Controlled Cationic Polymerization of N-Vinylcarbazol

Nuyken, O.; Rieß, G.; Loontjens, J.A.

Published in:
Journal of Macromolecular Science. Part A: Pure and Applied Chemistry

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1995

Citation for published version (APA):
Nuyken, O., Rieß, G., & Loontjens, J. A. (1995). Controlled Cationic Polymerization of N-Vinylcarbazol. *Journal of Macromolecular Science. Part A: Pure and Applied Chemistry*, *32*(1), 25-38.

MACROMOLECULAR REPORTS, A32(SUPPLS. 1&2), 25-38 (1995)

CONTROLLED CATIONIC POLYMERIZATION OF N-VINYLCARBAZOL

O. Nuyken*, G. Rieß
Lehrstuhl für Makromolekulare Stoffe
Technische Universität München
Lichtenbergstr. 4, D-85747 Garching, Germany
J.A. Loontjens
DSM, R & D, PO Box 18
NL-6160 MD Geleen, The Netherlands

ABSTRACT

Cationic polymerization of N-Vinylcarbazol (NVC) was initiated with 1-iodo-1-(2-methylpropyloxy)ethane (**1**) in the presence of $N(n\text{-}Bu)_4ClO_4$ and without addition of this activator. Furthermore, 1-chloro-1-(2-methylpropyloxy)ethane (**2**), with and without activator has been applied as initiator for NVC. These initiating systems show remarkable differences in activity, which are discussed in detail.

INTRODUCTION

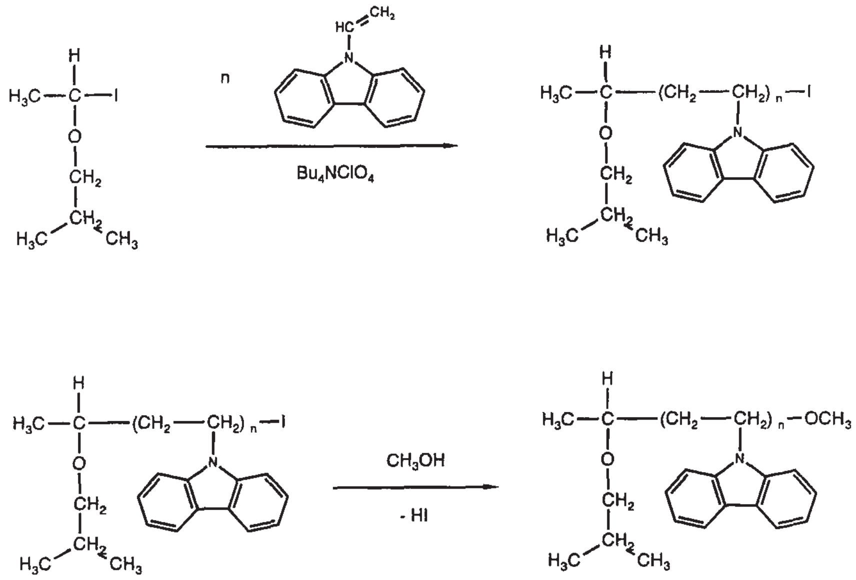
N-vinylcarbazol (NVC) is very reactive towards Brønsted and Lewis acids and other cationic initiators[1,2]. Due to this reactivity, its polymerization is rather fast and therefore difficult to control. Normally, low concentrations of monomer and initiators and low temperatures are applied. Neither molar masses nor their distribution were controlled. This situation has improved with the discovery of "living" systems for NVC by Higashimura et al[3-5]. Recently, an alternative route for cationic living polymerization was found in our laboratory[6-8], in which 1-iodo-1-(2-methylpropyloxy)ethane (1)/$N(n\text{-}Bu)_4ClO_4$ was used for the polymerization of vinylether.

Excellent control of molar masses over a wide range and narrow molar mass distributions observed for different vinylethers forced us to study scope and limitation of this initiating system for NVC.

RESULTS AND DISCUSSION

INITIATION OF NVC WITH **1**/$N(n\text{-}Bu)_4ClO_4$

The polymerization of NVC was carried out at low temperatures in dichloromethane according to the following reaction scheme:



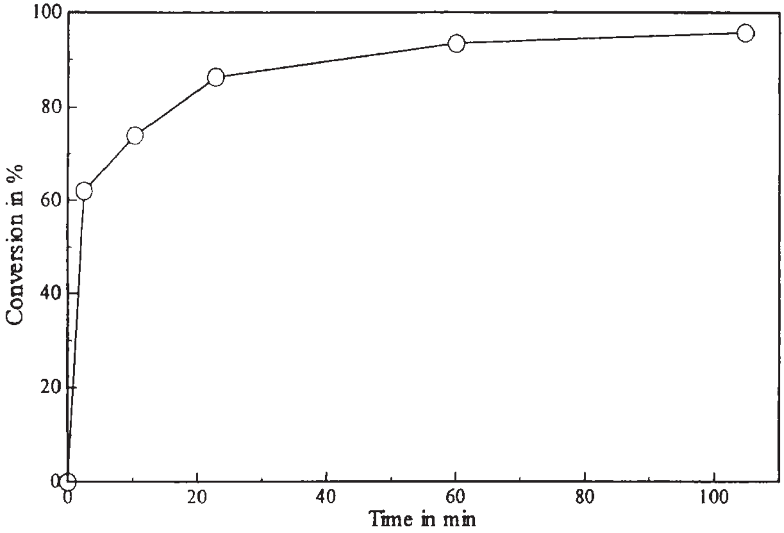


FIG. 1: Polymerization of NVC in CH_2Cl_2 at -70°C
$[NVC]_o = 0{,}46 \text{ mol l}^{-1}$, $[\mathbf{1}] = 0{,}0055 \text{ mol l}^{-1}$
$[N(n\text{-}Bu)_4ClO_4] = 0{,}0097 \text{ mol l}^{-1}$

A typical experiment is presented in FIG. 1 and TABLE 1. The theoretical molar masses were calculated on the basis of the following equations:

$$M_n(\text{calc.}) = M_M \bullet [M]_o/[I] \bullet C + M_{Head} + M_{End} \qquad (1)$$

M_M= molar mass of the monomer
M_{Head}= molar mass of the head group
M_{End}= molar mass of the end group
[I]= initial concentration of the initiator
$[M]_o$= initial concentration of the monomer
C = conversion
conversion was determined via ^{1}H NMR (Fig. 2)

$$I_1 + I_2 + I_3 = I_M + I_p \qquad (2)$$

I_1 = aromatic protons of monomer and polymer and <u>one</u> olefinic proton of the monomer

TABLE 1

Polymerization of NVC in CH_2Cl_2 at -70°C

$[NVC]_o$ = 0,46 mol l^{-1}, [**1**] = 0,0055 mol l^{-1}

$[N(n\text{-}Bu)_4ClO_4]$ = 0,0097 mol l^{-1}

t min	C %	M_n(GPC)[1)] g mol^{-1}	M_n(calc.) g mol^{-1}	M_w/M_n
25	62,6	1980	10250	4,55
10	73,9	2060	12080	5,0
22,5	86,6	3240	14130	4,45
60	93,5	3890	15240	3,97
105	96,1	4130	15660	3,83

---

1) calibrated with polystyrene standards

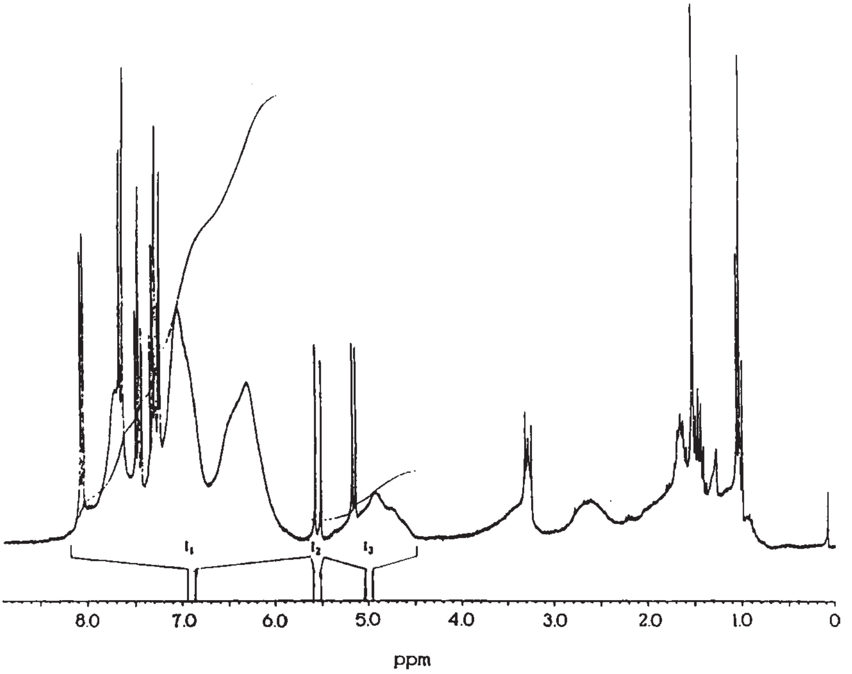


FIG. 2: ^1H NMR of Poly(NVC) in $CDCl_3$ after 86 % conversion

I_2 = one olefinic proton of the monomer

I_3 = olefinic protons of the monomer and aromatic protons of the polymer

I_M = all monomer protons (11H)

I_p = all aromatic polymer protons (8H)

$$I_M = 11 \times I_2 \qquad (3)$$

from (2) and (3) follows:

$$I_p = I_1 - 10I_2 + I_3 \qquad (4)$$

$$I_p(1) = I_p/8 \qquad (5)$$

(equivalent for <u>one</u> aromatic polymer proton)

$$\frac{n_M}{n_p} = \frac{I_M(1H)}{I_p(1H)} = \frac{I_2}{I_p(1H)} \qquad (6)$$

n_M = number of mole of M at t = t

n_p = number of mole of P (units in polymer) at t = t

$$\text{with } C = \frac{n_p}{n_M + n_p} \qquad (7)$$

$$C = \frac{1}{1 + I_2/I_p(1H)} \qquad (8)$$

$$= \frac{1}{1 + I_2/\left(\frac{I_1 - 10I_2 + I_3}{8}\right)} \qquad (9)$$

As one can see from table 1 molar masses are not controlled by the ratio [M] : [I] - they are smaller than calculated. These results can be explained on the basis of chain transfer reaction taking place under conditions applied here.

INITIATION WITH **1** (WITHOUT ACTIVATOR)

The main reason for the rather disappointing results described in the former chapter are most likely due to transfer reactions. These side reactions can be reduced by suppressing the activity of active center (e.g. assuming that ion pairs are less active than free ions). This concept is successfully applied to ionic polymerizations (cationic polymerization: addition of donors[9]; anionic polymerization: conversion of a carbanion into a Grignard reagents for controlled termination with CO_2[10]).

In case of the NVC polymerization, deactivation is realized by reducing of the activator (salt) concentration down to [activator] = 0. The polymerization characteristics can be explained by including a reversible termination step into the reaction scheme[11]:

Table 2 summarizes results of a NVC polymerization initiated with 1 but without $N(nBu)_4ClO_4$. The polymerization is slower as in the presence of the activating salt even at temperatures 20 to 30 degree higher than applied before (table 1).

It is interesting to note that no polymerization was observed in toluene. However, increasing of polarity by addition of dichloromethane to toluene allows polymerization which becomes faster with increasing amount of CH_2Cl_2. Simultaneous with polarity broadening of the molar mass distribution was observed. Relatively good agreement between calculated and observed molar masses was found in all cases.

Molar masses increase linearelly with conversion.

Conversion of the monomer was followed by GC using xylene as internal standard.

TABLE 2:

Polymerization of NVC with **1**

t = 2 hrs, $[NVC]_o$ = 0,15 mol l^{-1}

T °C	[1] mol l^{-1}	solvent	C %	M_n(GPC)	M_n(calc)[1)]	M_w/M_n
-50	0,0069	CH_2Cl_2	95	3940	4120	2,63
-50	0,0085	toluene	0	-	-	-
-50	0,0076	CH_2Cl_2/ toluene 1:3[2)]	22	1280	970	1,41
-50	0,0084	CH_2Cl_2/ toluene 3:1[2)]	53	1720	1960	1,33
-40	0,0073	CH_2Cl_2	100	5490	4100	2,31
-40	0,0073	toluene	0	-	-	-
-40	0,0075	CH_2Cl_2/ toluene 1:3[2)]	33	1470	1410	1,36
-40	0,0078	CH_2Cl_2/ toluene 3:1[2)]	67	2520	2620	1,27

1) calculated, using equ. 1

2) vol./vol. ratio

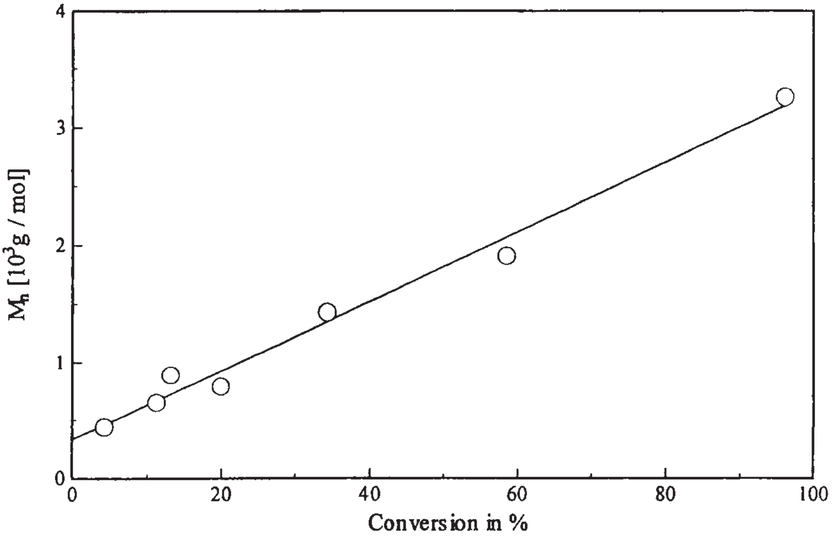


FIG. 3: Linear relationship between M_n and conversion for the polymerization of NVC in CH_2Cl_2/toluene at -50°C (3:1 vol. ratio) [M] = 0,15 mol l^{-1}, [I] = 0,01 mol^{-1} [salt] = 0

$$C = \frac{(A_M/A_{St})_o - (A_M/A_{St})_t}{(A_M/A_{St})_o} \qquad (10)$$

$(A_M/A_{St})_o$ = ratio of GC peaks of monomer/standard at t = 0

$(A_M/A_{St})_t$ = ratio of GC peaks of monomer/standard at t = t

The time conversion curve is given in Fig. 4.

Table 3 summarizes the results of a typical experiment. The discrepancy between calculated and observed molar masses is propably due to the calibration of the GPC with polystyrene standards.

M_n (GPC) and M_n (calc.) are getting closer with increasing molar masses meaning that the chemical nature

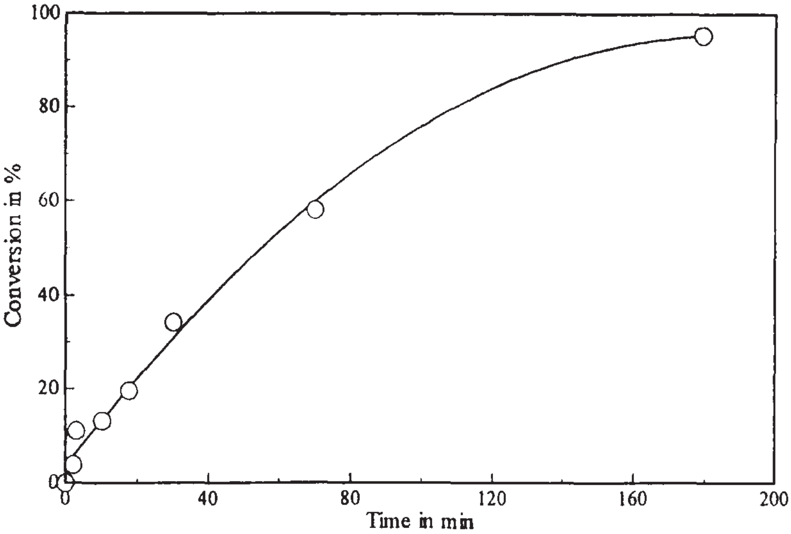


FIG. 4: Polymerization of NVC in CH_2Cl_2/toluene (3:1), at -50°C $[NVC]_o$ = 0,15 mol l^{-1}, [**1**] = 0,01 mol l^{-1}

TABLE 3:
Polymerization of NVC initiated by **1**
in CH_2Cl_2/toluene (3:1 (vol)).
$[NVC]_o$ = 0,15 mol l^{-1}, [**1**] = 0,01 mol l^{-1}, T = -50°C

t/min	2	3	10	15	30	70	180
C/%	4	11	13,1	19,6	34,1	58,3	95,8
M_n(GPC)	440	650	880	800	1440	1930	3200
M_n(calc)	250	450	510	700	1120	1820	2910
M_w/M_n (GPC)	1,55	1,50	1,48	1,45	1,45	1,43	1,40

becomes less important for the separation process of the GPC column with increasing molar masses.

The consumption of monomer follows first order kinetics (Fig. 5)

$$-d[M]/dt = k'[M] \qquad (11)$$

$$k' = k\ [\mathbf{1}] \qquad (12)$$

The growing chains remain active or can be activated again. This was clearly demonstrated by a monomer-addition-experiment in which, after 100%-consumption of a first portion of monomer a second portion leads to an increase of molar masses (Table 4).

This observation opens an interesting perspective for the synthesis of block copolymers by a sequential addition of different monomers[12].

INITIATION WITH 1-CHLORO-1(2-METHYLPROPYLOXYETHANE)(**2**) WITH AND WITHOUT $N(n\text{-}Bu)_4ClO_4$.

It would be of great advantage if initiator **1** could be replaced by **2**. **2** is not only cheaper then **1** but also more stable and therefore easier to handle. In contrast to **1** polymerization of NVC was observed only if **2** was used in combination with the activating salt.

However, broad molar mass distributions and discrepances between calculated and observed molar masses show that this reaction needs further optimization before it can be applied for a controlled polymerization (Table 5).

EXPERIMENTAL PART

INSTRUMENTS

IR: Digilab FTS-40; ^{1}H NMR: Bruker AC 250 (250 MHz); ^{13}C NMR: Bruker AC 250 (62,5 MHz); GPC: Waters 510, UV and RI detector (590); calibration with polystyrene'

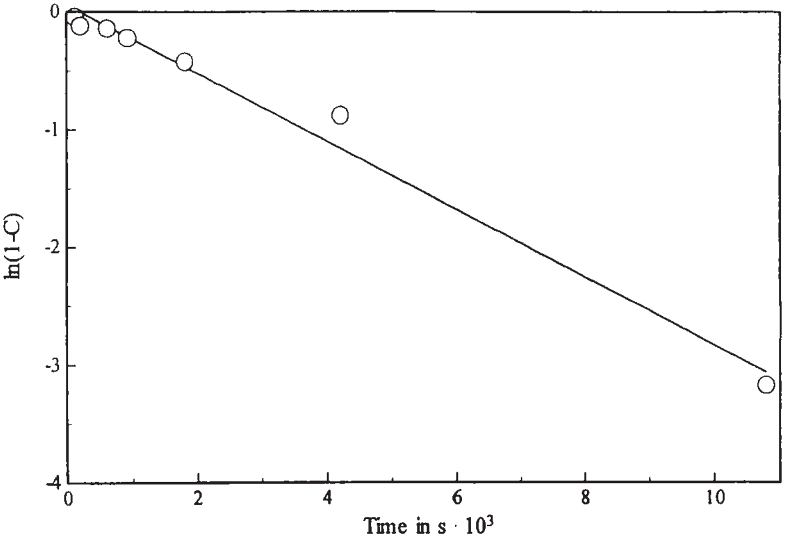


FIG. 5: First order kinetics for the polymerization of NVC with **1** in CH_2Cl_2/toluene (3:1) at -50°C

TABLE 4:
Polymerization of NVC initiated with **1**
in CH_2Cl_2/toluene (3:1 (vol.))
T = -50°C, t = 3,5 h for each portion of monomer

	NVC mol l^{-1}	[**1**] 10^3 mol l^{-1}	C %	M_n(GPC) g mol^{-1}	M_n(calc) g mol^{-1}	M_w/M_n
1.Add.	0,15	8,2	100	4430	3670	1,54
2.Add.	0,13	6,8[a)]	91	6980	7030	1,43

a) conc. decreases, because a monomer solution was added

TABLE 5:
NVC polymerization in CH_2Cl_2
initiated by **2**/$N(n\text{-}Bu)_4ClO_4$
[NVC] = 0,5 mol l^{-1}, [**2**] = 0,024 mol l^{-1}, t = 90 min

T °C	$N(n\text{-}Bu)_4ClO_4$ mol l^{-1}	C %	M_n(GPC)	M_n(calc)	M_w/M_n
-65 to -20	0,022	100	56000	4160	2,94
-65 to -20	0	0	-	-	-
-15 to 0	0,022	100	9100	4160	2,84
-15 to 0	0	0	-	-	-

standards, eluation with THF; GC: Varian GC 3700; column CP SIL 5CB, Chrompack 9000: Column CP SIL 5CB; Cryostate: Lauda UK 8 DN.

CHEMICALS

Toluene, xylene were distilled over sodium before use. CH_2Cl_2 was refluxed over CaH_2 and freshly distilled before each experiments.

N-vinylcarbazol (Fluka) was recrystallized from n-hexane. Isobutylvinyl ether (Fluka) was refluxed over CaH_2 and freshly distilled before use. $N(n\text{-}Bu)_4ClO_4$ (Fluka) was dried for 24 hrs under high vacuum conditions and stored under argon.

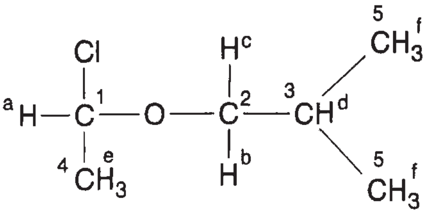
1-Iodo-1(2-methylpropyloxy)ethane (**1**)

It was synthesized as described in the literature[6].

1-Chloro-1(2-methylpropyloxy)ethane (**2**)

HCl-gas was bubbled through a solution of 16,5 g (0,125 mole) para aldehyde in 27,7 g (0,374 mole) 2-methyl-1-propanol for 1 hr. Two phases (organic phase and water) are formed at the end of the reaction. The organic phase

was dried over $CaCl_2$ and then the solvent was distilled off. Yield: 22 g (43%)
b.p. : 38-39°C (30 mbar)
^1H NMR ($CDCl_3$) δ (ppm): 5,05 (q, H^a), 3,67 (dd, H^b), 3,20 (dd, H^c), 1,95 (m, H^d), 1,76 (d, H^e), 0,90 (d, H^f)



^{13}C NMR ($CDCl_3$) δ (ppm): 96,3 (C^1), 77,1 (C^2), 27,9 (C^3), 26,7 (C^4), 1,91 (C^5)

POLYMERIZATION OF NVC

The thermostated polymerization apparatus equipped with thermostated dropping funnel, 3-way tap, thermometer septum and stirring bar was carefully dried before use (heated to 150°C for 12 hrs, cooled under dry argon). Then the apparatus was filled with monomer solvent, activator (if neccassary). The polymerization was started by the addition of prechilled solution of **1** (or **2**) in the corresponding solvent.
The reaction temperature was kept constant with a cryostate. Samples were taken through the septum during polymerization.

ACKNOWLEDGEMENT

The authors wish to thank DSM for financial support and Drs. v.d. Linde and Derks for helpfull discussions.

REFERENCES:

1. J. M. Rooney in G. Allen, J. C. Bevington, G. C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt (Ed.s) "Comprehensive Polymer Science" Vol. 3, p. 697, Pergamon Press Oxford 1989
2. D. R. Terrel, F. Evers, J. Polym. Sci. **20**, 2529 (1982)
3. T. Higashimura, H. Tearanski, M. Sawamoto, Polym. J. **12**, 393 (1980)
4. T. Higashimura, Y. X. Deng, M. Sawamoto, Polym. J. **15**, 385 (1983)
5. M. Sawamoto, J. Fujimoni, T. Higashimura, Macromolecules **20**, 916 (1987)
6. O. Nuyken, H. Kröner, Makromol. Chem. **191**, 1 (1990)
7. O. Nuyken, H. Kröner, S. Aechter, Makromol. Chem. Macromol. Symp. **32**, 181 (1990)
8. O. Nuyken, H. Kröner, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. **29** (2), 87 (1988)
9. G. Kaszas, J. E. Puskas, C. C. Chen, J. P. Kennedy Macromolecules **23**, 3909 (1990)
10. F. J. Burgess, D. H. Richards, Polymer **17**, 1020 (1976)
11. C. V. Freyer, J. Manz, O. Nuyken, Macromol. Chem. Theory and Simul., in print
12. O. Nuyken, G. Rieß, J. A. Loontjens, in preparation