. Sci. Pure Appl. Chem.* A34:1885
 b) Dawson DJ, Gless RD, Wingward, Jr. RE (1976) *J. Am. Chem. Soc.* 98:5996
2. Badesso, RJ, Nordquist, AF, Pinschmidt, Jr. RK, Sagl, DJ (1996) *Adv. Chem. Ser.* 248:489
3. a) US 5, 280, 077 (1994) Air products Chemicals, invs.: Carroll WE, Pinschmidt RU [CA 120:299557]
 b) DE 44 03519 (1994) Mitsubishi Kasai Corp., invs.: Kobayashi S, Uyama H, Sawayama S, Satoh K [CA 122:56829]
 c) US 5,373,076 (1994) Air products chemicals, invs.: Pinschmidt, Jr. RU, Carroll WE [CA 122:315375]
4. Spange S, Madl A, Eismann U, Utecht J (1997) *Macromol. Rapid Commun.* 18:1075
5. Madl A, Spange S, Waldbach T, Anders E, Mahr N (1999) *Macromol. Chem. Phys.* 200:1495
6. Okumara S, Higashimura T, Matsuda T (1966) *Kobunshi Kagaku* 23:273 [CA 66:18876]
7. Baccaredda M, Bruzzone M., Cesca S, DiMaina M (1973) *Chim. Ind. (Milan)* 55:109
8. Kennedy JP, Sivaram S (1973) *J. Macromol. Sci., Chem.* 7:969
9. Cook GA, Butler GB (1985) *J. Macromol. Sci., Chem.* A22:507
10. a) Higashimura T, Miyamoto M, Sawamoto S (1985) *Macromolecules* 18:611
 b) VanMeirvenne D, Haucourt N, Goethals EJ (1990) *Polym. Bull.* 23:185
 c) Nuyken O, Rieß G (1995) *Macromol. Reports* A32:25
11. W. Schrepp, BASF Aktiengesellschaft Ludwigshafen, unpublished results communicated to the authors
12. Madl A, Spange S (1999) *Macromolecules*, to be submitted
13. Gandini A, Cheredame H (1980) *Adv. Polym. Sci.* 34/35:4