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A Novel Approach to Branched Polymers via Latent Thiol Chain-transfer Polymerization

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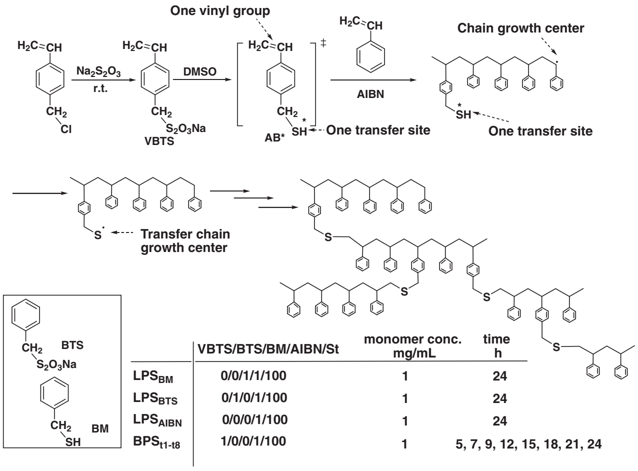
A novel sodium 4-vinylbenzyl thiosulfate (**VBTS**) monomer was designed and can be prepared effectively via the Bunte salt reaction in room temperature, which can be conveniently used as the latent chain-transfer monomer in the radical polymerization to prepare branched polymers.

Branched and hyperbranched polymers have captured considerable attention over the past few years because of their attractive features similar to dendrimers, such as high branching, multiple end groups, improved solubility, lower solution viscosity, and three-dimensional globular structure.[1] Typically, branched polymers can be synthesized conveniently via the random branch-on-branch propagation of AB_n-type monomers in large scale with relatively low cost. One of the most noteworthy and versatile approaches to branched polymers is self-condensing vinyl polymerization (SCVP) of the AB^* inimer.[2] And since Fréchet proposed this concept in 1995, this approach has been greatly expanded to various types of controlled polymerizations, such as reversible addition–fragmentation chain-transfer polymerization (RAFT), nitroxide-mediated radical polymerization (NMRP), and atom-transfer radical polymerization (ATRP).[3–5] However, many of those methods for synthesis of branched polymers also have significant drawbacks, including the need for complex monomers and harsh reaction conditions.[6]

Branched polymers can also be prepared via conventional free radical polymerization that uses only inexpensive and readily available starting materials.[7] The strategy involves the conventional free radical polymerization of vinyl monomers in the presence of a small amount of chain-transfer monomers or divinyl comonomer and thiols (–SH). However, it is very difficult to prepare a stable chain-transfer monomer containing –SH transfer group since the –SH group can easily react with vinyl under thermal condition or light irradiation. The optical alternative is to use latent sulfanyl groups (for example, the sodium thiosulfonyl group shown in Scheme 1) which can be effectively activated to release –SH transfer center and form branch points during the polymerization. We named this novel and convenient approach to branched polymers the latent thiol chain-transfer branched polymerization (**LTCTBP**).



	VBTS/BTS/BM/AIBN/St	monomer conc. mg/mL	time h
LPS_{BM}	0/0/1/1/100	1	24
LPS_{BTS}	0/1/0/1/100	1	24
LPS_{AIBN}	0/0/0/1/100	1	24
$BPS_{t1\text{-}t8}$	1/0/0/1/100	1	5, 7, 9, 12, 15, 18, 21, 24

Scheme 1. The basic concept of the latent thiol chain-transfer branched polymerization (**LTCTBP**).[11]

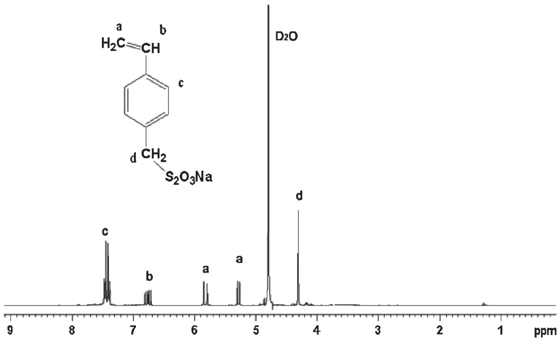


Figure 1. ^1H NMR spectrum of the sodium 4-vinylbenzyl thiosulfate (**VBTS**).

Scheme 1 outlines the basic concept of the named thiol chain-transfer branched polymerization. The synthesis of the chain-transfer monomer, i.e., sodium 4-vinylbenzyl thiosulfate (**VBTS**), was conveniently prepared via the Bunte salt reaction in room temperature.[8] As expected, a white precipitate can be easily collected after the mixture of 4-vinylbenzyl chloride and the aqueous sodium thiosulfate solution for 12 h. Figure 1 shows the ^1H NMR spectrum of the **VBTS** monomer. The peaks of sodium benzyl thiosulfate and vinyl groups can be clearly observed at 4.17–4.31, 5.27–5.30, 5.80–5.86, and 6.71–6.81 ppm. Furthermore, the sodium thiosulfate group can be effectively deprotected to release the active –SH in DMSO or DMF solvent or acidified by HCl, which can afford the **VBTS** monomer the latent chain-transfer ability in the free radical polymerization.[8]

To investigate the branched polymerization, DMSO was chosen as the polymerization solvent, more especially as the deprotection agent of the sodium thiosulfate group. As listed in Scheme 1, eight branched polymers of $\mathbf{BPS_{t1–t8}}$ were designed and prepared via one-pot synthesis at 70 °C by using **VBTS** as chain-transfer monomer, styrene (St) as common monomer, and AIBN as initiator with a constant ratio of **VBTS**/AIBN/St = 1/1/100. And for the **VBTS** chain-transfer monomer, there are two different on going polymerizations, i.e., the common radical polymerization and latent chain-transfer polymerization, at the same time. So it would be very difficult to investigate the deprotection-transfer step. For this reason, we also introduced

Table 1. The solution characteristics of the obtained polymers

	MW(GPC) $/10^4\,\mathrm{g\,mol^{-1}}$	PDI (GPC)	MW(LS) $/10^4\,\mathrm{g\,mol^{-1}}$	$[\eta]$ $/\mathrm{mL\,g^{-1}}$	$\alpha \times 10$
$\mathbf{LPS_{BT}}$	2.23	3.078	2.61	16.2	0.585 ± 0.004
$\mathbf{LPS_{BTS}}$	3.68	1.616	3.90	21.4	0.640 ± 0.006
$\mathbf{LPS_{AIBN}}$	4.67	1.642	4.93	24.3	0.624 ± 0.005
$\mathbf{BPS_{t1}}$	2.99	1.626	3.10	17.5	0.584 ± 0.006
$\mathbf{BPS_{t2}}$	2.95	1.587	3.08	16.9	0.550 ± 0.005
$\mathbf{BPS_{t3}}$	3.49	1.646	3.76	19.0	0.552 ± 0.005
$\mathbf{BPS_{t4}}$	3.75	1.702	4.18	19.7	0.559 ± 0.006
$\mathbf{BPS_{t5}}$	4.18	1.793	4.60	20.9	0.574 ± 0.005
$\mathbf{BPS_{t6}}$	5.28	1.967	6.24	23.6	0.567 ± 0.005
$\mathbf{BPS_{t7}}$	5.01	1.937	5.89	23.2	0.550 ± 0.005
$\mathbf{BPS_{t8}}$	6.34	2.185	7.86	25.3	0.554 ± 0.004

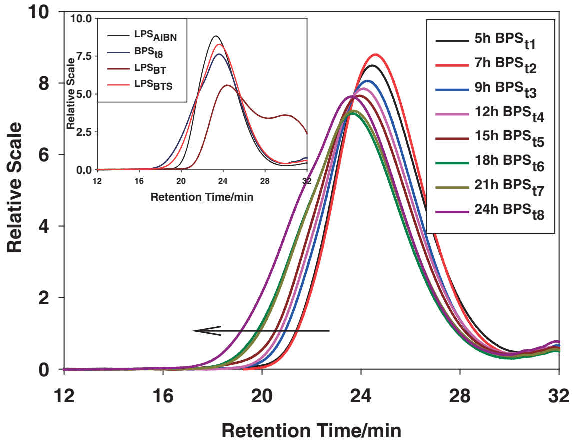


Figure 2. The GPC curves of the branched polymers along with polymerization time; the inset is the GPC curves of three linear polymers and a branched polymer $\mathbf{BPS_{t8}}$.

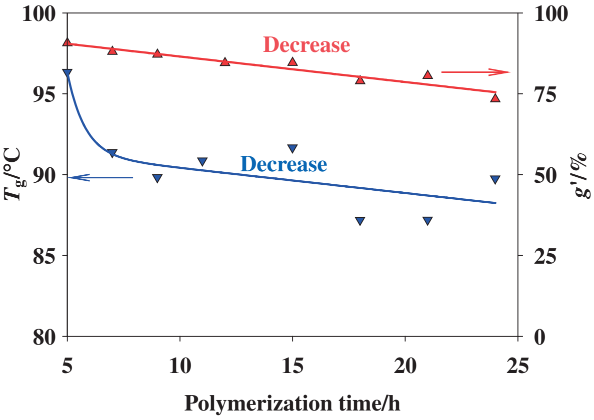


Figure 3. Plots of the branching magnitude of g' (red one) and the glass-transition temperature T_g (blue one) on polymerization time.

the analog chain-transfer compounds, sodium benzyl thiosulfate (**BTS**) and benzylthiol (**BT**) to prepare linear polymers of $\mathbf{LPS_{BTS}}$ and $\mathbf{LPS_{BT}}$, respectively. All the polymers were obtained without gelation and purified using the same method described in the experimental section and dried in vacuum oven for 12 h at 40 °C.

A Wyatt triple detector system equipped with a WATERS 1515 pump, a WATERS 2414 detector, a Wyatt miniDAWN TRISTAR detector, a Wyatt VicoStar viscometer detector, and Wyatt ASTRA Chromatography Software was used to determine the molecular weights, PDIs, and other solution characteristics of the obtained polymers. Additionally, all the polymers were also characterized by DSC and NMR.

Table 1 summarizes the typical characteristics of the obtained polymers. It is known that Mark–Houwink shape parameter ($[\eta] = \mathrm{K}M^{\alpha}$) of the branched polymers has lower values than those of their linear counterparts.[6] As expected, the PDI and α values of $\mathbf{LPS_{BTS}}$ are very near those of $\mathbf{LPS_{AIBN}}$ (which was prepared without any chain-transfer agent), which indicates the ongoing deprotection-transfer step of the sodium thiosulfonyl group in DMSO solvent. This can also be demonstrated from their GPC curves. And when transferred by the **VBTS** monomer, the branched polymers of $\mathbf{BPS_{t1\text{–}t8}}$ gained surprisingly low PDI values ranging between 1.587 and 2.185. As expected, the molecular weights of all branched polymers measured by GPC were much lower than those measured via light scattering (an absolute method for molecular weight determination). The obtained Mark–Houwink α-values range between 0.550 and 0.584 (Table 1, column 6). Which is consistent with the compact and globular shape of branched polymer compared to their linear counterpart.

Figure 2 compares the GPC curves of the branched polymers vs. the varied polymerization time. As expected, the leading peak shifted forward and the molecular weight distribution broadened along with the polymerization time. And interestingly, all the branched polymers gained high Gaussian-shaped curves without any shoulders or tailing peaks as the linear polymer $\mathbf{LPS_{AIBN}}$ and $\mathbf{LPS_{BTS}}$ did. The observed PDI values are quite lower (Table 1, column 3), which is very surprising for branched polymers prepared via one-pot polymerization.

It is well known that the solution properties of branched polymers, such as MW dependence of intrinsic viscosity ($[\eta]$) and the radius of gyration, are remarkably different from their linear analogs due to the compact character of the branched structure.[9] More specifically, the value of the exponential in the Mark–Houwink relation for branched polymer is apparently smaller than that for the linear one.[10] And the effect of architectural branching can also be expressed by the contracting factor, g' which is defined as $g' = [\eta]_b/[\eta]_l$, where $[\eta]_b$ and $[\eta]_l$ are the obtained intrinsic viscosity of branched polymers in solvent and the calculated one according to the Mark–Houwink equation ($[\eta] = \mathrm{K}M^{\alpha}$), respectively.[9,10] Here, we use the observed Mark–Houwink parameters of $\mathbf{LPS_{AIBN}}$ ($K_l = 3.042 \times 10^{-2}\,\mathrm{mL\,g^{-1}}$, $\alpha_l = 0.624$) and the absolute molecular weight MW(LS) of branched polystyrene (column 4, Table 1) measured by lighter scattering to calculate the $[\eta]_l$ values. As shown in Figure 3, the magnitude of g' decreased linearly along with the polymerization time and the branched polymer $\mathbf{BPS_{t8}}$ gained the lowest g' value of 73%, which indicates that much more **VBTS** monomers were copolymerized into the polymer chains to form branches along with the polymerization time. The decrease of the glass-transition temperature (T_g) on the varied polymerization time in Figure 3 also demonstrates this branch growth.

In summary, the novel sodium 4-vinylbenzyl thiosulfate (**VBTS**) monomer was designed and can be prepared effectively via the Bunte salt reaction in room temperature. And through the deprotection-transfer reaction of **VBTS** monomer in the radical polymerization, the named latent thiol chain-transfer branched polymerization (**LTCTBP**) can be approached conveniently. It is easy to envision that this general and convenient branched polymerization can readily be applied to many vinyl monomers. Therefore, as an extension of this work, we are currently preparing hyperbranched polymers with other functional vinyl monomers.

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