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Controlled radical polymerization of *p*-(iodomethyl)styrene—a route to branched and star-like structures

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Abstract

p-(Iodomethyl)styrene was polymerized under the action of a radical initiator (AIBN). The polymerization proceeds with degenerative chain transfer and leads to well defined branched polymers with functional primary and secondary iodomethyl groups as revealed by NMR studies. The obtained polymer can be further used as macroinitiator for radical polymerization of styrene. This polymerization proceeds in controlled way to polystyrene star polymers with reactive groups at the end of their arms. The characterization of branched and star structures was performed by NMR and GPC with absolute molar mass detection (MALLS).

Keywords: Controlled radical polymerization; Branched polymers; Star polymers

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1. Introduction

The principle of all controlled radical polymerizations consists of the fast and reversible transformation of the vast majority of the active centers into the inactive, 'dormant' ones, thus lowering the rate of bimolecular termination and transfer and making the chain growth to predominate, which results in the polymerization product like in all 'classical' living polymerizations.

Several methods of controlled radical polymerization are known and have been developed to a great perfection, allowing a variety of synthetic tasks to be carried out [1].

The degenerative chain transfer methods: iodine mediated chain transfer (further referred to as IDT), first described by Matyjaszewski [2,3] and later studied in detail by Goto [4] as well as reversible addition fragmentation transfer (RAFT) [5–7] are special ways to reversibly deactivate the growing radical at the chain end. In these reactions, the deactivation consists of the exchange of the terminal group between the 'living' and the dormant species (Scheme 1).

All the elementary reactions of the radical polymerization: the dissociation of the initiator (the formation of the radicals), the initiation, the chain transfer and (to a much lesser extent) the termination take place. However, the application of the chain transfer agent RX causes that the vast majority of the growing species is reversibly transformed into the dormant, inactive ones. This, together with the fast degenerative chain transfer (fast exchange of the ability to grow between the active and the dormant species) causes that the contribution of the bimolecular termination is greatly decreased and that the reaction behaves in the controlled manner, like a living system.

In the iodine mediated degenerative transfer method, the iodine atom is transferred directly, whereas in the RAFT the exchange proceeds via the reversible addition and fragmentation of dithioesters [5–7].

In spite of apparent similarities, the mechanism of the degenerative transfer is distinctly different from the metal mediated methods (ATRP) [1].

A number of chain transfer agents for the iodine mediated polymerization of styrene were studied [3]. When 1-phenyl ethyl iodide, perfluoroisopropyl iodide, perfluorohexyl iodide, iodoacetonitrile or iodoform are used, the control is achieved. Control of styrene polymerization was achieved also in the miniemulsion systems [8]. Well defined macromonomers of polystyrene [9] and block

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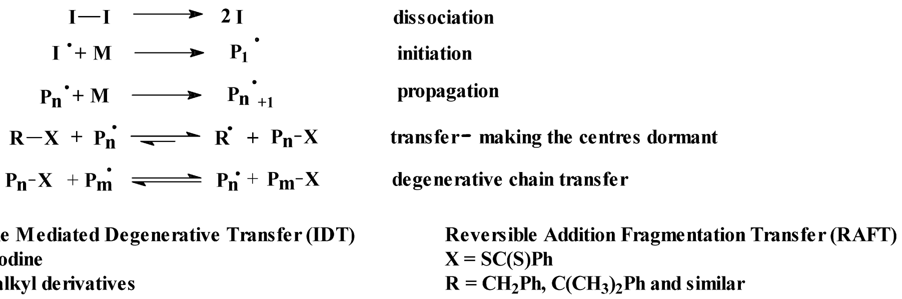


Scheme 1. Mechanism of degenerative chain transfer polymerization.

copolymers of styrene with acrylic monomers [3,10] were synthesized using this method.

When a monomer contains two sites, like a double bond and a halogen group, potentially active in the living radical polymerization and capable to generate a radical and to transfer the center of growth, branched structures may be formed in such a process, which is called self condensing vinyl polymerization (SCVP) [11–16]. This was evidenced in the ATRP of halogen containing monomers and in nitroxide mediated radical polymerizations and applied to obtain branched polyacrylates [17] and polystyrenes [11,18–20].

p-(Iodomethyl)styrene is a monomer, having two groups potentially active in the radical polymerization. If the iodomethylene group in this monomer is capable to act as the chain transfer agent in the degenerative chain transfer polymerization, branched structures containing reactive iodine groups will be obtained.

There are no conclusive data concerning the polymerizability of *p*-(iodomethyl)styrene. Gozdz [21] attempted to polymerize this monomer and reported to have obtained only ill-defined, insoluble products.

The aim of this work is to study the polymerization of *p*-(iodomethyl)styrene, to outline the mechanism of this process and the structure of the obtained polymer, and to use the resulting multifunctional branched polymers as initiators of the radical polymerization.

2. Experimental

2.1. Materials

Styrene (Merck, $>99\%$) was distilled over CaH_2 prior to use. The initiators; α,α′-azobis(isobutyronitrile) (AIBN, Fluka $>98\%$) and benzoyl peroxide (BPO, Fluka $>97\%$) were recrystallized from diethyl ether. Benzene and methanol were purified by distillation at atmospheric pressure.

p-(Iodomethyl)styrene (PIMS, caution: strong lachrymator, use well ventilated hood and personal safety wear) was synthesized from *p*-(chloromethyl)styrene according to Gozdz [21] via Finkelstein reaction. Benzyl iodide (BzI, caution: strong lachrymator, use well ventilated hood and personal safety wear) was synthesized from benzyl chloride in a similar manner.

2.1.1. General procedure

Benzyl chloride (6 g, 0.047 mol, Aldrich 99%) or *p*-(chloromethyl)styrene (7.32 g, 0.048 mol, Aldrich 90%) was added to a solution of NaI (10.7 g, 0.072 mol, Aldrich $>99\%$) in dry acetone (50 ml). The mixture was stirred at 50 °C for 2 h, cooled and filtered. Acetone was driven off under reduced pressure at room temperature, and to the solid residue 30 ml water and 50 ml diethyl ether were added. The aqueous layer was extracted additionally with ether, the combined ether extracts were washed with water containing sodium thiosulphate, and dried over $MgSO_4$. Ether was evaporated and the product was crystallized from cold *n*-hexane giving white (BzI) or yellow (PIMS) crystalline solid. Yield: 75% (BzI) and 50% (PIMS).

^1H NMR ($CDCl_3$, 300 MHz) for BzI: δ 4.46 (s, 2H), 7.3 (m, 5H)

^1H NMR ($CDCl_3$, 300 MHz) for PIMS: δ 4.44 (s, 2H), 5.23 (d, 1H), 5.71 (d, 1H), 6.65 (dd, 1H), 7.31 (m, 4H).

2.2. Measurements

2.2.1. Gas chromatography

In all polymerization experiments, conversions were determined by measurements of the residual monomer content by gas chromatography, with *p*-xylene as internal standard, using VARIAN 3400 gas chromatograph with a J and W Scientific DB-5 (30 m × 0.32 mm) column.

2.2.2. NMR

NMR spectra were recorded on a DRX-500 spectrometer (Bruker) operating at 500 MHz for ^1H and 125 MHz for ^{13}C and on an Unity-Inova spectrometer (Varian) operating at 300 MHz for ^1H. C_6D_6 was used as solvent. Resonances are given in ppm referenced to the solvent peak (δ (^1H) $=7.16$ ppm; δ (^{13}C) $= 128.7$ ppm). Proton NMR signals were used for quantitative analysis of the structural units, whereas signal assignment was achieved by means of DEPT as well as COSY, HMQC, and HMBC experiments using the DRX-500 spectrometer.

2.2.3. Size exclusion chromatography

The molecular weights and the polydispersities of obtained products were determined by GPC using PSS SDV 1×10^5 Å + 1×10^3 Å + 2×10^2 Å (Polymers Standards Service) 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 be 0.185 ml/g [22], for the poly[*p*-(iodomethyl)-styrene] in THF it was measured to 0.205 ml/g.

2.3. Polymerization of p-(iodomethyl)styrene

AIBN (0.0121 g, 0.07 mmol, $[I]_0 = 0.023$ M) and *p*-(iodomethyl)styrene (1.4409 g, 5.9 mmol $[M]_0 = 1.87$ M) were placed in a reactor and dissolved in benzene (1.65 ml). After degassing by three freeze-pump-thaw cycles, the polymerization was carried out at 67 °C. The samples were drawn and analyzed by gas chromatography and by the GPC without precipitation of the polymer. After full conversion was obtained the polymer was precipitated in methanol and dried.

^{1}H NMR (C_6D_6): δ 1.2–3.0 (CH, CH_2), 3.84 (CH_2I, b′), 4.05 (CH_2I, b), 4.4–5.05 (CHI, c–c‴), 5.09 and 5.63 (CH_2=, a), 6.4–7.3 (CH_{ar} and –CH=, a′). ^{13}C NMR (C_6D_6): δ 5.47 (CH_2I, b′), 6.4 (CH_2I, b), 30.1 (CHI), 33–35 (CHI, CH_2), 35–50 (CH, CH_2), 113.68 and 113.93 (CH_2=, a), 127–131 (CH_{ar}), 137.87 (–CH=; a′), 136–146 ppm (C_{ar}).

2.4. Polymerization of styrene in the presence of benzyl iodide in bulk

BPO (0.0313 g, 0.13 mmol, $[I]_0 = 0.01$ M), BzI (0.0845 g, 0.38 mmol, $[R-X]_0 = 0.03$ M) and styrene (1.35 g, 12.9 mmol) were placed in the reactor. After degassing by three freeze-pump-thaw cycles, the polymerization was carried out at 83 °C for 6 h. The polymer was precipitated in methanol and dried.

^{1}H NMR (C_6D_6): δ 1.4–1.9 (CH_2), 1.9–2.8 (CH), 4.66 and 4.80 (CHI), 6.4–7.3 (CH_{ar}). ^{13}C NMR (C_6D_6): δ 30.95 (CHI of end groups), 34–35 (CH_2 and CHI of end group), 41.7 (CH of PS), 42.5–49 (CH_2 of PS), 126–131 (CH_{ar} of PS and end group), 143.4 and 144.2 (C_{ar}, *ipso* to CHI), 146–148 (C_{ar} of PS).

2.5. Polymerization of styrene using α-benzyl-ω-iodo-polystyrene as a macroinitiator

α-Benzyl-ω-iodo-polystyrene (0.1 g, the concentration of iodine groups 0.05 M), BPO (0.0459 g, 0.19 mmol $[I]_0 = 0.01$ M) and styrene (2 g, 19.13 mmol) were placed in the 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. Polymerization of styrene using poly[p-(iodomethyl)styrene] as a macroinitiator

Poly[*p*-(iodomethyl)styrene] (0.2941 g, the concentration of iodine groups 0.05 M), AIBN (0.0395 g, 0.24 mmol, $[I]_0 = 0.01$ M) and styrene (2.52 g, 24.1 mmol) were placed in a reactor. After degassing by three freeze-pump-thaw cycles, the polymerization was carried out at 67 °C for 24 h. The polymer was precipitated in methanol and dried.

^{1}H NMR (C_6D_6): δ 1.4–2.0 ppm (CH_2), 2.0–3.1 (CH, CH_2), 4.05 (CH_2I, b), 4.68 and 4.82 (CHI, c), 4.92 (CHI, c″), 5.09 and 5.63 (CH_2=, a), 6.4–7.3 (CH_{ar} and –CH=, a′). ^{13}C NMR (C_6D_6): δ 6.6 (CH_2I, b), 31.0 (CHI, c), 34.4 (CH_2 and CHI, c‴), 35.0 (CHI, c), 41.7 (CH of PS), 42–51 (CH, CH_2), 133.56 (CH_2=, a), 126.5–131 (CH_{ar}), 136.28 (C_{ar}, *ipso* to vinyl group), 137.8–138.5 (C_{ar}, *ipso* to CH_2I, b, and –CH=, a′), 143.5–146 (C_{ar}, *ipso* to CHI, c, c‴), 146–147.5 (C_{ar} of PS).

3. Results and discussion

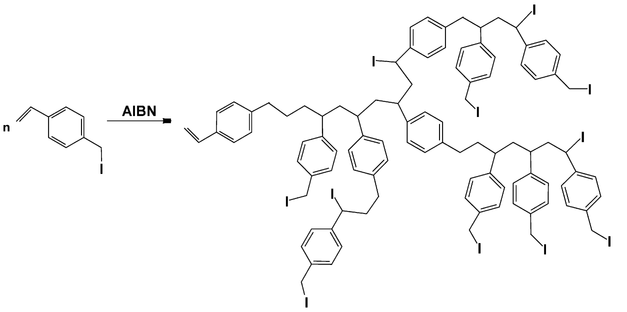
3.1. Radical polymerization of p-(iodomethyl)styrene

p-(Iodomethyl)styrene was heated in the presence of different radical initiators in highly concentrated benzene solution.

The experiments evidence that *p*-(iodomethyl)styrene may be polymerized radically under optimized conditions. The application of AIBN at a moderate temperature (67 °C) leads to fully soluble products (Scheme 2), which are sensitive to higher temperatures and oxygen. The application of BPO and the necessary higher temperature (80 °C) to generate the radicals leads to insoluble, dark colored products, probably due to the thermal instability of the monomer and the oxidizing action of the peroxide initiator.

The plot of $\ln([M]_0/[M])$ is linear in a wide range of conversion, which indicates that the concentration of the active centers is constant (Fig. 1).

Also the molar mass increases with conversion. Fig. 2



Scheme 2. Polymerization of *p*-(iodomethyl)styrene—a possible product.

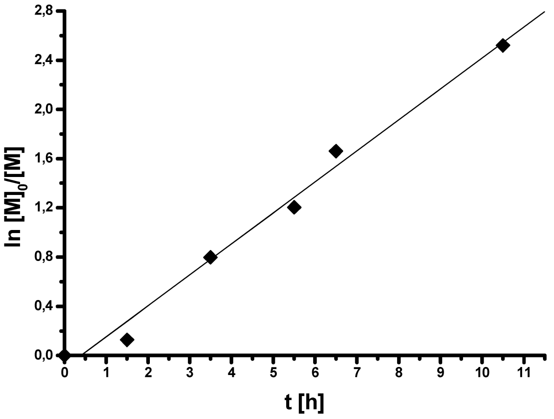


Fig. 1. Conversion versus time in the radical polymerization of *p*-(iodomethyl)styrene initiated with AIBN.

shows the GPC traces of samples drawn at different reaction times.

p-(Iodomethyl)styrene contains in a molecule two groups potentially active in the radical polymerization: the double bond and the iodomethyl group. If the degenerative chain transfer mechanism operates, the active radical may be generated on each group leading to branched structures. The fast exchange of iodine between the radical and the methyl iodide species has to be responsible for the activation–deactivation cycles and the controlled behavior of the polymerization as observed.

The determination of the molar masses and their distribution for low molecular, possibly highly branched polymers is a demanding task. We applied the GPC calibrated with linear polystyrene standards and the GPC coupled with multiangle light scattering detection. The results, collected in Table 1, have to be critically evaluated.

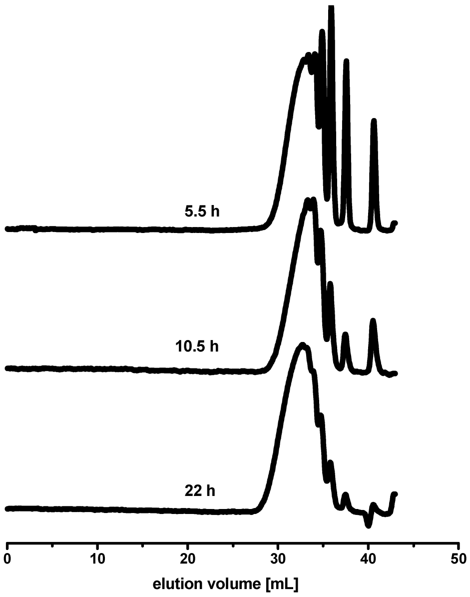


Fig. 2. GPC traces of the polymerization product of *p*-(iodomethyl)styrene initiated with AIBN.

The results obtained using the calibration with linear standards are obviously not reliable. There are two reasons for this. The studied polymers are highly branched (see the analysis of the NMR spectra further down) and therefore much more compact than the linear polymers used for the calibration. Also is the molar mass of the chain unit of poly[*p*-(iodomethyl)styrene] 2.5 times higher than that of styrene, but it does not occupy 2.5 times the volume, and the volume is what the GPC detects.

The light scattering detection should be expected to deliver correct values, although it is often stated that the light scattering cannot be applied for the analysis of low molar mass compounds. This limitation is not necessary true. The sensitivity of the contemporary equipment is high enough that even low molar masses are determined exactly, if the refractive index increment is high enough. Recently, Xie et al. have critically examined a number of methods for the determination of the molar masses of oligomers and found SEC MALLS to yield best results in the range between 1000 and 10,000 g/mol [23]. The refractive index increment for our polymers: $dn/dc = 0.205$ is one of the highest values ever observed and ensures sufficient scattering intensity. A danger of distortion is, however, the dependence of the refractive index increments upon the molar mass. The dn/dc value might be slightly different for each oligomer. This influences both the concentration detection and the molar masses calculated from the Debye equation. Probably the molar mass distribution would be influenced more than the molar masses themselves [24].

In one case the number average molar mass was calculated from the ^{1}H NMR spectrum, assuming one ‘focal point’ (the double bond) per molecule. The result is very close to the value obtained from the light scattering detection coupled with GPC, confirming the relative reliability of the light scattering measurements.

The polydispersity index measured is surprisingly low. Müller et al. predict theoretically for the ideal SCVP a polydispersity index roughly equal to the degree of polymerization [25]. In our case this would mean a polydispersity index between 6 and 10. Even if the values of M_w/M_n ratio measured by the GPC are not exact, the true values cannot be so much different being below 1.5. Such low polydispersities might indicate that linear chains are formed. However, the NMR clearly evidences a highly branched structure with the degree of branching equal to 0.36 (see below).

3.2. Model polymerization: radical polymerization of styrene in the presence of benzyl iodide

To check whether the iodomethyl group of *p*-(iodomethyl)styrene may be engaged in the chain transfer reaction a model polymerization was carried out (Scheme 3). The polymerization of styrene was initiated with BPO in the presence of benzyl iodide (BzI), a reagent containing a iodomethyl group supposed to mimic the behavior of such

Table 1
Polymerization of *p*-(iodomethyl)styrene initiated with AIBN in benzene

Sample	Time (h)	Conversion of PIMS (%)	Calibration with linear PS			GPC-MALLS		
			M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
1	1.5	12	–	–	–	–	–	–
2	3.5	55	–	–	–	–	–	–
3	5.5	70	890	1200	1.35	1300	1550	1.19
4	10.5	92	1060	1300	1.23	1980	2320	1.17
5[a]	18	95	1140	1440	1.28	2200	2870	1.30
6	22	100	1340	1760	1.31	2800	3140	1.12

[a] The number average molar mass calculated for this sample from ^{1}H NMR assuming one 'focal point' (double bond) per molecule is 2300 g/mol.

group in iodomethyl styrene. The activity of benzyl iodide in the IDT has never been tested before.

Two series of experiments were carried out: using AIBN and BPO as initiators. While no conversion was achieved when using AIBN at low temperatures (65 °C), the application of BPO and elevated temperature leads to a fast polymerization of styrene. These observed differences in polymerization behavior between styrene and *p*-(iodometyl)styrene has to be assigned to an activation of the double bond by the iodomethyl group in the para position to the latter. The molar ratio of the monomer (styrene) to BPO (generator of radicals) to BzI (transfer agent controlling the process) was chosen to 1:0.01:0.03.

The course of the reaction shows that it proceeds in a controlled way (Fig. 3).

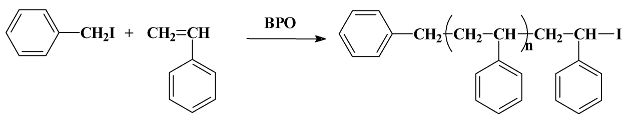
The molar masses increase with the conversion in qualitative agreement with the theoretical prediction $\mathrm{DP_{theor}} = \Delta[M]/([\mathrm{BzI}]_0 + \Delta[I])$; where $[M]$ denotes the monomer concentration, $[\mathrm{BzI}]_0$ the initial concentration of the chain transfer agent (in our case benzyl iodide) and $\Delta[I]$ the consumption of the radical initiator (BPO) [6,7]. Polymers with molar masses ranging from $M_n = 1500$ to $M_n = 4500$ g/mol and M_w/M_n up to 1.5 were obtained (Table 2).

The plot of $\ln([M]_0/[M])$ versus time indicates a constant concentration of active centers (Fig. 4).

The analysis of the ^{1}H NMR spectrum of the obtained polymer reveals the presence of the iodomethine end groups (Fig. 5, signals at $\delta = 4.6$–4.9 ppm) in an amount which agrees with the polymer molar mass determined from the GPC-MALLS (Fig. 4).

An additional evidence for the operation of the degenerative chain transfer mechanism yields the chain extension experiment. Here, the polystyrene ($M_n = 4500$ g/mol, $M_w/M_n = 1.22$, entry 6 in Table 2) obtained in the radical polymerization of styrene in the presence of benzyl iodide was used as the macroinitiator for the radical polymerization of styrene. The polymerization was carried out in the presence of BPO. The molar ratio of styrene to BPO and to the macroinitiator was 1:0.01:0.05. The GPC evidences clearly that a chain extension was achieved (Fig. 6).

Polystyrene of $M_n = 15,000$ g/mol and $M_w/M_n = 1.17$ was obtained. No measurable amount of the macroinitiator was detected by the GPC in the reaction product.



Scheme 3. Polymerization of styrene in the presence of benzyl iodide.

3.3. Structure of the poly[(*p*-iodomethyl)styrene] obtained in the radical polymerization

All the above discussed experiments indicate that the iodomethyl group is active in the radical polymerization of *p*-(iodomethyl)styrene, pushing the mechanism toward the degenerative chain transfer. Therefore a branched polymer is likely to result from the process. Taking into account the possible elementary reactions a structure like that schematically drawn in Scheme 4 should be expected.

The ^{1}H NMR spectrum (Fig. 7), even if no detailed analysis was achieved, allows to identify and to quantify the characteristic structural elements of the polymer as indicated in Scheme 4 and confirms the branched structure of poly[(*p*-iodomethyl)styrene] obtained via the radical polymerization. The signals of the vinyl CH$_2$ group in focal

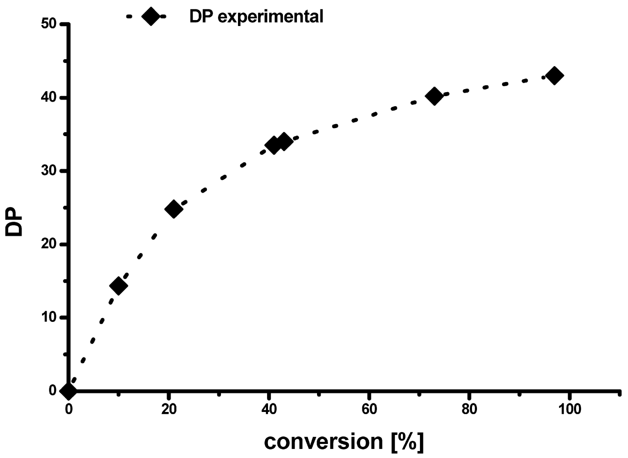


Fig. 3. Degree of polymerization versus conversion in the polymerization of styrene initiated with BPO in the presence of benzyl iodide (the dotted line is drawn as visualization aid only).

Table 2
Polymerization of styrene in the presence of benzyl iodide

Sample	Time	Conversion of styrene (%)	Conversion of BzI (%)	$M_{\mathrm{n\ GPC\text{-}MALLS}}$ (g/mol)	$M_{\mathrm{w\ GPC\text{-}MALLS}}$ (g/mol)	M_w/M_n
1	1 h	16	28	1500	2200	1.46
2	1 h 30 min	21	32	2200	3300	1.5
3	2 h 15 min	41	53	3500	5000	1.43
4	3 h 45 min	57	83	3550	4970	1.4
5	5 h 15 min	73	91	4200	5400	1.2
6	6 h	97	100	4500[a]	5600	1.24

[a] Calculated molar mass by NMR end group analysis (sample 6): $M_{\mathrm{n\ NMR}} = 4700$ g/mol.

units (**F**), coming from the initiating vinyl benzyl radical, are clearly seen at 5.1 and 5.6 ppm. The signal of the vinyl CH proton is overlapped by the signals of the aromatic protons. Iodomethine groups of $\mathbf{L_v}$ and **T** give rise to the signals in the range from 4.4 to 4.9 ppm (compare also Fig. 5). Structural differences (c–c‴) and tacticity effects result in several signals. Iodomethylene groups of linear ($\mathbf{L_v}$) and terminal (**T**) units can be distinguished by their ^{1}H NMR signals (4.0 ppm, b, and 3.8 ppm, b′, respectively). Small signals due to olefinic structures formed by dehydrohalogenation as described by Weimer et al. [19] are observed at about 3.3 and 6.3 ppm. In contrast to the branched poly[*p*-(chloromethyl)styrene] [18,19], it is possible to determine the fractions of **T**, $\mathbf{L_v}$, $\mathbf{L_c}$, and **D** structures from the signal integrals in the ^{1}H NMR spectrum. The signal integrals of protons b and b′ are representative for $\mathbf{L_v}$ and **T** units, respectively. The integral over all iodomethine protons represents $\mathbf{L_c}$ and **T**. It gives the $\mathbf{L_c}$ units if the **T** content is subtracted. The signal intensity of a proton in the focal unit (**F**) is the integral of one of the vinyl protons a. Finally, the signal intensity due to a dendritic group **D** can be calculated from the integral over all backbone CH and CH$_2$ corrected by the contributions of **F**, $\mathbf{L_c}$, $\mathbf{L_v}$, and **T** groups to this signal region

$$I(\mathbf{D}) = 1/5\{I(1.2\text{–}3.0\ \text{ppm}) - 2\times I(\mathbf{F}) - 3\times I(\mathbf{L_v}) - 4\times I(\mathbf{L_c}) - 2\times I(\mathbf{T})\} = 1/5\{I(1.2\text{–}3.0\ \text{ppm}) - 2\times I(5.09\ \text{ppm}) - 3/2\times I(b) - 4\times[I(c\text{–}c''') - 0.5\times I(b')] - I(b')\}.$$

It is obvious that $I(\mathbf{D})$ is more faulty than the other intensity values but accurate enough to allow conclusions with respect to the branched structure of poly[*p*-(iodomethyl)-styrene].

From these values the content of **T**, $\mathbf{L}(=\mathbf{L_v}+\mathbf{L_c})$, and **D** units and so the degree of branching (DB) according to Fréchet [26] can be calculated

$$\mathrm{DB} = \mathbf{T} + \mathbf{D}/(\mathbf{T} + \mathbf{L_v} + \mathbf{L_c} + \mathbf{D}).$$

From the spectrum depicted in Fig. 7 the following structural parameters were determined: $\mathbf{T} : \mathbf{L_v} : \mathbf{L_c} : \mathbf{D} = 0.24 : 0.46 : 0.18 : 0.12$ and DB = 0.36.

Besides the ^{1}H NMR spectra also ^{13}C NMR data (see Experimental Part) confirm the branched structure of the obtained poly[*p*-(iodomethyl) styrene] obtained via the radical polymerization. However, due to broad signals and signal overlapping in the ^{13}C NMR spectra quantitative results could only be obtained from the ^{1}H NMR experiments. It is important to note that different NMR

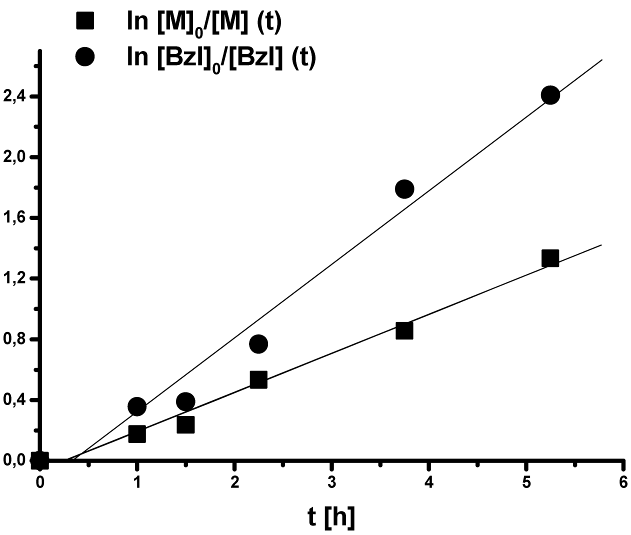


Fig. 4. Monomer and BzI consumption versus time in the polymerization of styrene initiated with BPO in the presence of benzyl iodide.

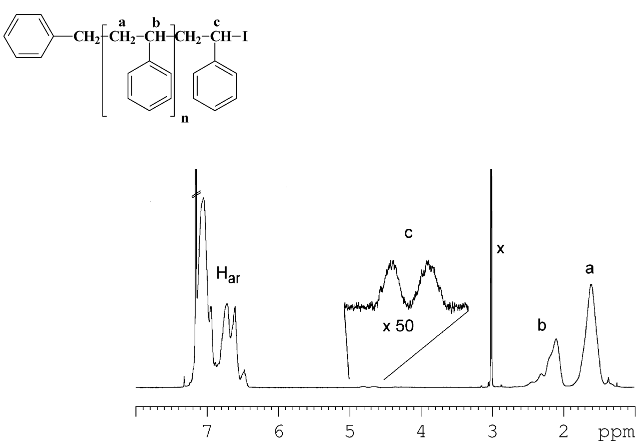


Fig. 5. ^{1}H NMR spectrum of α-benzyl-ω-iodo-polystyrene (500 MHz, C_6D_6); x—CH_3OH.

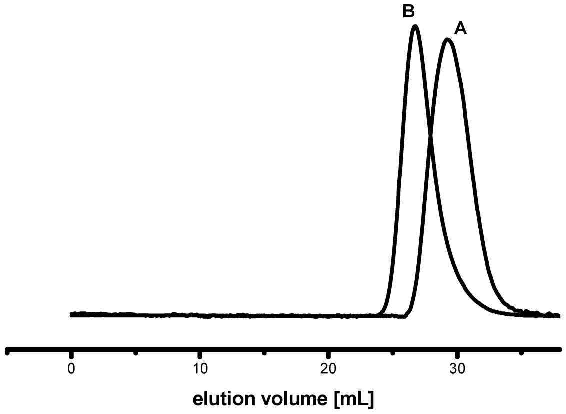


Fig. 6. GPC traces of: (A) α-benzyl-ω-iodo-polystyrene $M_n = 4800$ g/mol (see polymer 5 in Table 1), (B) product of the radical polymerization of styrene in the presence of (A).

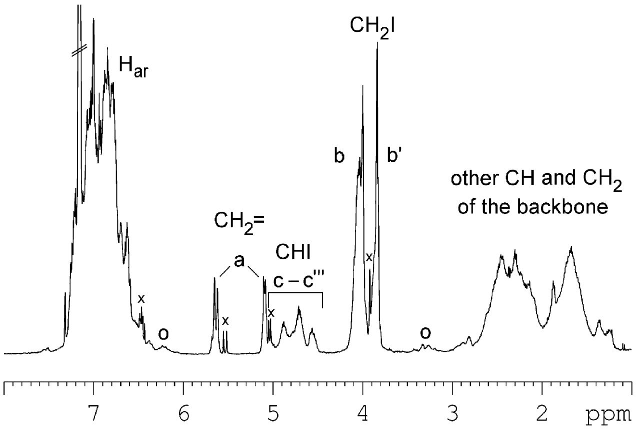


Fig. 7. ^1H NMR spectrum of poly[*p*-(iodomethyl)styrene] (500 MHz, C_6D_6). Signal assignment according Scheme 4; x—*p*-(iodomethyl)styrene and o-olefinic structures in the backbone.

techniques combining protons and carbons (DEPT as well as COSY, HMQC, and HMBC experiments) had to be used to confirm the assignment of the proton signals as given in Figs.7 and 10, but a full description of the NMR analysis cannot be the objective of the present study.

The gel permeation chromatography combined with light scattering detection and the independent measurements of the refractive index increment allow for a rather reliable determination of the molar mass and its distribution. For the polymer which NMR spectrum is shown on Fig. 7, the GPC-MALLS yields $M_n = 2800$ g/mol and $M_w/M_n = 1.2$, which corresponds to $DP = 10$. Therefore in average each macromolecule contains 10 iodine atoms. From the NMR results it can be concluded that about 60% of them are located in the iodomethylene groups.

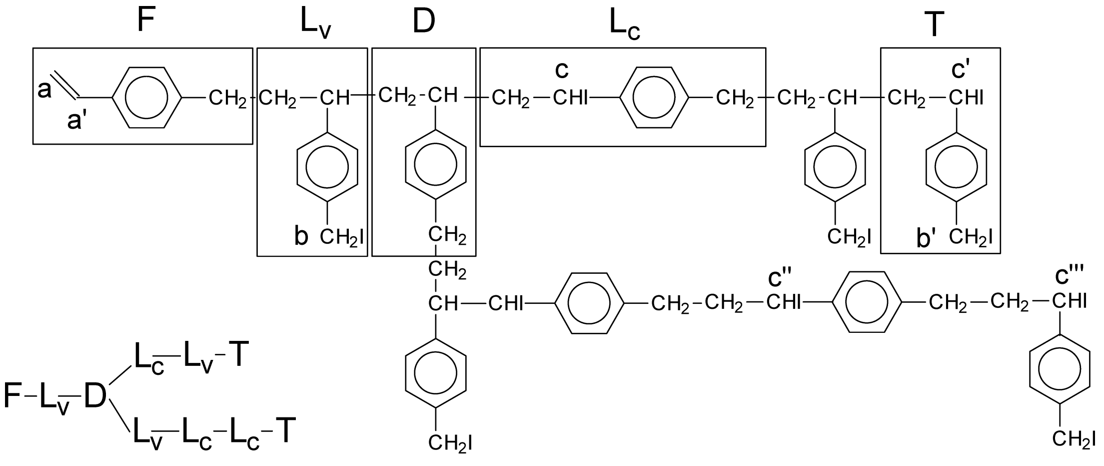
3.4. Poly[(*p*-iodomethyl)styrene] as chain transfer agent in the radical polymerization

As discussed above, benzyl iodide and iodine terminated polystyrene are efficient chain transfer agents, allowing to carry out the radical polymerization of styrene in a controlled way. Therefore it was decided to check the behavior of the poly[(*p*-iodomethyl)styrene] (sample 5 in Table 1) as a transfer agent in IDT. If it initiates the polymerization and acts as the agent of reversible degenerative chain transfer, multiarm star polymers should be obtained, as outlined in Scheme 5.

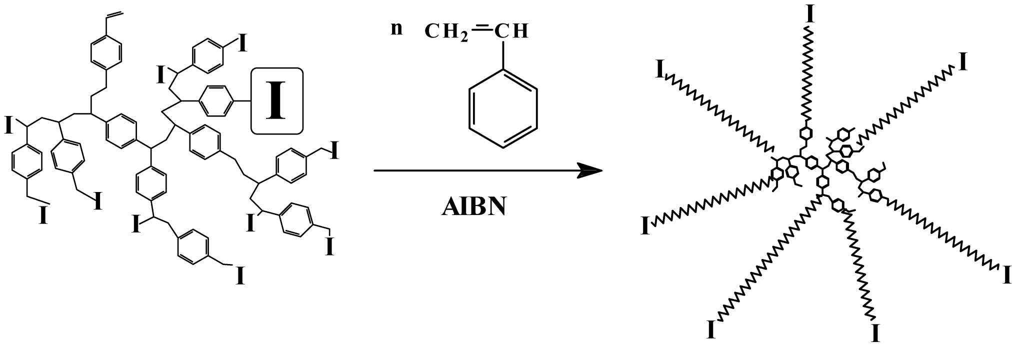
In the polymerization experiments a ratio of the iodine groups in the poly[*p*-(iodomethyl) styrene] to monomeric styrene 1 to 20 was chosen (20 mol styrene per mol iodine) together with AIBN as radical initiator (0.01 M).

The polymerization proceeds smoothly and is completed within 24 h at 67 °C. The gel chromatograms indicate an increase of the molar mass with increasing conversion (Fig. 8).

As long as the conversion does not exceed 50%, the peaks are monomodal. At low conversion, the molar masses increase linearly with the conversion (Fig. 9), indicating the living character of the polymerization and the operation of the degenerative chain transfer mechanism. At higher conversions, this linear relationship is not preserved anymore. It should be noted that at these conversions the chromatography indicates bimodal molar mass distribution.



Scheme 4. Possible structure of poly[*p*-(iodomethyl)styrene] showing the characteristic structural units.



Scheme 5. Radical polymerization of styrene in the presence of poly[*p*-(iodomethyl)styrene].

Probably the reason for the deviation of the M_n curve from the linearity and the complex shape of the chromatograms is the coupling of the growing macromolecules by recombination of the growing radicals and/or polymerization of focal double bond. As long as there are enough styrene monomer molecules in the system, the rates of these reactions remain slow compared to the growth of the star arms, they become, however, significant when the monomer is depleted.

The NMR spectra given in Fig. 10 confirm that the iodomethylene groups of the poly[(*p*-iodomethyl)styrene] take part in the polymerization. The CH_2I signal at 3.8 ppm and the CHI signal at 4.5 ppm disappear. Obviously, the terminal groups characterized by signals b′ and c′/c‴ are transferred in internal groups (b, c/c″ Scheme 6). Furthermore, the intensity ratio CHI to CH_2I increases, because the initiating CH_2I groups of the poly[*p*-iodomethyl]styrene] are replaced with CHI by reaction with styrene.

The gel permeation chromatography measurements further confirm the star-like structure, which follows also from the mechanistic considerations and NMR spectroscopy.

In Fig. 11 the number average molar masses of obtained star polymers so determined by the GPC with MALS detection are plotted versus conversion. In the same figure the molar masses for the same polymers determined by the GPC using the calibration with narrow linear polystyrene standards are marked.

In each case the true molar masses by MALS evaluation are higher than the molar masses calculated based upon calibration with linear standards (Table 3).

The value of $M_{nGPC\text{-}calibr}/M_{nGPC\text{-}MALLS}$ is in most cases close to 0.5.

There are many well founded reports that for the branched structures the measurements of molar masses based on the calibration with the linear standards yield much lower values than true molar masses of such polymers [27–32]. It has been evidenced that this effect is due to the significantly more compact structure and therefore much lower hydrodynamic volume of the branched structures than their linear counterparts of the same molar mass.

The ratio $M_{nGPC\text{-}calibr}/M_{nGPC\text{-}MALLS}$ decreases with the increasing conversion, to reach 0.34 for the sample of the highest molar mass. The elugram of this sample indicates the bimodal mass distribution (see Fig. 8). This lowered ratio may be due to the coupling of the macromolecules at high conversion, resulting in more complex and compact star architectures.

4. Conclusions

We could demonstrate that the controlled radical polymerization of *p*-(iodomethyl)styrene is possible and leads to fully soluble branched products. The study of this polymerization and of its model, the polymerization of styrene in the presence of benzyl iodide, proves that the iodine mediated chain transfer mechanism operates: iodine is transferred in a fast and reversible reaction from the iodobenzyl group to the growing chain end, which causes the controlled course of this polymerization and allows also

Table 3
Molar masses of the polystyrene samples obtained in the radical polymerization in the presence of poly[(*p*-iodomethyl)styrene]

Conversion of styrene (%)	$M_{n\ GPC\text{-}calibr}$ from PS calibration (g/mol)	$M_{n\ GPC\text{-}MALLS}$ (g/mol)	$M_{nGPC\text{-}calibr}/M_{nGPC\text{-}MALLS}$
10	2400	5000	0.47
26	4300	7700	0.55
46	6750	14,200	0.47
67	10,400	24,000	0.43
100	11,900	34,200	0.34

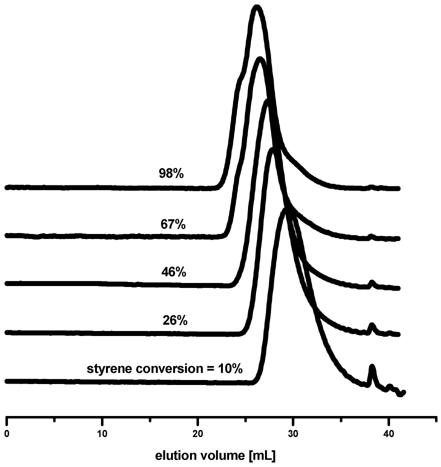


Fig. 8. GPC traces of the products of the radical polymerization of styrene in the presence of poly[*p*-(iodomethyl)styrene].

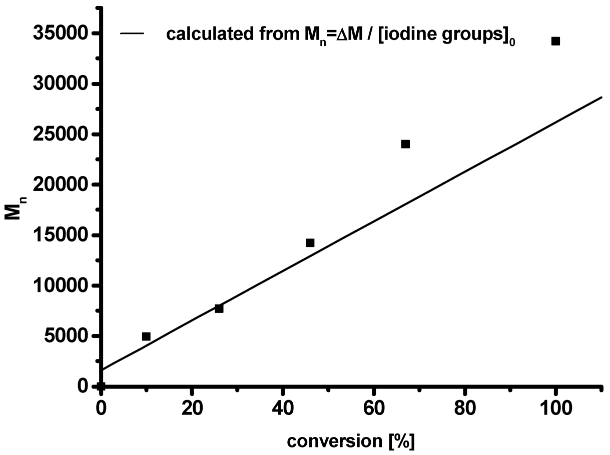


Fig. 9. M_n versus conversion in the radical polymerization of styrene in the presence of poly[*p*-(iodomethyl)styrene.

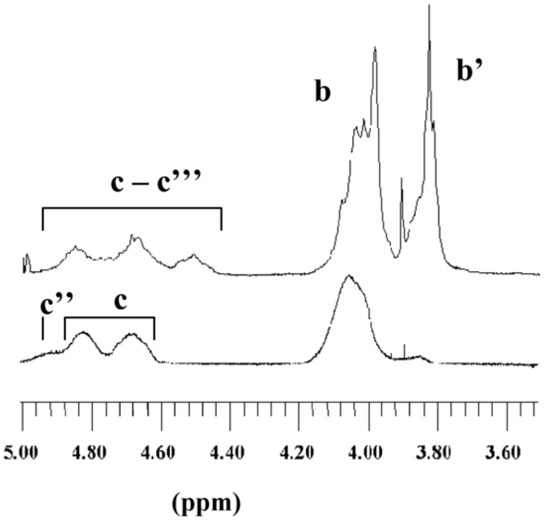
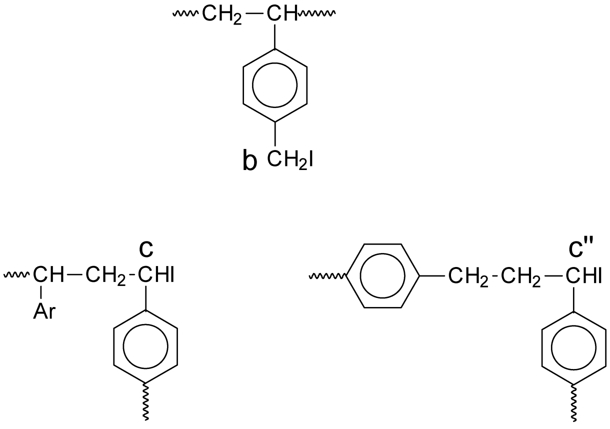


Fig. 10. ^{1}H NMR spectrum (CH_2I and CHI signals) of the poly[(*p*-iodomethyl)styrene] (upper trace) and of the product of the radical polymerization of styrene in the presence of polyPIMS (lower trace) (500 MHz; C_6D_6).



Scheme 6. Iodine-containing structures formed from poly[*p*-(iodomethyl)-styrene] after reaction with styrene.

successful chain extension experiments. *p*-(Iodomethyl)-styrene behaves similar to an inimer in the radical polymerization and therefore, this new case of the SCVP yields branched polymers, as evidenced by the NMR studies.

Branched polymers of *p*-(iodomethyl)styrene of M_n varying from 1500 to 3000 g/mol are obtained. These polymers contain reactive iodomethyl groups and may be subject of further transformations. One example of such transformation is described: when styrene is polymerized radically in the presence of poly[*p*-(iodomethyl)styrene] so obtained, the polymerization proceeds in a controlled manner and yields star-like polymers with poly[*p*-(iodomethyl)styrene] core and polystyrene arms. The length of the arms can be controlled by changing the styrene to poly[(*p*-iodomethyl)styrene] ratio and conversion.

Further reaction of and with the branched poly[(*p*-iodomethyl)styrene] are under investigations.

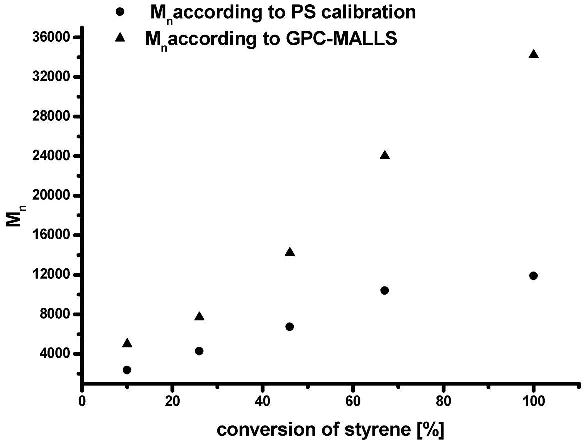


Fig. 11. Molar masses of the products of the radical polymerization of styrene in the presence of poly[*p*-(iodomethyl)styrene]: determined using SEC coupled with multiangle light scattering detector (triangles) and calculated from calibration of SEC with linear polystyrene standards (dots).

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