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Core-shell polyacrylate and polystyrene-*block*-polyacrylate stars

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Abstract

The polymerization of *p*-(iodomethyl)styrene (PIMS) yields well-defined branched polymers with reactive iodomethyl groups. The branched poly[*p*-(iodomethyl)styrene] was used as the transfer agent in the iodine mediated radical polymerization of vinyl monomers. The polymerization proceeds in a controlled way and yields polystyrene and poly(*t*-butyl acrylate) star polymers with reactive groups at the end of their arms. Polymers so obtained were also used to prepare stars with block copolymer arms: polystyrene-*block*-poly(*t*-butyl acrylate). The characterization of star structures was performed by NMR and gel permeation chromatography with absolute molar mass detection (MALLS). Preliminary characterization of the thermal properties of these novel materials is reported.

Keywords: Controlled radical polymerization; Degenerative transfer; Branched polymers

1. Introduction

Star polymers are branched structures in which linear homopolymer or copolymer chains are covalently bound to one central element of the functionality from three to dozens. The preparation methods and properties of star polymers were widely reviewed [1–4].

Star shaped polymers are frequently classified according to the structure of their arms to: A_n type with n homopolymer arms ($n>2$), $(AB)_n$ type with n AB block copolymer arms and A_nB_m type with n arms of homopolymer A and m arms of homopolymer B.

Stars with chemically different arms in respect to chemical nature, molar masses, functional groups or topology of building blocks are called heteroarm or miktoarm stars from the Greek *μικτοσ*-mixed.

The core of the star polymer can be composed of a multifunctional low molar mass compound [5–8], a dendrimer [9], a hyperbranched polymer [10,11], an arborescent structure [12] and a crosslinked microgel [13,14]. When the core is big enough the stars obtained are called core–shell structures. They exhibit interesting properties, especially when the chemical differentiation between internal and external parts occurs.

The literature classifies the general methods of the synthesis of the star-shaped macromolecules into three categories. The ‘arm-first’ method is based on the termination of the living monofunctional polymer chains by a multifunctional terminating agent [15–17]. In the ‘core-first’ method groups of the polyfunctional core initiate the polymerization of the monomer, thus forming the arms [18,19]. The multistage methods are usually used for the preparation of the star polymers with chemically various arms [20–22]. The most common combination of these two methods is called ‘mixed’, ‘three step’ or ‘in-out’ synthesis and leads to well defined miktoarm stars.

All methods described above require the control of every step of the star synthesis: both of the synthesis of the arms and of the synthesis of the core irrespective which element of structure is obtained first. For the analysis of properties of the core-shell star polymers a precise control of their structure is needed and therefore the use of living/controlled polymerizations is desired.

In our previous paper [23] the polymerization of the *p*-(iodomethyl)styrene (PIMS) under the action of a radical initiator (AIBN) was described for the first time. Polymerization proceeds via the degenerative chain transfer

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reaction. A branched polymer (polyPIMS) with up to 10 primary and secondary reactive iodomethyl groups is obtained. This polymer was further used as the transfer agent in the radical polymerization of styrene, yielding well defined polystyrene stars. Here, we want to report a new route to core-shell type A_n stars with polyacrylate arms and of $(AB)_n$ stars with polystyrene-*block*-polyacrylate arms. Both types of arms are connected to a branched polyPIMS core. The iodine mediated controlled radical polymerization was applied for the syntheses. The thermal properties of the synthesized star polymers were also investigated.

2. Experimental

2.1. Materials

p-(Iodomethyl)styrene (PIMS) was synthesized from *p*-(chloromethyl)styrene according to Gozdz [24] via the Finkelstein reaction. Styrene (Merck, >99%) and *t*-butyl acrylate (Aldrich, 98%) were distilled over CaH_2 prior to use. The initiator: α,α'-azobis(isobutyronitrile) (AIBN) (Fluka, >98%) was recrystallized from diethyl ether. Benzene and methanol were purified by distillation at atmospheric pressure.

2.2. Measurements

2.2.1. Gas chromatography

Gas chromatography was used to determine the conversions by measurements of the residual monomer content with *p*-xylene as internal standard, using VARIAN 3400 gas chromatograph with the J&W Scientific DB-5 ($30\,m\times 0.32\,mm$) column.

2.2.2. NMR

NMR spectra were recorded on Unity-Inova spectrometer (Varian) operating at 300 MHz for ^{1}H. C_6D_6 was used as the solvent. The resonances are given in ppm referenced to the solvent peaks for C_6D_6 (δ (^{1}H) = 7.16 ppm).

2.2.3. Gel permeation chromatography

The molar masses and the dispersities of obtained products were determined by GPC using polymer standard service (PSS) column SDV $1\times10^5+1\times10^3+2\times10^2$ Å columns with differential refractive index detector Δn-1000 RI WGE Dr Bures and a multiangle light scattering detector DAWN EOS of Wyatt Technologies. Measurements were performed in THF as the solvent at 30 °C with a nominal flow rate of 1 mL/min. Results were evaluated using the ASTRA software from Wyatt Technologies and WINGPC software from PSS.

Refractive index increment for polystyrene in THF was assumed to 0.185 mL/g [27], for the poly[*p*-(iodomethyl)-styrene] in THF to 0.205 mL/g [23]. For poly(*t*-butyl acrylate) it was measured in THF to 0.055 mL/g. Where conventional calibration was used, it was established using the polystyrene (Polymer Laboratories) and poly(*t*-butyl acrylate) (PSS) standards.

2.2.4. Differential scanning calorimetry (DSC)

The TA Instruments DSC 2910 with cooling head assembly and liquid nitrogen cooling accessory (LNCA) was used to perform DSC heating and cooling cycles. For all DSC experiments, about 10 mg of the sample were crimped into standard aluminum DSC pans. Nitrogen purged the DSC cell area at 50 mL/min. The samples were heated from room temperature at 20 °C/min to 50 °C above the first glass transition temperature. Next they were aged for 10 min, cooled down at 50 °C/min (quenching) and reheated at 10 °C/min. The obtained data points were collected using Universal Analysis NT Software. The same software was used to calculate results.

2.3. Syntheses of branched polymer of *p*-(iodomethyl)styrene and star polymer with poly[*p*-(iodomethyl)styrene] core and polystyrene arms

The syntheses were carried out using iodine mediated controlled radical polymerization as described in our previous report [23] yielding polyPIMS of $M_n = 2400$ g/mol and polystyrene stars of M_n up to 14,000 g/mol.

2.4. Synthesis of star polymer with poly[*p*-(iodomethyl)styrene] core and poly(*t*-butyl acrylate) arms

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

^{1}H NMR (C_6D_6, 300 MHz): δ 1.2–1.6 ppm (CH_3), 1.6–1.9 (CH_2), 3.7–4.7 (CHI and CH_2I), 5.2, 5.9 and 6.3 (CH_2=, –CH=), 6.6–7.4 (CH_{ar}).

2.5. Extension of the arms of the star polymer

Polystyrene star of $M_n = 5400$ g/mol (0.2 g), AIBN (0.0109 g, 0.07 mmol) obtained as described under 2.3 and styrene (0.6966 g, 6.66 mmol) were placed in a reactor. After degassing by three freeze–pump–thaw cycles, the polymerization was carried out at 83 °C for 2 h. The polymer was precipitated in methanol and dried.

2.6. Synthesis of star polymers with polystyrene-block-poly(*t*-butyl acrylate) arms

Polystyrene star of $M_n = 14,000$ g/mol (0.1 g, 0.071 mmol of iodine groups), AIBN (0.0042 g,

Table 1
The molar masses of star polymers with polyPIMS core and poly(*t*-butyl acrylate) arms

Sample	Conversion of *t*BuA (%)	GPC–MALLS			$M_{n\ \text{GPC-calib}}$ from poly(*t*BuA) calibration (g/mol)	$M_{n\ \text{GPC-calib}}/M_{n\ \text{GPC-MALLS}}$
		d*n*/d*c* (mL/g)	M_n (g/mol)	M_w/M_n		
1	6	0.090	21,800	1.46	15,000	0.68
2	20	0.068	30,700	1.43	21,200	0.69
3	60	0.060	97,200	2.20	36,200	0.37
4	77	0.058	105,400	1.37	46,200	0.44
5	99	0.055	127,500	1.91	66,200	0.52

$P_n^{\bullet} + M \longrightarrow P_{n+1}^{\bullet}$ **propagation**

$R{-}I + P_n^{\bullet} \rightleftharpoons R^{\bullet} + P_n{-}I$ **transfer reaction**

$R^{\bullet} + M \longrightarrow RP_1^{\bullet}$ **propagation on the transfered centre**

$P_n{-}I + P_m^{\bullet} \rightleftharpoons P_n^{\bullet} + P_m{-}I$ **degenerative chain transfer**

R = alkyl derivatives

Scheme 1. Mechanism of the iodine mediated degenerative chain transfer polymerization.

0.026 mmol) and *t*-butyl acrylate (0.3291 g, 2.57 mmol) were placed in the reactor. After degassing by three freeze–pump–thaw cycles, the polymerization was carried out at 83 °C for 5 h. The obtained polymer was dried under vacuum.

3. Results and discussion

3.1. Synthesis of star polymers with poly[p-(iodomethyl)styrene] core and poly(t-butyl acrylate) arms

Iodine mediated controlled radical polymerization was applied to synthesize the core of all stars discussed in this work.

The polymerization of vinyl compounds in the presence of alkyl iodides belongs, next to the RAFT, to the group of the degenerative chain transfer methods. Basically, it proceeds according to Scheme 1.

We were able to show [23] that if *p*-(iodomethyl)styrene was used as monomer and AIBN as initiator, a degenerative chain transfer mechanism via self condensing vinyl polymerization operates and yields highly branched product of the degree of branching DB = 0.36. According to the polymerization mechanism every macromolecule contains in its structure one double bond [25,26] and in average up to 10 iodine groups.

We have also shown that if styrene is polymerized radically in the presence of these macromolecules, the polymerization is controlled and leads to stars containing up to 10 arms. The details are given in Ref. [23].

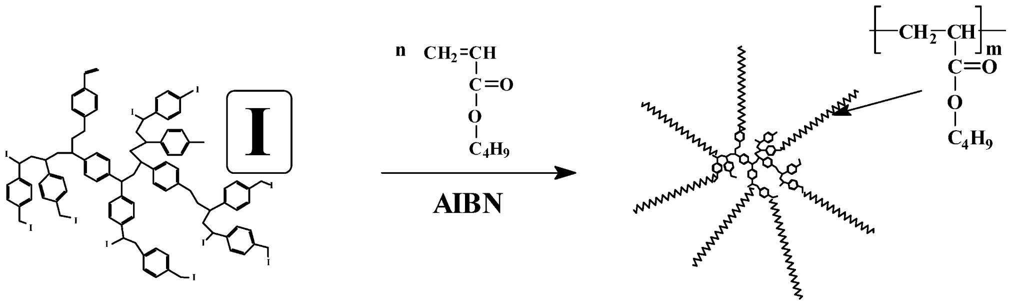
Here, it was attempted to polymerize radically other vinyl monomer, *t*-butyl acrylate, in the presence of the branched polyPIMS core. The polymerization was expected to proceed as shown in the Scheme 2.

PolyPIMS of $M_n = 2400$ g/mol and the ratio of iodomethyl groups to *t*-butyl acrylate of 1–100 was used. It turned out that the polymerization proceeds in a controlled manner.

The ^{1}H NMR spectrum (Fig. 1) evidences the structure of the obtained product. The aromatic protons signals of the core are clearly seen in the range from 6.4 to 7.2 ppm, while the proton signals coming from the poly(*t*-butyl acrylate) arms are at 2.0–2.4 ppm (a), 1.7 ppm (b) and 1.5 ppm (c), respectively.

The plot of $\ln([M]_0/[M])$ as the function of time is shown in the Fig. 2.

The GPC measurements of the obtained polymers (Fig. 3, Table 1) evidence the increase of the molar mass with increasing conversion. Monomodal molar mass distribution indicates that the coupling of macromolecules by recombination reactions and/or via polymerization of the double



Scheme 2. The approach to star polymers with branched polystyrene core and poly(*t*-butyl acrylate) arms.

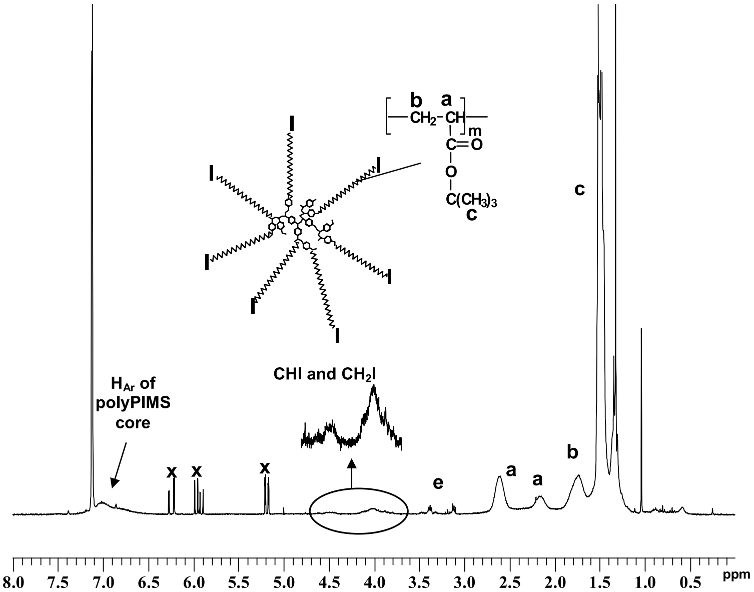


Fig. 1. ^{1}H NMR spectrum of the product of the radical polymerization of *t*-butyl acrylate in the presence of polyPIMS (sample 2, Table 1), x-monomer signals, e-impurities (300 MHz, C_6D_6).

bonds present in polyPIMS cores is negligible. This is different from what was observed for polystyrene stars at higher conversions [23]. Also no homopolymers of *t*-butyl acrylate (possibly formed in the degenerative transfer process), were detected by GPC, which indicates that they are not present in any significant amounts.

The molar masses of the obtained polymers are summarized in the Table 1.

For the evaluation of the GPC–MALLS results the values of the refractive index increment of every sample are needed. They were calculated basing upon the composition of polymers and assuming refractive index increment for the poly[*p*-(iodomethyl)styrene] in THF to 0.205 mL/g [23]. For poly(*t*-butyl acrylate) it was measured in THF to 0.055 mL/g (Section 2).

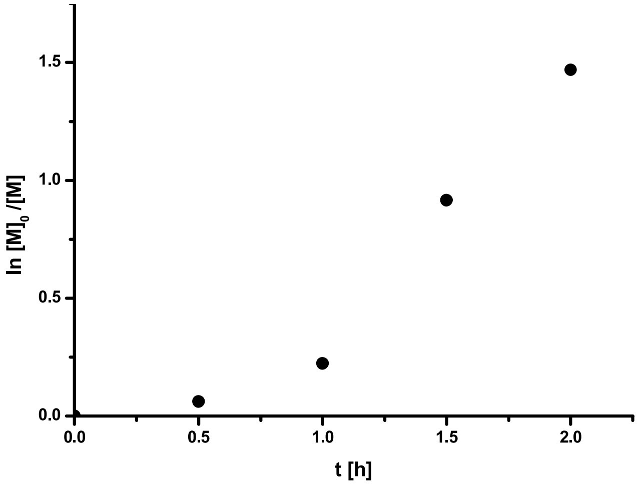


Fig. 2. Monomer consumption versus time in the polymerization of *t*-butyl acrylate using poly[*p*-(iodomethyl)styrene] as the transfer agent.

The obtained values confirm that the iodine mediated degenerative transfer mechanism operates and that control the molar masses of the star polymer is possible over a wide range. Polymers of M_n up to 130,000 g/mol have been obtained.

In the Fig. 4 the comparison between measured molar masses and the molar masses calculated is shown. The molar masses were calculated basing upon the monomer conversion according to the equation:

$$M_{\text{n star}} = M_{\text{core}} + \left(\left(\frac{[C_{t\text{BuA}}]_0}{[C_{\text{core}}]_0} \right) \Delta C_{t\text{BuA}} M_{t\text{BuA}} \right)$$

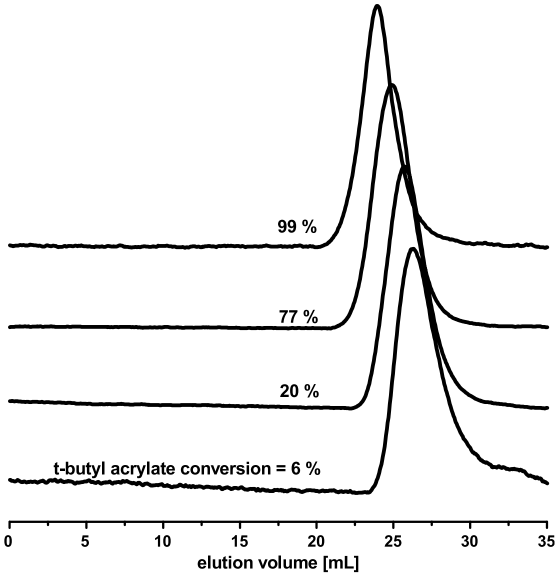


Fig. 3. GPC traces of the products of the radical polymerization of *t*-butyl acrylate in the presence of poly[*p*-(iodomethyl)styrene] (THF, 1 mL/min).

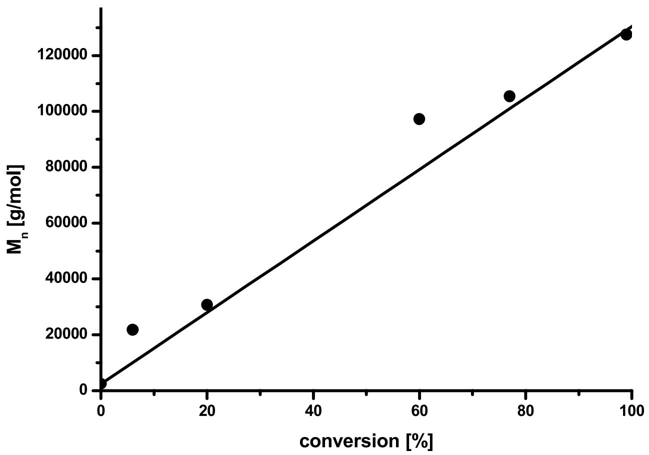


Fig. 4. M_n versus conversion in the radical polymerization of *t*-butyl acrylate in the presence of poly[*p*-(iodomethyl)styrene (THF, 1 mL/min), (—) calculated, (●) measured.

where $M_{n\ star}$, the molar mass of the star polymer; M_{core}, the molar mass of polyPIMS; $[C_{tBuA}]_0$, the initial molar concentration of *t*-butyl acrylate; $[C_{core}]_0$, the initial molar concentration of the polyPIMS; ΔC_{tBuA}, the consumption of *t*-butyl acrylate; M_{tBuA}, the molar mass of *t*-butyl acrylate.

The molar mass of the polymers obtained increases linearly with the conversion in quantitative agreement with the masses theoretically calculated.

The GPC–MALLS measurements confirm the star-like structure of the obtained polymers. In the Fig. 5 the number average molar masses of the obtained polymers determined by GPC–MALLS are plotted versus conversion. In the same figure the molar masses for the same polymers determined using the calibration with narrow linear poly(*t*-butyl acrylate) standards are shown.

In each case the molar masses from GPC–MALLS evaluation are higher than the molar masses calculated based upon the calibration with linear poly(*t*-butyl acrylate) standards. This effect is due to more compact structure and therefore lower hydrodynamic volume of the branched macromolecules as compared with the linear counterparts of the same molar mass. Similar effect was observed for the star polymers with polystyrene arms [23].

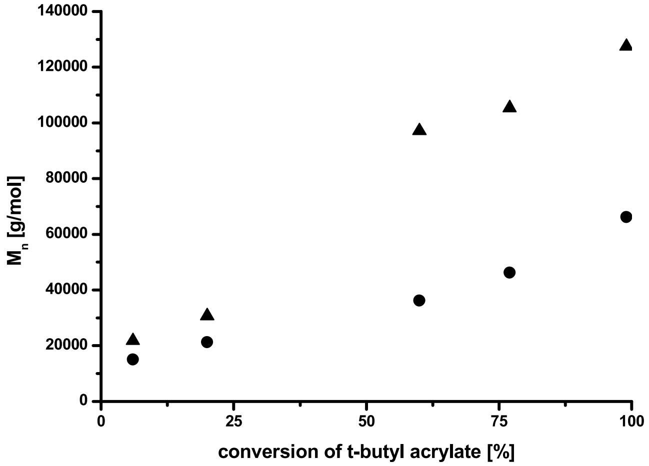


Fig. 5. Molar masses of the products of the radical polymerization of *t*-butyl acrylate in the presence of poly[*p*-(iodomethyl)styrene]: determined using GPC coupled with multiangle light scattering detector (▲) and calculated from calibration with linear poly(*t*-butyl acrylate) standards (●) (THF, 1 mL/min).

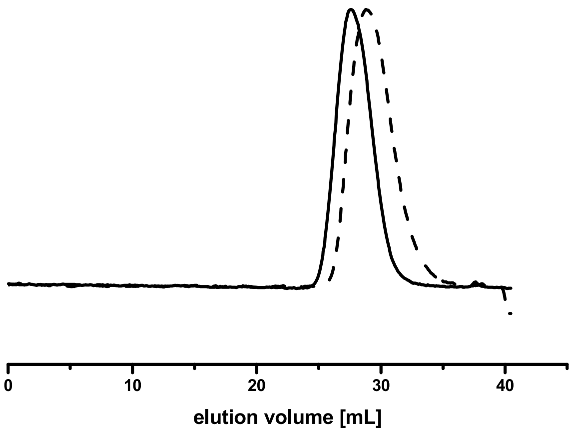


Fig. 6. GPC traces of the polystyrene star of $M_n = 5400$ g/mol (- - -) and the product of radical polymerization of styrene in the presence of this polystyrene star (—), (THF, 1 mL/min).

3.2. Synthesis of star polymers with poly[p-(iodomethyl)styrene] core and polystyrene-block-poly(t-butyl acrylate) arms

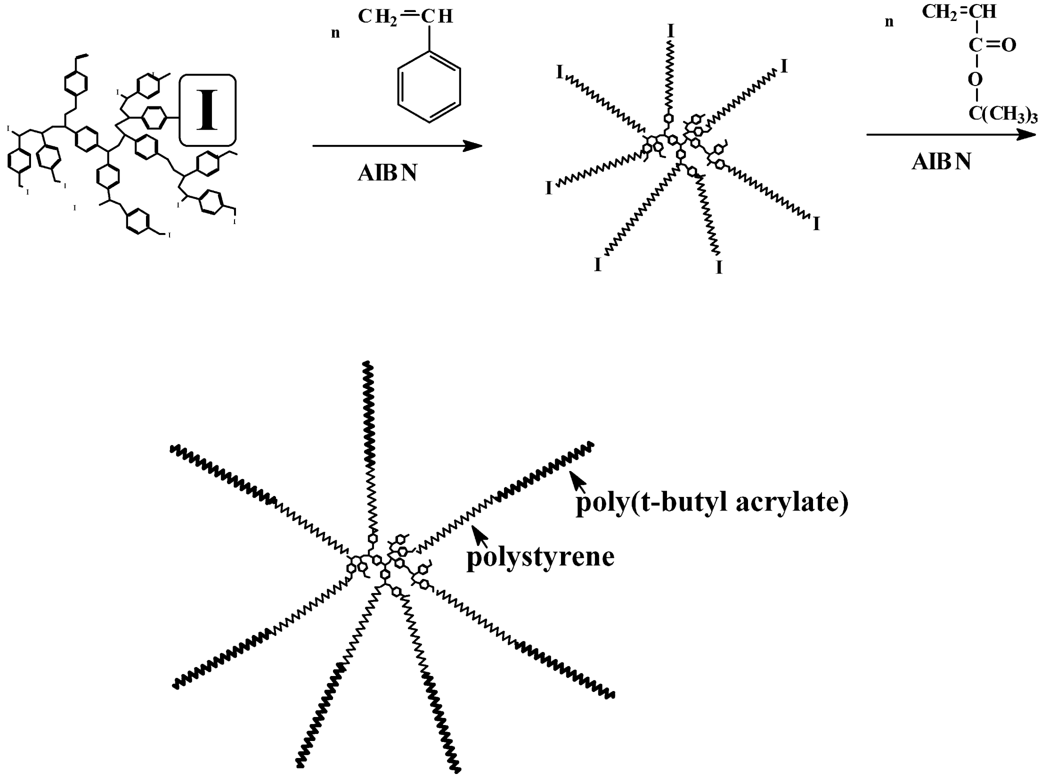
3.2.1. The extension of the arms of polystyrene stars

The polystyrene stars, obtained by the radical polymerization of styrene in the presence of poly[*p*-(iodomethyl)-styrene] core contain iodomethylene groups at the ends of the polystyrene arms [23]. If these groups are capable to act as chain transfer agent in the iodine mediated radical polymerization, the route to star with block copolymer arms would be open.

To check this possibility, we first tried to extend the arms of a polystyrene star. For this, a (iodine terminated) polystyrene star of $M_n = 5400$ g/mol was used as the transfer agent for the polymerization of styrene initiated with AIBN. The GPC indicates a very clean extension of the arms of the star. An evaluation of the GPC–MALLS data indicates that a star polymer of $M_n = 14{,}000$ g/mol and M_w/M_n equal to 1.44 is formed (for the conversion of styrene 50%). The theoretical molar mass is $M_{n(theor)} = 15{,}800$ g/mol, calculated for the same monomer conversion. No significant amount of the polyPIMS was detected in the product (Fig. 6).

3.2.2. Synthesis of star polymers polystyrene-block-poly(t-butyl acrylate) arms

Having thus proven the chain transfer ability of the terminal iodomethylene group of the polystyrene star we attempted to obtain stars with arms, consisting of polystyrene-*block*-poly(*t*-butyl acrylate) arms.



Scheme 3. A route to star polymers with polystyrene-*block*-poly(*t*-butyl acrylate) arms.

Table 2
The molar masses of stars with polyPIMS core and polystyrene-*block*-poly(*t*-butyl acrylate) arms

Sample	Time (h)	Conversion of *t*BuA (%)	M_n (GPC–MALLS)	M_w/M_n	$M_{n(theor)}$
1	1.5	70	40,800	1.58	46,290
2	3.5	90	46,300	1.66	55,520
3	5	100	48,000	1.66	60,140

The refractive index increments were calculated using d*n*/d*c* value calculated from the composition assuming d*n*/d*c* for the polystyrene 0.185 mL/g and for poly(*t*-butyl acrylate) 0.055 mL/g.

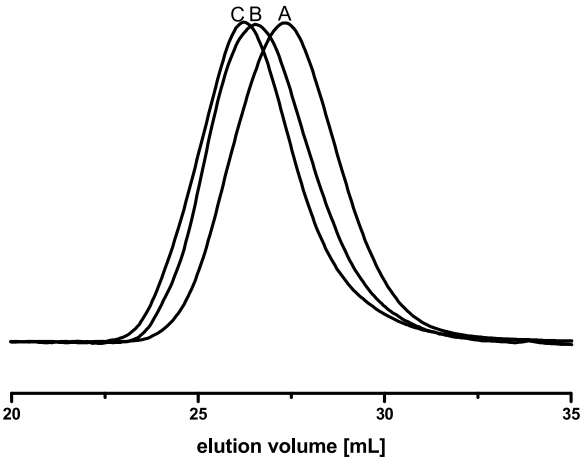


Fig. 7. GPC traces of the polystyrene star (A) and the products of the radical polymerization of *t*-butyl acrylate in the presence of this polystyrene star (B, C—samples 1 and 3, Table 2) (THF 1 mL/min).

For this, we first synthesized a polystyrene star. Branched poly[*p*-(iodomethyl)styrene] of $M_n = 2400$ g/mol was used as the transfer agent and the styrene was polymerized in the presence of this core, yielding polystyrene star of $M_n = 14{,}000$ g/mol. Then the iodine sites of polyPIMS were used to obtain stars with polystyrene-*block*-poly(*t*-butyl acrylate) copolymers arms by initiation of the polymerization of *t*-butyl acrylate monomer (Scheme 3).

No measurable amount of the initial PS star polymer has been detected in the reaction product (Fig. 7) which indicates that the polyPIMS was used up in the polymerization.

The GPC–MALLS measurements evidenced that the polymerization of the *t*-butyl acrylate using polystyrene star as the transfer agent in the iodine mediated controlled polymerization yields the products of the molar masses up to 46,000 g/mol (Table 2).

The star polymers with hydrophobic branched polystyrene core and polyacrylate shell may be transformed into

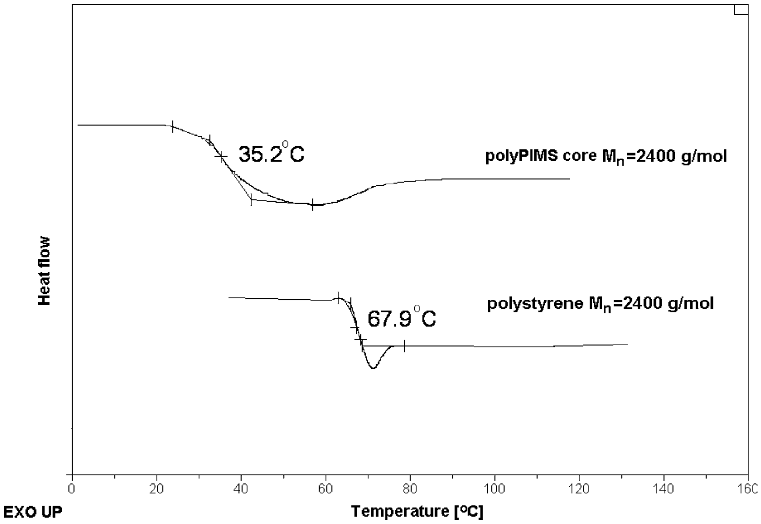


Fig. 8. DSC curves of the poly[*p*-(iodomethyl)styrene] core of $M_n=2400$ g/mol and of the polystyrene standard of $M_n=2400$ g/mol.

Table 3
DSC of the polystyrene star polymers and of the linear counterparts of the arms

Polymer	M_n (GPC–MALLS) (g/mol)	M_n[a] of the arms	First glass transition (°C)	Second glass transition (°C)
Polystyrene	570	–	−22	–
Polystyrene	1300	–	39	–
Star with PS arms	10,000	760	35	88
Star with PS arms	14,000	1160	34	94

[a] Assuming that stars consists of 10 arms.

amphiphilic ones by the hydrolysis of esters groups of external acrylate shell. The investigations are in progress.

3.3. Thermal properties of obtained star polymers

Non-linear polymers almost always exhibit the glass transition, but its source is not fully understood. In the case of linear polymers T_g is related to cooperative motion of relatively large chain segments. Above a certain molar mass the end groups have no influence upon the glass transition temperature of linear chains. For branched structures the T_g is strongly influenced by the number and the nature of functional end groups, the number of branching points and the architecture of the branched structure [28–34].

The thermal properties of the star polymers have been studied for different types of stars. The stars of A_n type usually show only one glass transition temperature connected with the movement of the arm segments [35–39]. It

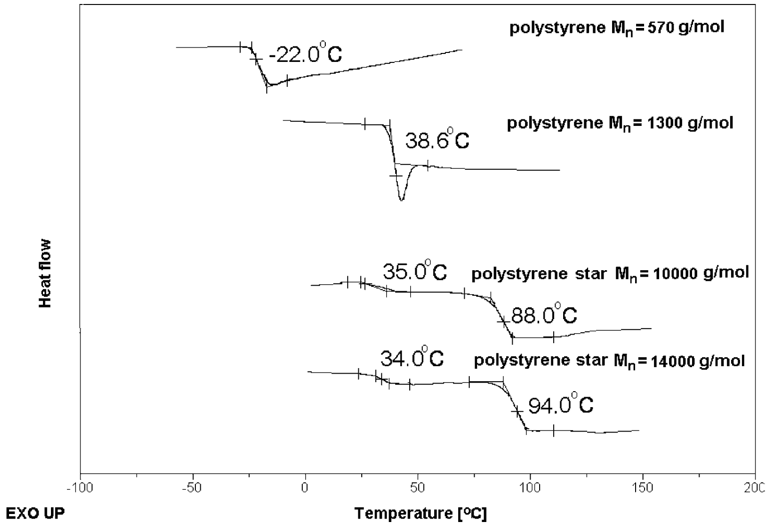


Fig. 9. DSC curves of the polystyrene standards and of the polystyrene star polymers.

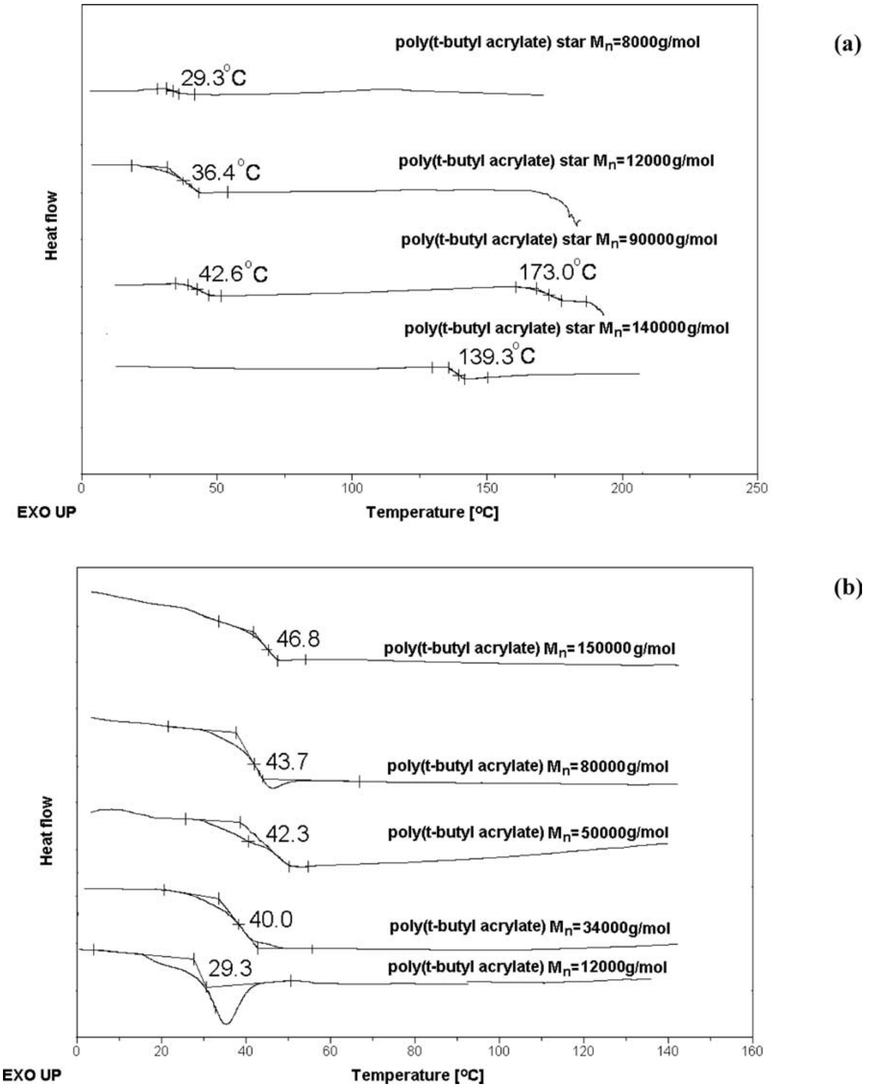


Fig. 10. DSC curves of linear poly(*t*-butyl acrylates) (a) and of the star polymers with poly(*t*-butyl acrylate) arms (b).

was reported that for the polymers of the core-shell structure T_g was also observed. In such structures T_g in comparison with the linear counterparts of arms can be shifted to higher values because of the arm interactions with 'the walls' of the core or to lower values because of the loose packing of the chains constituting the arms [39].

Here, we report the preliminary thermal properties of star-shaped polymers with branched polystyrene core and with polystyrene or poly(*t*-butyl acrylate) arms investigated by differential scanning calorimetry and compared with those of linear counterparts.

All thermogram curves were obtained for the samples in the second heating run, after clearing their thermal history.

First, the thermogram of branched poly[*p*-(iodomethyl)-styrene], the core of the stars, was examined and compared with the thermal behavior of the linear polystyrene standard of the same molar mass (Fig. 8). The T_g of core (M_n= 2400 g/mol) at ca. 35 °C is significantly lower then the glass transition of the linear polymer (68 °C).

All investigated polystyrene stars exhibit two second order transitions (Fig. 9, Table 3). The first one can be assigned to the movement of the star arms in the region of 34 °C. In the Fig. 9 the star thermograms are compared to those of low molar mass polystyrene standards of $M_n = 570$ and 1300 g/mol. The first T_g of stars is slightly lower than the value measured for the low molecular polystyrene standard of $M_n = 1300$ g/mol. The second transition was observed at about 90 °C and possibly corresponds to the motion of the whole star.

The thermograms of linear poly(*t*-butyl acrylates) are shown in the Fig. 10(a) and for the stars with poly(*t*-butyl acrylate) arms in the Fig. 10(b). The T_g values of the star polymers with poly(*t*-butyl acrylate) arms are collected in Table 4.

For the polyacrylate stars two glass transitions are observed, if the length of the arms exceeds a certain value. The comparison with the values measured for the linear poly(*t*-butyl acrylate) samples indicates that the first

Table 4
DSC of the poly(*t*-butyl acrylate) star polymers and linear counterparts of the arms

Polymer	M_n (GPC–MALLS) (g/mol)	M_n[a] of the arms	First glass transition (°C)	Second glass transition (°C)
Poly(*t*-butyl acrylate)	12,000	–	30	–
Poly(*t*-butyl acrylate)	34,000	–	40	–
Poly(*t*-butyl acrylate)	50,000	–	42	–
Poly(*t*-butyl acrylate)	80,000	–	44	–
Poly(*t*-butyl acrylate)	150,000	–	47	–
Star with polyacrylate arms	8000	770	29	–
Star with polyacrylate arms	12,000	1280	36	Cannot be established
Star with polyacrylate arms	90,000	9000	43	173
Star with polyacrylate arms	140,000	14,000	–	139

[a] Assuming that star polymer contains 10 arms.

transition, occurring in the range 29–43 °C may be attributed to the segmental motion of the arms of the star. The values are similar to those measured for the linear polymers. We were not able to detect the first transition in the case of the star of $M_\mathrm{n}=140{,}000$ g/mol, which may suggest that the arms are highly entangled.

The polyacrylate stars undergo thermal degradation above 180 °C. For two of the studied stars the second transition appears at 173 °C ($M_\mathrm{n}=90{,}000$ g/mol) and 139 °C ($M_\mathrm{n}=140{,}000$ g/mol), below the degradation begins. This order is surprising. We cannot give a well-founded rationalization at present. The high temperature transition is most likely due to the reorientation motion of the whole star, the surprising order of the transition temperatures may indicate differences in the packing of macromolecules and the morphology of the sample.

4. Conclusions

The iodine mediated controlled radical polymerization is a convenient route to the synthesis of well defined star polymers of core-shell structure, comprising polystyrene core and polyacrylate arms of well defined length. The core may easily be obtained by self condensing vinyl polymerization of *p*-(iodomethyl)styrene, which yields highly branched oligomer containing reactive iodomethyl groups. This core, if applied as the chain transfer agent in the iodine mediated radical polymerization, initiates the growth of poly(*t*-butyl acrylate) or polystyrene arms. Arms may be extended using the same polymerization mechanism.

Acknowledgements

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