Star-Like Polymers of *tert*-Butyl Acrylate via Controlled Radical Polymerization – Synthesis and Properties

Andrzej Dworak,[1,2] *Agnieszka Kowalczuk,*[1] *Barbara Mendrek,*[1,2]
*Barbara Trzebicka**[1]

Summary: Star polymers with different numbers and lengths of poly(*tert*-butyl acrylate) arms were obtained by the core-first method via atom transfer and iodine mediated radical polymerization. Multifunctional initiators with different numbers of initiating groups (from 3 to 28) were used to initiate the polymerization of *tert*-butyl acrylate, yielding stars with different numbers of arms. The structures of the stars were characterized by NMR and gel permeation chromatography with refractive index, multiangle laser light scattering and viscosimetric detectors.

Keywords: branching parameters; controlled radical polymerization; core-shell polymers; poly(*tert*-butyl acrylate); star polymers

Introduction

Star polymers are branched structures consisting of a central core connected to linear chains.[1] The compact structure of stars is reflected in their solution and solid-state properties. For instance, stars have a lower hydrodynamic volume, smaller size and higher segment density than linear polymers of the same molar mass.[1,2] Well defined star structures are intensively investigated to determine the effect of the number of arms on the properties of polymers in solution and in the melt. Stars containing poly(*tert*-butyl acrylate) arms are especially interesting because pH sensitive covalently bonded spherical particles can be obtained after hydrolysis of the *tert*-butyl acrylate groups.[3–6]

In general, three methods are commonly employed for the preparation of stars.[7] The arm-first method is based on the termination of living monofunctional polymer chains by a multifunctional terminating agent. In the core-first approach, a polyfunctional core initiates monomer polymerization, which forms the arms of the star. In the core-first approach, the number of arms in the star can be predefined, functional end groups can be easily introduced into the arms and unreacted linear chains are not observed if transfer reactions do not occur. Mixed, three step or in-out syntheses are a combination of arm-first and core-first methods that lead to well-defined miktoarm stars with chemically variable arms.[7] In the aforementioned methods, every step of the synthesis must be controlled, including the synthesis of the arms and the core, regardless of which structure is obtained first. To analyze the properties of stars, precise control of their architecture is required. Significant advancements in the field of controlled radical polymerization techniques have opened new routes to the synthesis of well-defined star structures by all three methods.[8–11]

Non-linear polymers are characterized by determining the branching parameters, g and g',[12,13] and the shape factor, ρ.[14–16]

---

[1] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland
E-mail: btrzebicka@cmpw-pan.edu.pl

[2] University of Opole, Faculty of Chemistry, Oleska 48, 45-052 Opole, Poland

Moreover, the relationship between the branching parameters and the molar mass and the number of arms must be established, and the measured values should be compared to the predicted values.[1,2,17]

In this work, star polymers with poly(*tert*-butyl acrylate) arms were synthesized by atom transfer radical polymerization (ATRP) and iodine mediated radical polymerization (IDT), and the dilute solution properties of the stars were determined.

Results and Discussion

Star polymers with poly(*tert*-butyl acrylate) arms were obtained by the core-first method. Polymer cores with various number of halogenated functional groups were synthesized to initiate the controlled radical polymerization of *tert*-butyl acrylate (Scheme 1), yielding star polymers with 3 to 28 arms.

Pentaerythritol derivatives with 3, 4 and 6 bromoester groups, calix[4]arenes based on pyrogallol with 12 and 16 bromoester groups[18] and hyperbranched poly(arylene oxindole) with an average of 28 bromoester groups ($M_n = 20000$ g/mol and $M_w/M_n = 1.70$ from GPC-MALLS)[19] were used as multifunctional initiators of ATRP. Hyperbranched poly[p-(iodomethyl)styrene] with an average of 10 iodine groups ($M_n = 2400$ g/mol and $M_w/M_n = 1.83$ from GPC-MALLS)[20] was used as to initiate IDT polymerization.

The structure of multifunctional initiators with different number of functional groups was characterized by NMR and MS.[18–20]

The structure of multifunctional initiators is shown in Scheme 2.

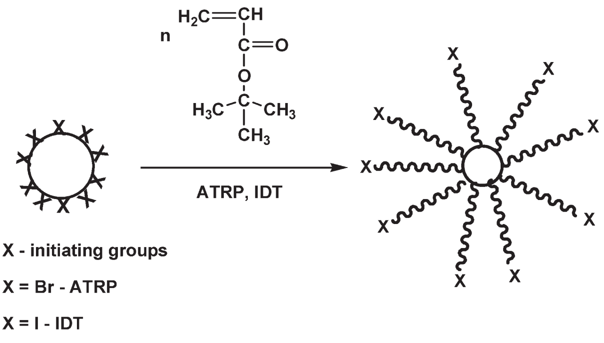
Polymerizations of *tert*-butyl acrylate initiated by multifunctional cores proceeded in a controlled manner. The ratio of initiating groups to *t*BuA was varied to prepare stars with arms of varying lengths (Table 1). The polymerizations were stopped at less than 80% conversion to avoid star-star coupling, which would drastically affect the molar mass distribution.

However, in the polymerization of poly[p-(iodomethyl)styrene] via IDT (I-10, Scheme 2), star-star coupling was not observed, and 100% conversion of monomer was achieved.

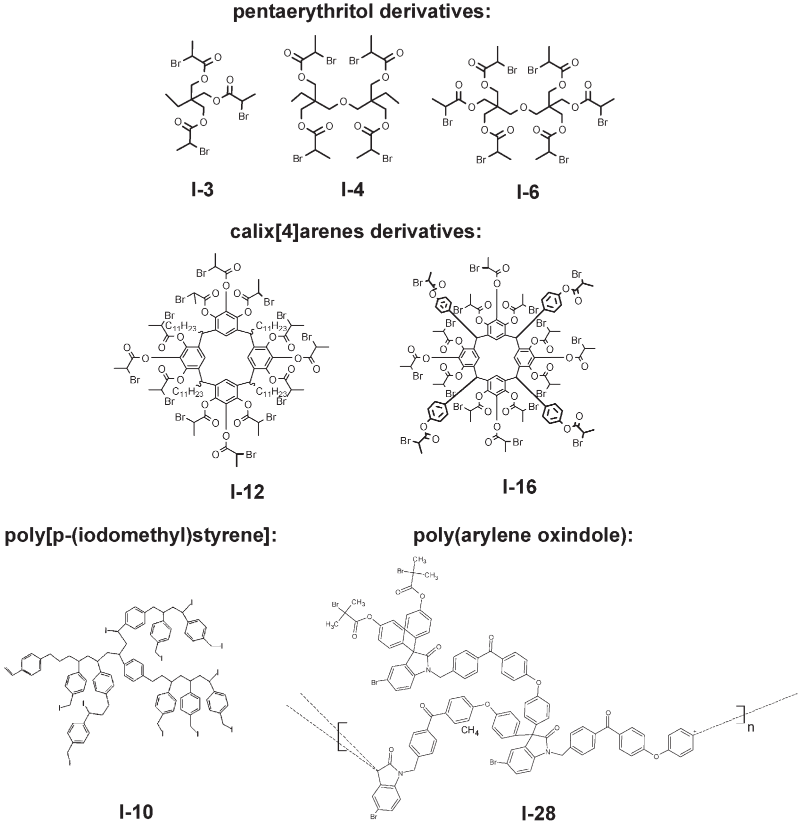
The chromatograms of the stars produced via ATRP and IDT were monomodal and symmetrical. Furthermore, the molar mass of the products increased with an increase in monomer conversion.

As an example, the chromatograms of star polymers with six poly(*tert*-butyl acrylate) arms are provided in Figure 1.

To determine the average molar mass, dispersity and intrinsic viscosity of the star polymers and their linear analogues, the polymers were characterized by gel permeation chromatography (GPC) with differential refractive index (RI), multiangle laser light scattering (MALLS) and viscosimetric (Visco) detectors.



Scheme 1.
Polymerization of tert-butyl acrylate.



Scheme 2.
The structure of multifunctional initiators used as star cores.

Because the polymerizations of *tert*-butyl acrylate were controlled, the theoretical molar mass was calculated based on the conversion of monomer, according to equation 1:

$$M_{theor.star} = M_i + ([C_{tBuA}]_0/[C_i]_0) \times \Delta C_{tBuA} \times M_{tBuA}) \tag{1}$$

where:

$M_{theor.star}$ – the theoretical molar mass of the star polymer
M_i – the molar mass of the initiator
$[C_{tBuA}]_0$ – the initial molar concentration of *tert*-butyl acrylate
$[C_i]_0$ – the initial molar concentration of the initiator
ΔC_{tBuA} – the consumption of *tert*-butyl acrylate
M_{tBuA} – the molar mass of *tert*-butyl acrylate

The results obtained from GPC and GC analyses of P*t*BuA stars with different arm lengths and numbers of arms are provided in Table 1.

Only minor discrepancies between the number of average molar masses obtained through GPC-MALLS and the theoretical values based on the conversion of monomer were observed (Table 1); thus, both ATRP and IDT polymerizations of *tert*-butyl acrylate with multifunctional initiators were controlled. The dispersities of the molar masses of stars derived from I-3, I-4, I-6, I-12 and I-16 were measured by GPC-MALLS, and the experimental results were rather low (less than 1.26, Table 1). The dispersities of the stars synthesized from hyperbranched cores I-10 and I-28 were greater than those obtained from low molar

Table 1.
Characteristics of P*t*BuA star polymers.

Initiator	*f**	$[M_o]/[I_o]$	conversion [%]	$M_{the\ or}$	$M_{n\ GPC\text{-}MALLS}$[a] [g/mol]	M_{n_calib}[b] [g/mol]	M_w/M_n
I-3	3	300	10	4400	4500	3000	1.18
			21	8600	7800	5800	1.26
			37	14700	13900	9900	1.14
			49	19400	18600	12400	1.05
			59	23200	22200	14000	1.05
I-4	4	400	32	17200	18000	15200	1.16
			57	30000	30800	22000	1.18
			62	32600	33100	24500	1.18
			66	34600	34600	25600	1.19
			75	39200	39900	30400	1.20
		16000	8	164800	156000	–	1.07
			17	349400	365000		1.10
			22	452000	440000		1.13
			37	759600	752000		1.13
			41	840800	822600		1.13
I-6	6	600	21	17200	17600	14400	1.08
			29.5	23750	23300	20500	1.08
			36	28700	27700	22800	1.08
			38.5	30600	30400	25500	1.08
			42.5	33700	36800	29000	1.09
I-10	10	1000	6	10000	21800	15000	1.46
			20	28000	30700	21200	1.43
			60	79300	97200	36200	2.20
			77	101900	105400	46200	1.37
			99	129100	127500	66200	1.91
I-12	12	540	18.5	15600	16700	9600	1.05
			27	21500	22200	14600	1.07
			34.5	26700	27300	19200	1.04
			38.6	29500	28000	21600	1.08
			41	31200	28700	21900	1.08
			55.7	41300	39200	26400	1.06
I-16	16	760	17	19600	21200	8500	1.06
			24	26400	27000	12000	1.03
			28	30300	28900	13400	1.03
			31	33200	33500	15400	1.02
			35	37200	35000	15200	1.02
			39	41000	38000	17700	1.03
I-28	28	2800	10	54600	54700	47500	1.75
			19	91680	77900	53200	1.85
			32	129231	110500	58000	1.90
			41	160518	134700	77200	1.78
			52	201649	151700	91000	2.36
			60	235040	168100	100600	1.82

* *f*-arm number[a]molar mass measured by GPC with multiangle light scattering detection[b]molar mass measured by GPC with standard calibration based on P*t*BuA standards

mass initiators due to the high dispersities of the hyperbranched cores (I-10: $M_w/M_n = 1.83$; I-28: $M_w/M_n = 1.70$), which resulted in a rather broad distribution of the number of arms.

The compactness of the star structures in solution was determined via GPC analysis using calibration with linear poly(*tert*-butyl acrylate) standards. All of the average molar masses were calculated from the calibration curve (apparent molar masses) and were lower than the absolute molar masses obtained from GPC-MALLS analysis (Table 1), confirming that the stars were more compact in THF than their corresponding linear analogues.

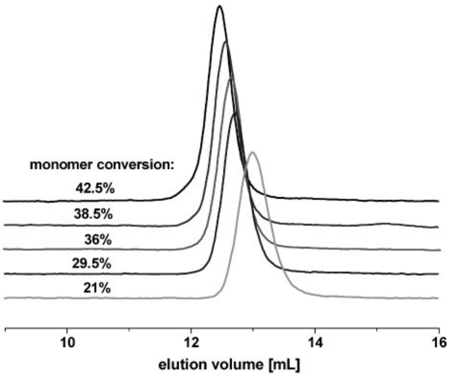


Figure 1.
Chromatograms (RI traces) of 6-arm stars formed via ATRP of *tert*-butyl acrylate using I-6 as an initiator (THF, 1 mL/min).

The total intrinsic viscosity of the P*t*BuA stars and their linear analogues were measured using GPC with a viscosimetric detector connected online to the system. The integral of the measured slice viscosities over concentration yielded the viscosity of the complete sample.[18]

The total intrinsic viscosities of the stars were compared to those of linear P*t*BuA (Figure 2).

The results indicated that star polymers possessed lower intrinsic viscosities than their linear analogues. For stars with the same molar mass, the intrinsic viscosity increased with an increase in the number of arms. However, a plot of the intrinsic viscosity versus the weight average molar mass revealed that a similar relationship was observed in stars and linear polymers. Thus, linear P*t*BuA ($K = 0.0042$ and $\alpha = 0.78$ in THF at 35 °C[18,19]) and stars with a fixed number of arms provided nearly identical (ranging from 0.74 to 0.79) α values in the Kuhn-Mark-Houwink-Sakurada equation. A similar relationship was observed for inter-alia polybutadiene,[21] polyisoprene[22] and poly(ethylene oxide) stars.[23]

Based on the total intrinsic viscosity, the branching parameter ($g' = \frac{[\eta]_{branched}}{[\eta]_{linear}}|_{at\ the\ same\ M}$) of the stars was determined in THF, which is a good solvent for P*t*BuA.[24] The average values of g' for stars with the same number of arms are shown in Table 2.

Table 2 also displays the values of g', which were calculated from the equations of Zimm and Kilb[13] (equation 2), Roovers[2]

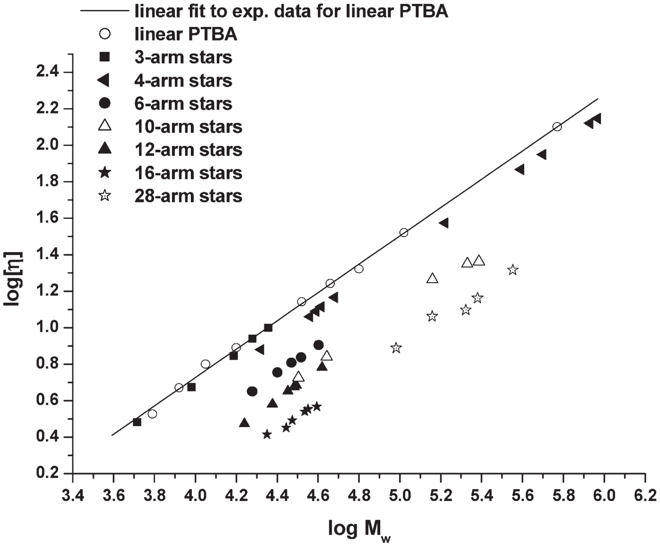


Figure 2.
Mark-Houwink plots of linear P*t*BuA and P*t*BuA stars with different numbers of arms.

Table 2.
Experimental and calculated values of the branching parameter (g') for stars with different numbers of arms.

F	g'_{av}	g' (eq. 2)	g' (eq. 3)	g' (eq. 4)
3	0.97	0.935	0.95	0.83
4	0.76	0.83	0.76	0.71
6	0.49	0.71	0.55	0.56
10	0.38	0.57	0.36	0.39
12	0.36	0.53	0.31	0.33
16	0.24	0.46	0.25	0.25
28	0.23	0.35	0.16	0.12

(equation 3) and Douglas et al.[25] (equation 4).

$$g' = \frac{(2/f)^{1.5}[0.396(f-1)+0.196]}{0.586} \tag{2}$$

$$\log g' = 0.36 - 0.8 \log f \tag{3}$$

$$g' = \left[\left(\frac{3f-2}{f^2}\right)^{0.58} \right] \times \left[\frac{1-0.276-0.015(f-1)}{1-0.276} \right] \tag{4}$$

where:

f – number of arms

The experimental values of the branching parameter, g', decreased with an increase in the number of arms, indicating that the star structure became more compact as the number of arms increased. The average branching ratio, g', was in agreement with the empirical predictions of Roovers[2] and Douglas et al.[25] for star polymers in a good solvent; however, the results obtained in this study were lower than those predicted by the theoretical model of Zimm and Kilb for stars in a θ solvent (equation 4).[13]

The average values of the branching parameters were similar to those obtained for different types of stars with the same number of arms. For example, the branching parameters of the stars in this study were similar to those of polybutadiene stars,[2,21] poly(ethylene oxide) stars[23] and polystyrene stars.[1,2,8]

Conclusion

Precise syntheses of star-like polymers from multifunctional initiators via controlled radical polymerizations allowed the number of arms and the molar mass of the polymers to be accurately controlled, leading to well defined macromolecules. Moreover, the solution properties of well-defined poly(*tert*-butyl acrylate) stars were studied, and the parameters of the Kuhn- Mark-Houwink-Sakurada (KMHS) equation were determined. When the chain length of the arms of star-like macromolecules increased and the number of arms remained constant, the value of the α parameter in the KMHS equation was similar to that of the corresponding linear polymer. Moreover, the values of the α parameter and the branching parameters agreed with theoretical and empirical predictions.

Experimental Part

Materials

N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA, 99%) and copper (I) bromide (CuBr, 99.999%) were purchased from Aldrich and were used as received. α,α'-Azobis(isobutyronitrile) (AIBN) (Fluka, >98%) was recrystallized from diethyl ether. *tert*-Butyl acrylate (*t*BuA, 98%), anisole (99%) and *p*-xylene (99%) were purchased from Aldrich and purified by distillation prior to use. Acetone (pure p.a.) was purchased from POCh and was used without purification. Benzene and methanol were purified by distillation at atmospheric pressure.

The protonated form of DOWEX MARATHON MSC ion exchange resin (Aldrich) was obtained by reaction with 1.6 M HNO_3.

Characterization

Gas Chromatography

To determine the conversion of the monomers, gas chromatography was used to measure the concentration of residual monomer in solution. Anisole or *p*-xylene were used as an internal standard, and GC analyses were conducted on a VARIAN 3400 gas chromatograph equipped with a J&W Scientific DB-5 (30 m × 0.32 mm) column.

Gel Permeation Chromatography

GPC was used to determine the molar mass, molar mass distribution and solution viscosities of the polymers. GPC was performed in THF at 35°C with a nominal flow rate of 1 mL/min using a differential refractive index detector (Δn-2010 RI WGE, Dr. Bures) a viscosimetric detector (η-2010 WGE, Dr. Bures) and a multiangle light scattering detector (DAWN EOS from Wyatt Technologies). four SDV columns (1×10^5 Å, 1×10^3 Å and 2×10^2 Å) and was obtained from Polymer Standard Service (PSS). The results were evaluated with ASTRA software from Wyatt Technologies and WinGPC Unity software from PSS. The *dn/dc* value of P*t*BuA star polymers and linear P*t*BuA was measured independently.

Synthesis of the Cores

The synthesis and characterization of ATRP low molar mass multifunctional initiators of *tert*-butyl acrylate were performed as described previously.[18] The synthesis and characterization of hyperbranched poly(arylene oxindole)[19] and poly[p-(iodomethyl)styrene] was performed according to.[20]

Synthesis of PtBuA Star Polymers - ATRP

The initiator (I-3, I-4, I-6, I-12, I-16, I-28) (20 mmol), CuBr (1.43 g, 10 mmol), PMDETA (1.73 g, 10 mmol, 2.08 mL) and acetone or anisole (10–50% v/v of monomer, sufficient to dissolve the initiator) were placed in a Schlenk flask. The solution was stirred until the Cu complex formed and the solution turned green. Subsequently, an appropriate amount of *tert*-butyl acrylate was added to the solution to obtain the desired monomer to initiator ratio. The mixture was degassed by conducting three freeze-vacuum-thaw cycles and was placed in an oil bath (60 °C for acetone and 80 and 90 °C for anisole). After the desired conversion (measured by gas chromatography) was obtained, THF (20 mL) was added and the solution was passed through a column containing DOWEX-MSC-1 ion exchange resin to remove copper from solution. The polymer was precipitated from a methanol/water mixture (1:1) and dried.

Synthesis of PtBuA Star Polymers - IDT

Poly[p-(iodomethyl)styrene] (I-10) (0.2941 g, 1.2 mmol of iodine groups), AIBN (0.0197 g, 0.12 mmol) and *tert*-butyl acrylate (15.3804 g, 120 mmol) were placed in a reactor. The resulting mixture was degassed by three freeze-pump-thaw cycles, and the polymerization was conducted at 67 °C. The polymer was precipitated from a methanol/water mixture (1:3) and dried.

Acknowledgements: The authors would like to thank Dr. Mario Smet (University of Leuven, Belgium) for the sample of hyperbranched poly(arylene oxindole).

[1] W. Burchard, *Adv. Polym. Sci.* **1999**, *143*, 113–194.
[2] J. Roovers, in "*Star and Hyperbranched Polymers*" M. K., Mishra, S. Kobayashi, editors, Marcel Dekker, Inc., Basel, New York **1999**.
[3] F. Plamper, H. Becker, M. Lanzendorfer, M. Patel, A. Witteman, M. Ballauff, A. H. E. Mueller, *Macromol. Chem. Phys.* **2005**, *206*, 1813–1825.
[4] T. Furukawa, K. Ishizu, *Macromolecules* **2005**, *38*, 2911–1917.
[5] C. Burguiere, S. Pascual, C. Bui, J.-P. Vairon, B. Charleux, K. Davis, K. Matyjaszewski, *Macromolecules* **2001**, *34*, 4439–4450.
[6] S. Hou, E. Chaikof, D. Taton, Y. Gnanou, *Macromolecules* **2003**, *36*, 3874–3881.
[7] M. Mishra, S. Kobayashi, red. "*Star and hyperbranched polymers*", Marcel Dekker, Inc., New York, Basel **1999**.
[8] S. Angot, K. S. Murthy, D. Taton, Y. Gnanou, *Macromolecules* **2000**, *33*, 7261–7274.
[9] H. Gao, K. Matyjaszewski, *Macromolecules* **2006**, *39*, 7216–7223.
[10] H. Gao, S. Ohno, K. Matyjaszewski, *J. Am. Chem. Soc.* **2006**, *128*, 15111–15113.
[11] H. Gao, K. Matyjaszewski, *J. Am. Chem. Soc.* **2007**, *129*, 11828–11834.

[12] B. H. Zimm, W. H. Stockmayer, *J. Chem. Phys.* **1949**, *17*, 1301–1314.
[13] B. H. Zimm, R. W. Kilb, *J. Polym. Sci.* **1959**, *37*, 19–42.
[14] S. Rangelov, B. Trzebicka, M. Jamóz-Piegza, A. Dworak, *J. Phys. Chem. B* **2007**, *111*, 11127–11133.
[15] S. Park, T. Chang, I. C. H. Park, *Macromolecules* **1991**, *24*, 5729–5731.
[16] S. Stradman, S. Hietala, V. Aseyev, B. Koli, S. J. Butcher, H. Tenhu, *Polymer* **2006**, *47*, 6524–6535.
[17] S. Grest, L. Fetters, J. S. Huang, D. Richter, *Adv. Chem. Phys.* **1996**, *XCIV*, 67–163.
[18] B. Mendrek, B. Trzebicka, *Eur. Polym. J.* **2009**, *45*, 1979–1993.
[19] A. Kowalczuk, A. Vandendriessche, B. Trzebicka, B. Mendrek, U. Szeluga, G. Cholewiński, M. Smet, A. Dworak, W. Dehaen, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 1120–1135.
[20] A. Kowalczuk-Bleja, B. Trzebicka, H. Komber, B. Voit, A. Dworak, *Polymer*, **2004**, *45*, 9–18.
[21] J. Roovers, L. Zhou, P. M. Toporowski, M. Zwan, H. Iatrou, N. Hadjichristidis, *Macromolecules* **1993**, *26*, 4324–4331.
[22] B. J. Bauer, L. J. Fetters, W. Graessley, N. Hadjichristidis, G. F. Quack, *Macromolecules* **1989**, *22*, 2337–2347.
[23] B. Comanita, B. Noren, J. Roovers, *Macromolecules* **1999**, *32*, 1069–1072.
[24] R. Jerome, V. Desreux, *Eur. Polym. J.* **1970**, *6*, 411–421.
[25] J. Douglas, J. Roovers, K. Freed, **1990**, *23*, 4168–4180.