Single-Step Synthesis of Internally Functionalizable Hyperbranched Polyethers

Raj Kumar Roy, S. Ramakrishnan

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India
Correspondence to: S. Ramakrishnan (E-mail: raman@ipc.iisc.ernet.in)

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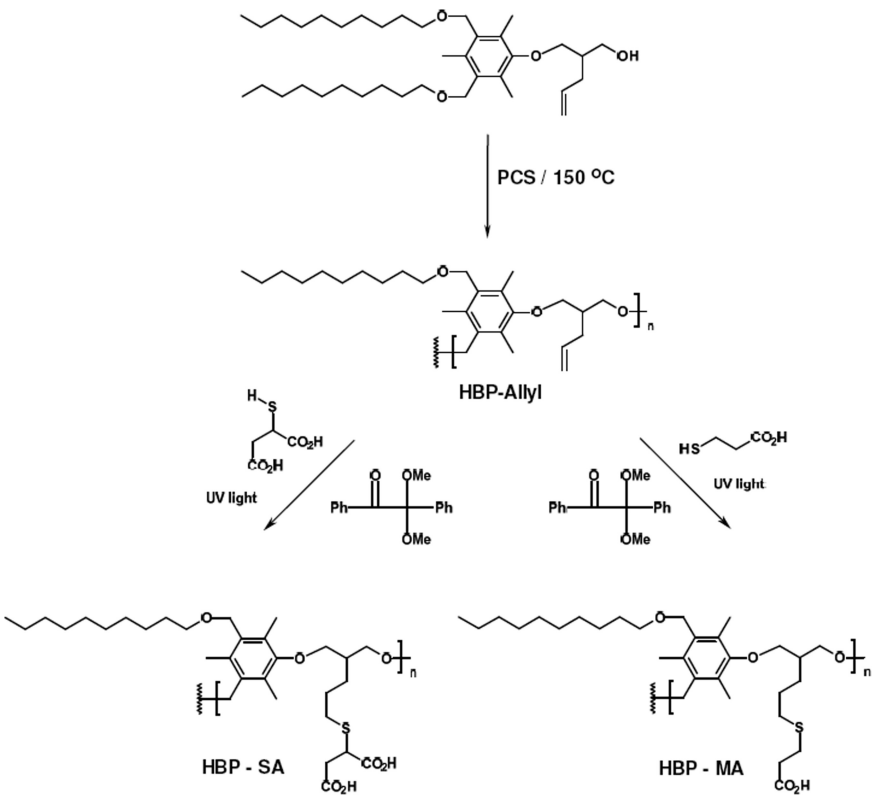
ABSTRACT: Radical catalyzed thiol-ene reaction has become a useful alternative to the Hüisgen-type azide-yne click reaction as it helps expand the variability in reaction conditions as well as the range of clickable entities. In this study, the direct generation of a hyperbranched polyether (HBPE) having decyl units at the periphery and a pendant allyl group on every repeat unit of the polymer backbone is described; the allyl groups serve as a reactive handle for postpolymerization modifications and permits the generation of a variety of internally functionalized HBPEs. In this design, the AB_2 monomer carries two decylbenzyl ether units (B-functionality), an aliphatic —OH (A-functionality) and a pendant allyl group within the spacer segment; polymerization of the monomer readily occurs at 150 °C via melt transetherification process by continuous removal of 1-decanol under reduced pressure. The resulting HBPE has a hydrophobic periphery due to the presence of numerous decyl chains, while the allyl groups that remain unaffected during the melt polymerization provides an opportunity to install a variety of functional groups within the interior; thiol-ene click reaction with two different thiols, namely 3-mercaptopropionic acid and mercaptosuccinic acid, generated interesting amphiphilic structures. Preliminary field emission scanning electron microscope (FESEM) and Atomic Force Microscopy (AFM) imaging studies reveal the formation of fairly uniform spherical aggregates in water with sizes ranging from 200 to 400 nm; this suggests that these amphiphilic HBPs is able to reconfigure to generate jellyfish-like conformations that subsequently aggregate in an alkaline medium. The internal allyl functional groups were also used to generate intramolecularly core-crosslinked HBPEs, by the use of dithiol crosslinkers; gel permeation chromatography traces provided clear evidence for reduction in the size after crosslinking. In summary, we have developed a simple route to prepare core-clickable HBPEs and have demonstrated the quantitative reaction of the allyl groups present within the interior of the polymers; such HB polymeric systems that carry numerous functional groups within the core could have interesting applications in analyte sequestration and possibly sensing, especially from organic media. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4125–4135

KEYWORDS: amphiphiles; core–shell; crosslinking; hyperbranched; nanoparticles; polyethers

INTRODUCTION Dendrimers are highly branched, symmetric, monodisperse macromolecules with several unique features that are uncharacteristic of conventional macromolecules.[1] These unusual features have attracted researchers to explore their potential applications in biotechnology, nanotechnology, and so forth.[2] The unique architecture of dendrimers is very useful for mimicking some of the nature's complex functions; for example, site-isolation,[3] light-harvesting,[4] catalysis,[5] and so forth. Several applications of dendrimers rely on the compartmentalization of the core and shell.[6] Recently, researchers have also begun to explore site-specific functionalization of the core region to develop newer applications.[2(h)] Several interesting properties of internally functionalized dendrimers, in conjunction with peripheral functionalization, have been developed; for instance, energy cascading from periphery to the core of the dendrimer,[7] catalytic process,[8] and so forth. Owing to the step-wise synthesis of dendrimers, functional groups can also be selectively incorporated at various locations, such as the core, periphery or even within specific internal layers of the Dendrimer. Conversely, hyperbranched polymers (HBPs) that are prepared by a single-step methodology do not have a distinct core or periphery; therefore, it is a challenging task to design suitable monomers for internal functionalization. Although HBPs contain numerous linear defects, amphiphilic HBPs have been shown to reconfigure to create distinct core and shell domains.[9] Therefore, exploring methodologies to install specific functional groups within the core of reconfigured HBPs could create interesting application potentials.

Some years ago, Haag et al.[10] exploited the presence of two types of hydroxyl groups in HB polyglycerol, one an isolated

Additional Supporting Information may be found in the online version of this article.



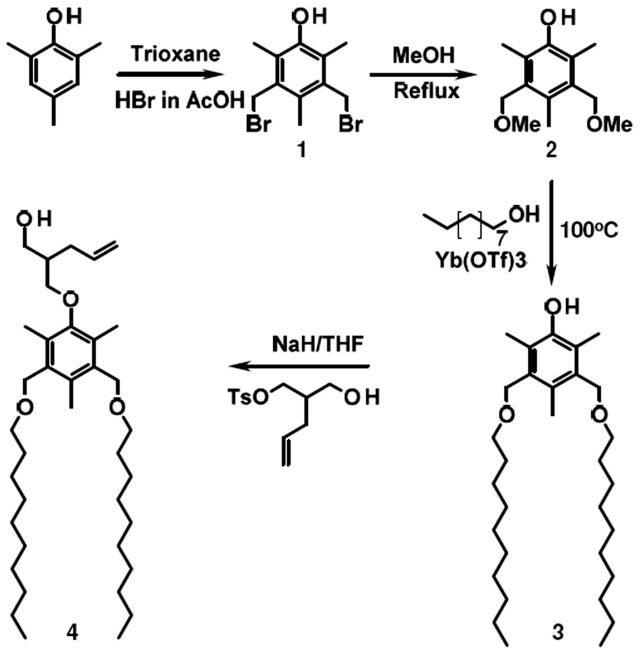
SCHEME 1 Synthesis of the internally clickable HBP and its derivatization.

—OH groups in the linear defect sites and the other the vicinal diols at the terminal units, for selective functionalization. They used the acetal or ketal forming reaction to discriminate between the linear and terminal units; this enabled them to create core–shell architectures in the hyperbranched polymer. Ambade and Kumar[11] prepared a potentially functionalizable hyperbranched polyurea from a suitably designed carbonyl azide-based AB_2 monomer; here N-allyl groups were present in every repeat unit of the hyperbranched polymer. Later, using a suitable capping agent, they decorated the periphery with long chain hydrocarbon units. The N-allyl groups within the HBP could, in principle, have been transformed to a variety of interesting functional groups making this polymer one of the early examples of potentially functionalizable HBPs; however, the authors do not appear to have explored this possibility.

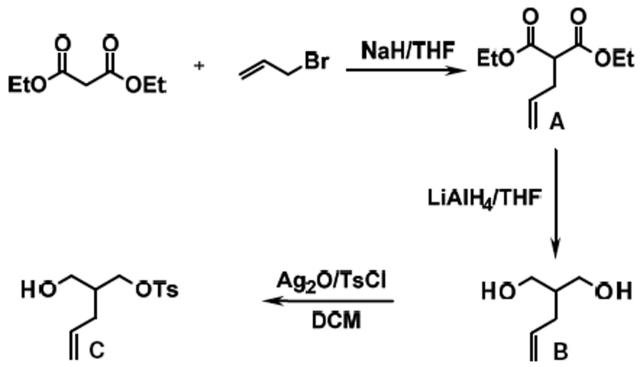
In an effort to prepare internally functionalized hyperbranched polymers, we selected the thiol-ene click reaction to confer the interior of the HBP with variety of functional groups. Although the thiol-ene reaction is over a century-old reaction, interest in this reaction has been revived recently because of the mild reaction conditions, quantitative yield, absence of side-products, and so forth.[12] More importantly, comparison of this reaction with the Cu-catalyzed azide-yne click reaction reveals some distinct advantages: (a) the thiol-ene reaction can be done in the absence of a metal ion, and (b) it can be initiated photochemically in the absence of a radical initiator.[13] Given the merits of the thiol-ene reaction and its wide range of applicability, it would be useful to develop simple single-step strategies to synthesize hyperbranched polymers that carry numerous thiol-ene clickable allyl groups within the interior. We have recently demonstrated that HBPs carrying numerous allyl groups at their periphery can be readily synthesized in a single step and subsequently used to access a wide range of peripherally functionalized structures using the thiol-ene click process.[14] In this report, we describe a single-step preparation of a peripherally hydrophobic hyperbranched polyether (HBPE) with clickable internal functionality, using a suitably design AB_2 monomer. Further, we demonstrate that these HBPEs can be readily transformed to amphiphilic systems by reaction with polar thiols that renders the core hydrophilic; we have then examined the solution behavior and aggregation properties of these interesting class of HBPs, in addition to exploring intramolecular core-crosslinking.

RESULTS AND DISCUSSIONS

Over a decade ago, we developed a simple strategy for preparing HBPs via a novel melt transetherification process, wherein the AB_2 monomer carried two methoxybenzyl groups (B type) and an aliphatic —OH group (A type).[15] The polymerization was performed under mildly acidic conditions using pyridinium camphorsulfonate (PCS) as the catalyst, at 150 °C. As the transetherification is a reversible reaction similar to transesterification, removal of low boiling methanol drives the equilibrium in the forward direction to



SCHEME 2 Synthesis of the AB_2 (**4**) monomer carrying pendant allyl group.



SCHEME 3 Synthesis of the allyl-containing spacer (**C**).

generate the HBPE. Subsequently, we had also shown that the polymerization process is not only limited to methoxybenzyl group but is equally applicable to propargyloxybenzyl[16] and allyloxybenzyl groups.[14] Thus, it became evident that the transetherification process can be readily exploited for polymer synthesis as long as the removal of the condensate, that is, the alcohol, is feasible under the polymerization conditions. Based on these earlier studies, we designed a novel AB_2 monomer (Scheme 1) that carries two decyloxybenzyl groups and an aliphatic —OH group; the unique feature of this design is inclusion of a pendant allyl group in the spacers segment. It may be expected that this monomer will undergo melt condensation under standard acid-catalyzed transetherification conditions at 150 °C; the equilibrium would be driven to polymer formation by the continuous removal of 1-decanol under reduced pressure. The AB_2 monomer in turn was prepared as outlined in Scheme 2; the bis(methoxymethyl) Mesitol derivative (2) was transformed to the corresponding decyloxy analogue (3) by transetherification in the presence of a very effective Lewis acid catalyst, namely yitturbium triflate; an excess of 1-decanol was used to prevent the possibility of premature polymerization. Compound 3 was then coupled with the allyl-carrying spacer (synthesized as per Scheme 3) to give the required AB_2 monomer (4). The monomer was then polymerized under standard melt transetherification conditions.[15]

The proton NMR spectra of the monomer **4** and the parent HBPE (**HBP-Allyl**) are shown in Figure 1, along with the peak assignments. One of the salient differences in the polymer spectra is the decrease in the relative intensity of the peaks belonging to the decyloxy group; the ratio of the terminal methyl protons of the decyl units (peak **l**) to the benzylic protons (peak **c**) changes from 1.5:1, in the monomer, to nearly 0.75:1, in the polymer. This implies that one equivalent of the decyl group has been lost as decanol and confirms that high conversion has indeed been achieved. Further, the benzylic methylene peak splits in two due to the presence of both backbone and terminal benzylic units. Most importantly, it is also evident that the pendant allyl groups remain unaffected during the high temperature melt polymerization process; the relative intensities of the peaks due to the allyl units match well with the expected value (**a**:**l** is 1:3). The molecular weight of the polymer was determined using gel permeation chromatography (GPC), which was coupled to a triple detector system, and Mn was found to be around 12,000 based on the Universal calibration method. Although the degree of branching was difficult to establish in this case, it could be assumed to be similar to those containing a simple alkylene spacer,[17] which was found to be around 0.5, along expected lines.

One of the virtues of generating HBPs that carry internal allyl groups is that it provides an opportunity to generate a wide range of polymers with distinct properties by simply clicking with different organic thiols. Of the various approaches to carry out thiol-ene reactions, the photochemically initiated approach, using 2,2-dimethoxy 2-phenyl acetophenone as the radical-initiator, is often the method of choice. Hence, in this study, a solution of the parent polymer **HBP-Allyl** and the required thiol was taken along with the initiator in chloroform and irradiated using a Hg-vapor lamp for about 4 h. The isolated polymers were analyzed using ^{1}H NMR and GPC.

Two different thiols (3-mercaptopropionic acid [**PA**] and mercaptosuccinic acid [**SA**]) were clicked onto the HBPE in this study; and the samples thus obtained were labeled **HBP-PA** and **HBP-SA**, respectively. In both cases, our objective was to prepare an amphiphilic hyperbranched polymer having hydrophobic shell and hydrophilic core. The expected structures of these clicked hyperbranched polymers are shown in Scheme 1. The ^{1}H NMR spectra of the parent polymer, along with the two clicked polymers, are shown in Figure 2; the region where the allyl proton signals is expected has been expanded to reveal the absence of residual allyl groups in the polymer, thereby confirming that the

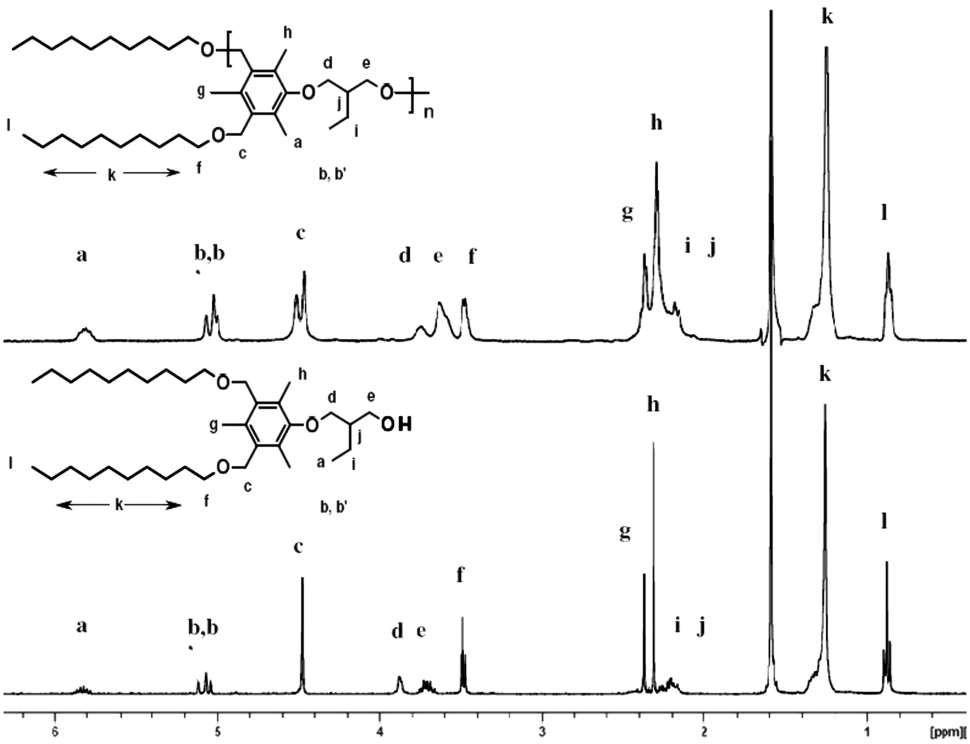


FIGURE 1 ^{1}H NMR spectra of monomer **4** and the HBP, **HBP-Allyl**.

click reaction has proceeded to near completion in both the cases. In addition to the disappearance of the allyl proton signals, the relative intensities of the signals arising from the clicked moiety also matched well with the expected values for quantitative conversion. These observations clearly suggest that HBPs bearing allyl groups within the core can indeed serve as compact *hyperscaffolds,* within the core of which a variety of function-performing units could be ligated under mild conditions.

It is well-known that the thermal properties of HBPs depend strongly on the nature of the peripheral functional groups.[18] However, little is known about the dependence of Tg on the nature of functional groups within the core of HBPs. The DSC thermograms of the two clicked HBPEs, along with that of the parent polymer **HBP-Allyl**, are shown in Supporting Information Figure S1. The parent hyperbranched polymer exhibited a sharp peak at −45 °C and a broad one at −15 °C; these were very weak and could reflect the melting (and some associated transition) of the segregated decyl chains, although unequivocal interpretation of this is not possible without further characterization. However, both the internally functionalized HBPEs were found to be completely amorphous and exhibited only a glass transition temperature; the Tg of **HBP-SA** (−10 °C) was slightly lower than that of **HBP-PA** (0 °C). The amorphous nature of these derivatives is intriguing; this may be due to the intramolecular H-bonding within the core region that renders a single chain nanoparticle-like nature to these polymers and consequently the improper segregation of the peripheral decyl chains could hinder their crystallization. Thus, it is clear that the presence of internal functional groups, especially those that can interact strongly, could modify the thermal properties in fairly unexpected ways to generate amorphous system.

When compared with dendrimers, hyperbranched polymers contain numerous structural defects and are typically highly polydisperse; thus formation of uniform aggregated structures appears would be difficult. However, recent studies suggest that the HBPs also self-assemble to form fairly uniform and interesting structures; for instance, micelles, vesicles, microscopic tubes, fibers, and so forth, have been reported using amphiphilic hyperbranched polymers.[19] The interest in self-assembled structures based on HBPs is primarily because of the relatively straightforward methodology used for their synthesis, which makes them more readily accessible.

Very recently, we showed that hyperbranched polymers, randomly functionalized with PEG (polyethylene glycol) and docosanol (C-22) at their periphery, adopt a Janus structure;[20] the immiscibility of docosyl and PEG segments and the crystallization of docosyl units into a paraffinic lattice were shown to be the driving motivation for the formation of self-segregated Janus structures. In this study, the HBPEs carrying long chain hydrocarbon (decyl unit) at the periphery and either mercaptopropionic acid (**HBP-PA**) or SA (**HBP-SA**) units within the interior were examined for their aggregation behavior.

All the polymers were readily soluble in a wide range of solvents, such as chloroform, THF, hexane, and so forth.

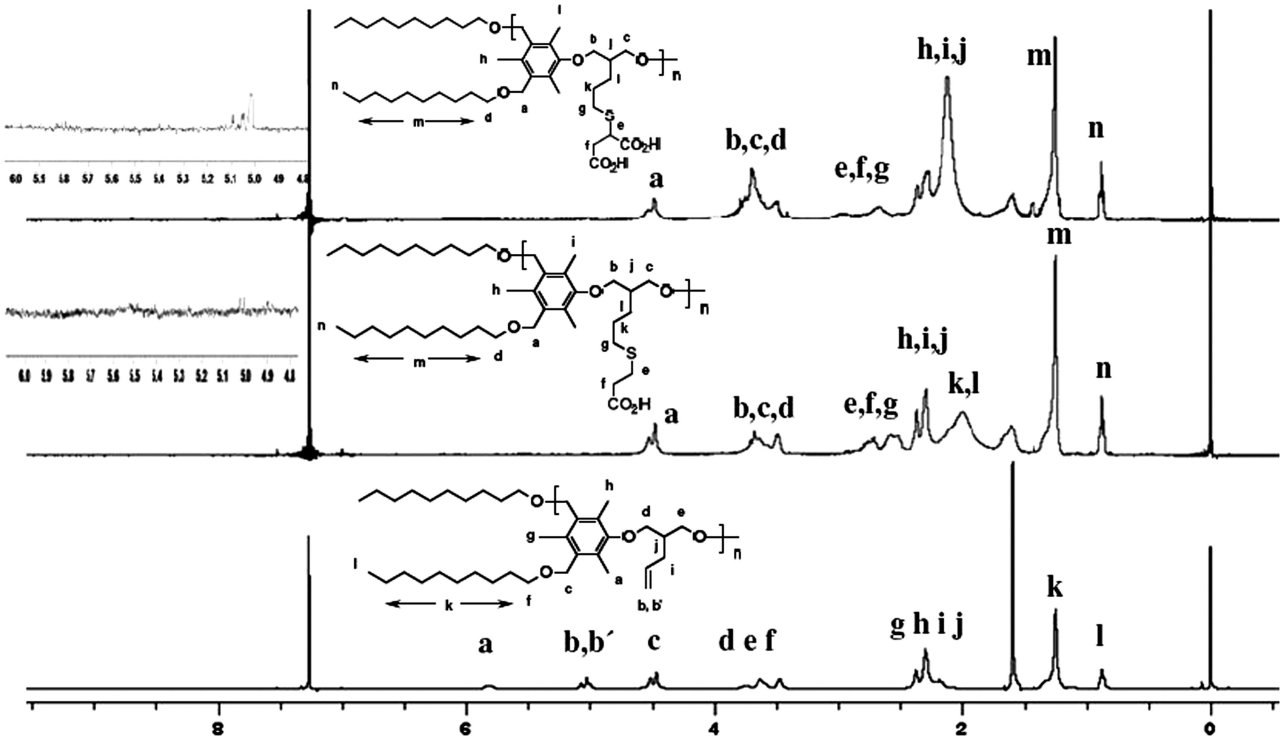


FIGURE 2 ^{1}H NMR spectral stack plot of parent polyether **HBP-Allyl** (bottom), and those clicked with 3-mercaptopropanoic acid **HBP-PA** (middle) and mercaptosuccinic acid **HBP-SA** (top). The expanded region shows the near completion disappearance of the allyl protons.

HBP-PA was completely insoluble in water, whereas **HBP-SA** was partially soluble; however, both of them were completely soluble in aqueous alkali due to the ionization of the internal carboxylic acid groups. The solubility in aqueous alkaline medium indicates that the internally functionalized HBPEs are able to invert so that the carboxylate groups are solvated in water; such inverted amphiphilic structures could then self-assemble to form variety of aggregates. To examine the nature of aggregates formed, ~1 mg of the polymer was taken in 2 mL of water containing the required amount of $NaHCO_3$; the solution was sonicated until a clear solution is formed, filtered through a 0.47 μm filter and a few drops of this solution was cast on a substrate and allowed to dry. Visualization under field emission scanning electron microscope (FESEM) clearly showed the formation of spherical aggregates (Fig. 3) with reasonably uniform sizes (~200–400 nm). To ascertain the sizes of these self-assembled structures in solution, we carried the dynamic light scattering (DLS) measurements, which showed that the average size of the

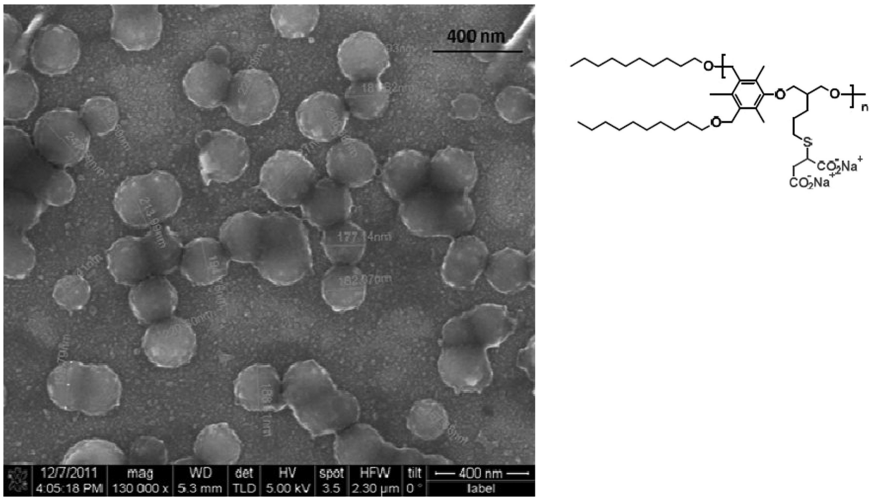


FIGURE 3 FESEM image of **HBP-SA**.

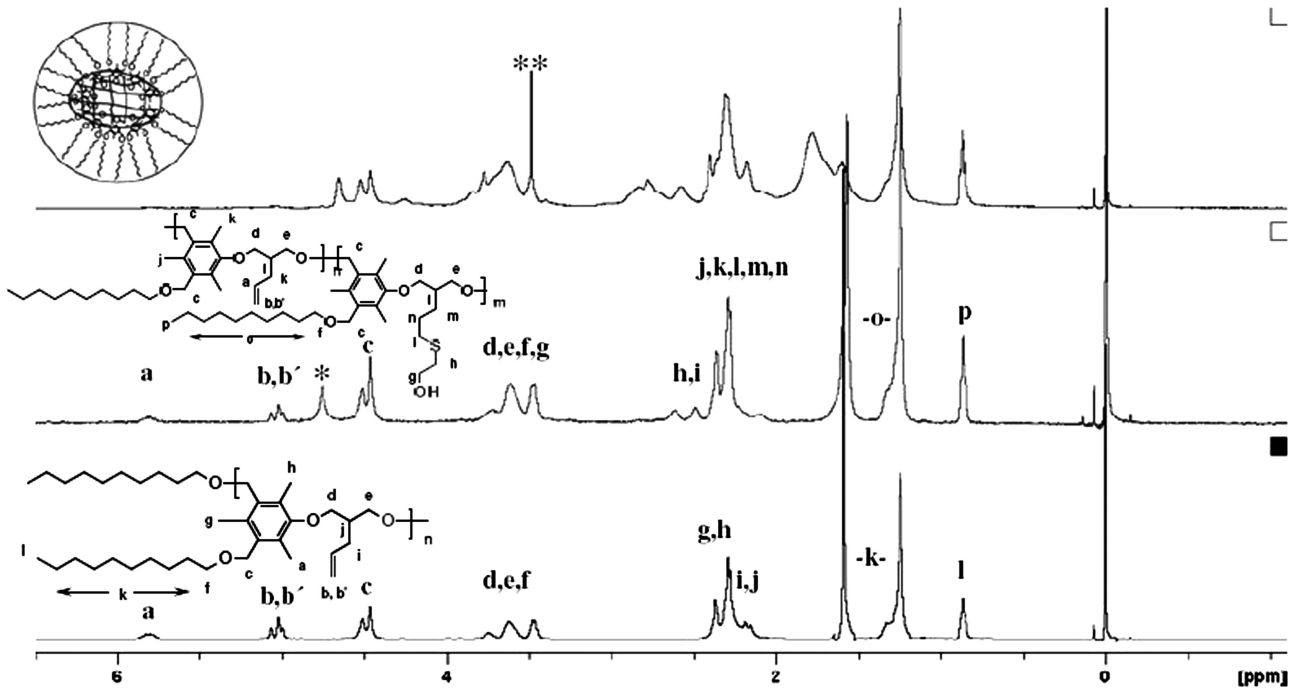


FIGURE 4 ^{1}H NMR spectral stack plot of parent polymer HBP-Allyl (bottom); partially clicked HBPE (middle); and core-crosslinked HBPE (top). Peaks marked with an * are due to OH from —SCH_2CH_2OH and those with an ** due to residual MeOH (used for reprecipitation of polymer).

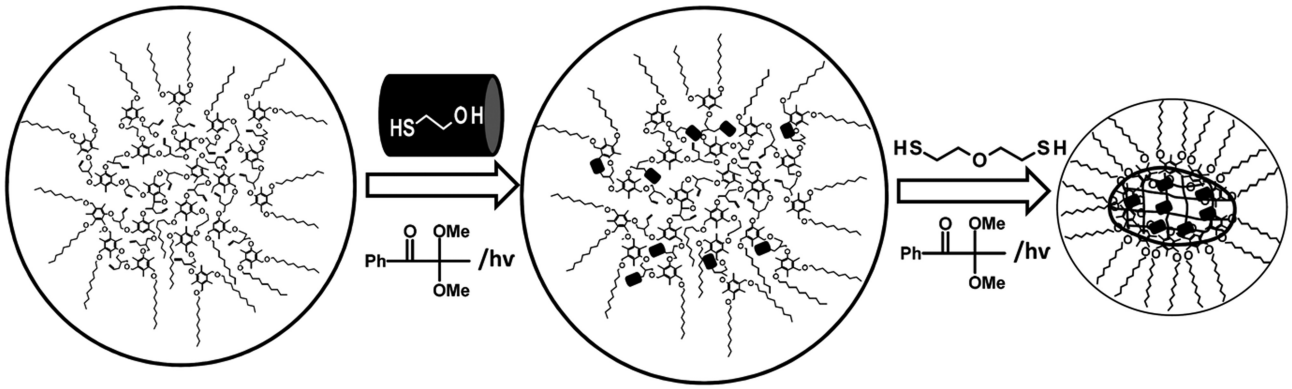
aggregates were about ~240 nm (Supporting Information Fig. S2), which is in fair agreement with the FESEM data.

Atomic Force Microscopy (AFM) images of the same sample also confirmed the formation of spherically aggregates structures (Supporting Information Fig. S2); however, the concentration of the aggregates was far higher and hence substantial particle overlap was seen. The line scan in the AFM image reveals that the average size of these spherical aggregates is around 200 nm. Given the fairly large size of these aggregates, they could be either vesicular or a multimicellar aggregate. In aqueous alkaline medium it might be expected that the internally carboxylated HBPs would turn inside-out and generate a jelly-fish like structure with alkyl groups sticking out; such reconfigured entities can then aggregate to form micelles. It is clear that simple micelles formed by such inverted molecular entities cannot exceed 10 nm in size; hence, the large aggregates must be built of several such micelles that aggregate together to for these giant structures.[21]

Intramolecular Core Crosslinking

One of the other objectives in this study was to use the internal allyl groups to generate core-crosslinked hyperbranched polymers; this could be achieved by performing the thiol-ene click reaction in the presence of a dithiol. However, our first attempts to do so under normal conditions led to the formation of some insoluble cross-linked products; this clearly suggested that intermolecular process could not be completely precluded. Core and shell-crosslinked dendrimers have been previously reported, wherein the crosslinking reactions were performed under very dilute conditions.[22] To devise a simple method to preclude crosslinking, we considered an alternate strategy wherein the dithiol crosslinker would have an intrinsic preference to reside within the core-region of the amphiphilic HBPE, thereby reducing the probability of interchain reactions. To achieve this, we conceived of a two-step process (Scheme 4); in the first step, we transformed the parent polymer **HBP-Allyl** to an amphiphilic core–shell system by installing numerous hydroxyl groups within the core by reacting the parent polymer with 2-mercaptoethanol; however, care was taken to ensure that a reasonable fraction of the allyl groups were left unreacted. The resulting polymer carried a very hydrophobic periphery due to the dodecyl chains and a hydrophilic core due to the presence of a large number of hydroxyl groups within the core. In the second step, the core-modified polymer was dissolved in a nonpolar solvent, like hexane, and a relatively polar dithiol crosslinker, namely diethylene dithioglycol (Scheme 4), was introduced; under these conditions, it may be expected that the crosslinker will preferentially partition within the polar core of the HBPE, wherein the residual allyl groups would also be present. The photo-initiated crosslinking resulted in the generation of the core-crosslinked HBPE; despite this precaution, a small amount of insoluble product was formed due to some crosslinking, which was removed by filtration using a 0.45 μm filter.

The ^{1}H NMR spectra of the partially clicked amphiphilic HBPE along with core-crosslinked HBPE are shown in Figure 4; the extent of mercaptoethanol incorporation was readily estimated by comparing the signal intensity of the allyl peak (**a**) with that of the benzylic peak (**c**), and it was established



SCHEME 4 Schematic representation of the formation of core-crosslinked HBP; the first step renders hydrophilicity to the core and the second step crosslinks the core.

that about ~70% of the allyl groups was transformed in the first step, leaving behind about 30% for the second crosslinking step. The spectrum of the polymer after the second intramolecular crosslinking step revealed a near complete disappearance of allyl proton signals, thereby confirming that the thiol-ene crosslinking process within the core had occurred effectively. Furthermore, in the case of the core-crosslinked polymer, a considerable broadening of the peaks associated with the backbone segments also possibly reflects the decreased mobility of the core segments due to crosslinking. Finally, comparison of the GPC traces (Fig. 5) of the partially clicked amphiphilic HBPE with that of the sample after core-crosslinking clearly reveals a substantial reduction in the hydrodynamic volume; the apparent molecular weights retrieved from this run were $M_w = 72{,}000$ and $M_w = 50{,}000$, respectively. Although one does not expect a change in the PDI, as per its definition, a slight decrease after crosslinking reflects the lowering of the dispersity in the hydrodynamic sizes upon crosslinking, which is the parameter that GPC measures. This crosslinking studies reveal an interesting strategy to access core-crosslinked hyperbranched polymers utilizing a preferential partitioning of the crosslinker within the core of a suitably funtionalized HBP; one important feature of this process is that the polar functionality installed in the first step could be chosen to perform other specific functions, such as specific analyte sequestration, and possibly sensing.

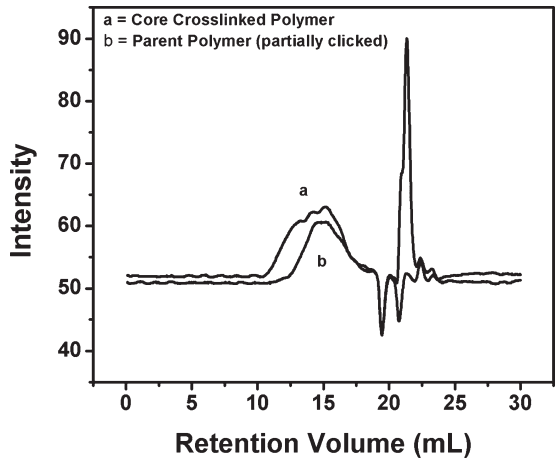


FIGURE 5 GPC traces of partially clicked parent hyperbranched polymer; core crosslinked hyperbranched polymer.

CONCLUSIONS

In conclusion, a novel AB_2 monomer carrying a pendant allyl group in the spacer segment was designed; the monomer carried two decyloxybenzyl groups and a single hydroxyl group at the far end of the spacer, such that the melt condensation polymerization under standard acid-catalyzed transetherification conditions directly yielded a HBPE that bore numerous decyl chains on the periphery and a number of allyl groups within the core. The allyl groups were readily clicked using photo-initiated thiol-ene reaction to install a large number of carboxylic acid groups within the core-region of the HBP; two thiols, namely PA and SA, were used for the click reaction, and in both cases nearly complete transformation of the allyl groups was achieved. The clicked HBPs represent an interesting category of polymers where the periphery is hydrophobic while the core is hydrophilic; the flexibility of the HBP backbone confers the macromolecule the adaptability to generate segregated amphiphilic entities that could self-assemble, like normal amphiphiles. DLS, AFM, and FESEM studies clearly demonstrate the formation of fairly uniform spherical aggregates, which are believed to be multimicellar aggregates based on their large dimensions of ~200 nm. The numerous core allyl groups were also used to generate core-crosslinked HBPs (CCHBPs); to achieve this with minimum formation of interchain crosslinked products, a novel strategy was developed wherein partial transformation of the allyl groups rendered core–shell amphiphilicity to the system, and, subsequently, preferential partitioning of a relative polar crosslinker into the core of the HBP dissolved in a nonpolar solvent substantially enhanced the intrachain crosslinking process yielding soluble core-crosslinked HBPs. One novel feature of this process is generation of single-chain core–shell nanoparticle-like entities,

with the potential for varying the nature of the internal functionality for specific applications. We are presently examining the possibility of using this strategy for creating single-chain core-crosslinked polymeric nanoparticles for analyte sequestration and sensing.

EXPERIMENTAL

2,4,6-Trimethylphenol, 1-decanol, 2-mecaptoethanol, trioxane, p-toluene sulfonyl chloride, lithium aluminum hydride, sodium hydride, and camphor sulfonic acid were purchased from Sigma-Aldrich Chemical Company and used directly. Allyl bromide, diethyl malonate, metallic sodium, $AgNO_3$, and 33% acetic acid solution of HBr were purchased from Spectrochem and used directly. 3,5-Bismethoxymethyl-2,4,6-trimethyl phenol was synthesized from Mesitol using previously reported procedure.[23] Common organic solvents were purchased locally and distilled prior to use. ^{1}H NMR spectra were recorded using a 400 MHz Bruker spectrometer using $CDCl_3$ as solvent, unless mentioned otherwise. DSC measurements were performed on a Mettler Toledo instrument at a heating rate of 10°/min; the samples were first heated to melt, cooled, and the subsequent heating and cooling runs were recorded. For FESEM measurement, the polymer samples are drop-casted on mica substrate; imaging was performed using FESEM, FEI Nova-Nano SEM-600, The Netherlands. AFM measurements of the polymer samples were performed using Nanoscope IVA multimode AFM (Digital Instrument, Santa Barbara, CA). All the images presented are tapping mode height images, recorded using a tip of force constant 2.8 N/m and resonance frequency of 75 kHz. Image analysis was performed using the software provided along with the Nanoscope IVA. GPC was performed using a Viscotek TDA model 300 system, which is coupled to refractive-index, differential viscometer, and light scattering detectors in series. The separation was achieved using two mixed-bed PL gel columns (5 μm, mixed C) maintained at 35 °C; tetrahydrofuran (THF) was used as the eluent. The molecular weights were estimated using a universal calibration curve based on polystyrene standards.

Synthesis of Monomers

Diethyl, 2-Allylmalonate (A)

To a suspension of NaH (9.6 g, 60%, 240 mmol) in THF, diethyl malonate (76 g, 480 mmol) was slowly added in the ice-cold condition; excess malonate was used to minimize the formation of the diallyl product. After 1 h, allyl bromide (29.1 g, 240 mmol) was added to the reaction mixture and the mixture was stirred for 12 h at room temperature. The reaction was quenched by addition of saturated solution of ammonium chloride and extracted in ethyl acetate. The ethyl acetate layer was washed with brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. Fractional distillation yielded the pure product as the second fraction (yield = 80% with respect to allyl bromide).

^{1}H NMR (δ, ppm, $CDCl_3$): 1.27 (6H, t, —$CO_2\mathbf{CH_2}CH_2\mathbf{CH_3}$); 2.66 (2H, m, $CH_2CH\mathbf{CH_2}CH$—); 3.42 (1H, t, $CH_2CHCH_2\mathbf{CH}$—); 4.21 (4H, q, —$CO_2\mathbf{CH_2}CH_3$); 5.08 (2H, m, $\mathbf{CH_2}CHCH_2CH$—); 5.76 (1H, m, $CH_2\mathbf{CH}CH_2CH$—).

2-Allylpropane-1,3-diol (B)

6.84 g (180 mmol) of $LiAlH_4$ was added to the dry THF in the ice-cold condition. To this, 18 g (90 mmol) of **A** (Scheme 3) was added in dropwise manner and the reaction mixture was refluxed for 10 h. The reaction was then quenched very carefully by adding 10% aqueous NaOH. The dense-white slurry was filtered under suction, the filtrate was collected, concentrated, and subject to distillation in Kugelrohr under reduced pressure (100 °C at 2 torr) to yield the required product. Yield = 55%.

^{1}H NMR (δ, ppm, $CDCl_3$): 1.91 (1H, m, $CH_2CHCH_2\mathbf{CH}$—); 2.12 (2H, m, $\mathbf{OH}CH_2CH$—); 2.12 (2H, m, $CH_2CH\mathbf{CH_2}CH$—); 3.66–3.83 (4H, m, $OH\mathbf{CH_2}CH$—); 5.06 (2H, m, $\mathbf{CH_2}CHCH_2CH$—); 5.81 (1H, m, $CH_2\mathbf{CH}CH_2CH$—).

2-(Hydroxymethyl)pent-4-enyl 4-Methylbenzenesulfonate (C)

6.8 g (58.6 mmol) of **B** along with 20.4 g (88 mmol) of freshly prepared Ag_2O and a catalytic amount of KI were taken in 150 mL of DCM. To the ice-water bath cooled reaction mixture, 12.3 g (64.5 mmol) p-toluene sulfonyl chloride was slowly added using a solid addition funnel; the progress of the reaction was monitored by TLC and the reaction was stopped when the ditosylated product begins to form. After completion, the reaction mixture was filtered through a celite-pad and the filtrate was concentrated under reduced pressure. The monotosylated product was purified by column chromatography using petroleum ether and ethyl acetate (60:40) as the eluent. Yield = 58%.

^{1}H NMR (δ, ppm, $CDCl_3$): 1.91 (1H, m, $CH_2CHCH_2\mathbf{CH}$—); 2.12 (1H, m, $\mathbf{OH}CH_2CH$—); 2.12 (2H, m, $CH_2CH\mathbf{CH_2}CH$—); 3.61 (2H, m, $OH\mathbf{CH_2}CH$—); 4.09 (2H, m, —$CH\mathbf{CH_2}$OTs); 5.03 (2H, m, $\mathbf{CH_2}CHCH_2CH$—); 5.72 (1H, m, $CH_2\mathbf{CH}CH_2CH$—); 7.35 (2H, d, Ar**CH**—); 7.80 (2H, d, Ar'**CH**).

3,5-Bisdecyloxymethyl-2,4,6-trimethyl phenol (3)[24]

3 g (17.85 mmol, 1 eq.) of monomer **2** (Scheme 4) was taken in 5 mL of 1-decanol; to this, 0.11 g (0.178 mmol, 0.01 eq.) of $Yb(OTf)_3$ was added and the system was purged with dry N_2 for 15 min. The solution was then heated to 100 °C with continuous N_2 purging for 4 h. After removal of excess decanol under reduced pressure, ~15 mL of water was added and the mixture was extracted with 50 mL of $CHCl_3$. The chloroform layer was dried using anhydrous sodium sulfate, filtered, and concentrated under reduced pressure; distillation using a Kugelrohr apparatus yielded the pure product. Yield = 79%.

^{1}H NMR (δ, ppm, $CDCl_3$): 0.88 (6H, t, $ArCH_2OCH_2CH_2(CH_2)_7\mathbf{CH_3}$); 1.26 (28H, m, $ArCH_2OCH_2CH_2\mathbf{(CH_2)_7}CH_3$); 1.59 (4H, m, $ArCH_2OCH_2\mathbf{CH_2}(CH_2)_7CH_3$); 2.31 (6H, s, $Ar\mathbf{(CH_3)_2}$); 2.35 (s, 3H, $Ar\mathbf{CH_3}$); 3.48 (t, 4H, $ArCH_2O\mathbf{CH_2}CH_2(CH_2)_7CH_3$); 4.47 (s, 4H, $Ar\mathbf{CH_2}OCH_2CH_2(CH_2)_7CH_3$); 4.72 (s, 1H, ArO**H**).

2-((3,5-Bis((decyloxy)methyl)−2,4,6-trimethylphenoxy)methyl)pent-4-en-1-ol (4)

NaH (0.18 g, 60%, 4.41 mmol) was taken in 60 mL of THF, the solution was purged with dry N_2 for a few minutes and then the monomer **3** (2.1 g, 4.41 mmol) was slowly added to it. 1.90 g (7.1 mmol, 1.6 eq.) of **C** was added dropwise to the reaction mixture and the contents were refluxed for 72 h under N_2 atm. The reaction was quenched by adding 50 mL of water and then extracted in diethyl ether. To remove unreacted **3**, the ether layer was washed with 10% NaOH solution. The ether layer was dried using anhydrous sodium sulfate and concentrated under reduced pressure. The product was purified by the column chromatography using petroleum ether and ethyl acetate (75:25) as the eluent. Yield = 47%.

^{1}H NMR (δ, ppm, $CDCl_3$): 0.88 (6H, t, $ArCH_2OCH_2CH_2(CH_2)_7\mathbf{CH_3}$); 1.26 (28H, m, $ArCH_2OCH_2CH_2\mathbf{(CH_2)_7}CH_3$); 1.59 (4H, m, $ArCH_2OCH_2\mathbf{CH_2}(CH_2)_7CH_3$); 1.91 (1H, m, $CH_2CHCH_2\mathbf{CH}$—); 2.12 (2H, m, $CH_2CH\mathbf{CH_2}CH$—); 2.31 (6H, s, $Ar\mathbf{(CH_3)_2}$); 2.35 (s, 3H, $Ar\mathbf{CH_3}$); 3.48 (t, 4H, $ArCH_2O\mathbf{CH_2}CH_2(CH_2)_7CH_3$); 3.72 (2H, m, $OH\mathbf{CH_2}CH$—); 3.86 (m, 2H, $ArO\mathbf{CH_2}CH$—); 4.47 (s, 4H, $Ar\mathbf{CH_2}OCH_2CH_2(CH_2)_7CH_3$); 5.03 (2H, m, $\mathbf{CH_2}CHCH_2CH$—); 5.72 (1H, m, $CH_2\mathbf{CH}CH_2CH$—).

Synthesis of Polymers

HBP-allyl: Monomer **4** (1.1 g, 1.916 mmol) along with 2 mol % of pyridinium camphorsulfonate (PCS) was taken in a test-tube shaped polymerization vessel. The mixture was degassed for 10 min and maintained at a temperature of 110 °C under continuous N_2 purge, to ensure homogeneous mixing of catalyst and monomers. The polymerization was then performed at 150 °C under N_2 for 2 h with constant stirring. Subsequently, using a Kugelröhr apparatus, the polymerization was continued for an additional period of 45 min at 150 °C under reduced pressure (2 torr), with continuous mixing of the melt by rotation. The resultant polymer was dissolved in THF, the acid-catalyst was neutralized with solid $NaHCO_3$, and then the solution was filtered. The filtrate was concentrated under reduced pressure to a viscous solution and precipitated in methanol. The polymer was further purified twice by dissolution in THF and reprecipitation into methanol (yield = 70%; molecular weight M_n = 12,000).

^{1}H NMR (δ, ppm, $CDCl_3$): 0.87 (3H, t, $ArCH_2OCH_2CH_2(CH_2)_7\mathbf{CH_3}$); 1.25 (14H, m, $ArCH_2OCH_2CH_2\mathbf{(CH_2)_7}CH_3$); 1.59 (2H, m, $ArCH_2OCH_2\mathbf{CH_2}(CH_2)_7CH_3$); 1.91 (1H, m, $CH_2CHCH_2\mathbf{CH}$—); 2.12 (2H, m, $CH_2CH\mathbf{CH_2}CH$—); 2.31 (6H, s, $Ar\mathbf{(CH_3)_2}$); 2.35 (s, 3H, $Ar\mathbf{CH_3}$); 3.48 (t, 2H, $ArCH_2O\mathbf{CH_2}CH_2(CH_2)_7CH_3$); 3.63 (2H, m, —$O\mathbf{CH_2}CH$—); 3.74 (m, 2H, $ArO\mathbf{CH_2}CH$—); 4.47 (s, 4H, $Ar\mathbf{CH_2}OCH_2CH_2(CH_2)_7CH_3$); 5.03 (2H, m, $\mathbf{CH_2}CHCH_2CH$—); 5.72 (1H, m, $CH_2\mathbf{CH}CH_2CH$—).

Thiol-ene Reaction with PA (HBP-PA)

A mixture of **HBP-Allyl** (100 mg, 0.23 mmol) and PA (74 mg, 0.69 mmol) were taken in 5 mL $CHCl_3$, along with the photo-initiator, 2,2-dimethoxy 2-phenyl acetophenone (2 mg, 0.008 mmol). The contents were irradiated using a 150 W Hg-vapor lamp for 4 h. The polymer solution was then concentrated under reduced pressure and precipitated in methanol; the polymer was further purified by dissolution in $CHCl_3$ and reprecipitation into methanol to yield the **HBP-PA** (yield = 64%; molecular weight: M_n = 13,400).

^{1}H NMR (δ, ppm, $CDCl_3$): 0.87 (3H, t, $ArCH_2OCH_2CH_2(CH_2)_7\mathbf{CH_3}$); 1.25 (14H, m, $ArCH_2OCH_2CH_2\mathbf{(CH_2)_7}CH_3$); 1.62 (2H, m, $ArCH_2OCH_2\mathbf{CH_2}(CH_2)_7CH_3$); 1.91 (1H, m, —$SCH_2CH_2CH_2\mathbf{CH}$—); 2.01 (2H, m, —$SCH_2CH_2\mathbf{CH_2}CH$—); 2.12 (2H, m, —$SCH_2\mathbf{CH_2}CH_2CH$—); 2.28 (6H, s, $Ar\mathbf{(CH_3)_2}$); 2.35 (s, 3H, $Ar\mathbf{CH_3}$); 2.57 (t, 2H, $CO_2H\mathbf{CH_2}CH_2SCH_2$—); 2.57 (t, 2H, $CO_2HCH_2CH_2S\mathbf{CH_2}$—); 2.75 (m, 2H, $CO_2HCH_2\mathbf{CH_2}SCH_2$—); 3.48 (t, 2H, $ArCH_2O\mathbf{CH_2}CH_2(CH_2)_7CH_3$); 3.63 (2H, m, —$O\mathbf{CH_2}CH$—); 3.74 (m, 2H, $ArO\mathbf{CH_2}CH$—); 4.5 (s, 4H, $Ar\mathbf{CH_2}OCH_2CH_2(CH_2)_7CH_3$).

Thiol-ene Reaction with SA (HBP-SA)

A mixture of **HBP-Allyl** (100 mg, 0.23 mmol) and 2-SA (104 mg, 0.69 mmol) were taken in 5 mL $CHCl_3$, along with the photo-initiator, 2,2-dimethoxy 2-phenyl acetophenone (2 mg, 0.008 mmol). The contents were irradiated using a 150 W Hg-vapor lamp for 4 h. The polymer solution was then concentrated under reduced pressure and precipitated in diethyl ether; the polymer was further purified twice by dissolution in $CHCl_3$ and reprecipitation into diethyl ether to yield **HBP-SA** (yield = 73%; molecular weight M_n = 12,700).

^{1}H NMR (δ, ppm, $CDCl_3$): 0.87 (3H, t, $ArCH_2OCH_2CH_2(CH_2)_7\mathbf{CH_3}$); 1.25 (14H, m, $ArCH_2OCH_2CH_2\mathbf{(CH_2)_7}CH_3$); 1.62 (2H, m, $ArCH_2OCH_2\mathbf{CH_2}(CH_2)_7CH_3$); 1.91 (1H, m, —$SCH_2CH_2CH_2\mathbf{CH}$—); 2.01 (2H, m, —$SCH_2CH_2\mathbf{CH_2}CH$—); 2.12 (2H, m, —$SCH_2\mathbf{CH_2}CH_2CH$—); 2.31 (6H, s, $Ar\mathbf{(CH_3)_2}$); 2.35 (s, 3H, $Ar\mathbf{CH_3}$); 2.65 (q, 2H, $CO_2H\mathbf{CH_2}CH(CO_2H)SCH_2$—); 2.65 (t, 2H, $CO_2HCH_2CH(CO_2H)S\mathbf{CH_2}$—); 2.95 (m, 1H, $CO_2HCH_2\mathbf{CH}(CO_2H)SCH_2$—); 3.48 (t, 2H, $ArCH_2O\mathbf{CH_2}CH_2(CH_2)_7CH_3$); 3.63 (2H, m, —$O\mathbf{CH_2}CH$—); 3.74 (m, 2H, $ArO\mathbf{CH_2}CH$—); 4.5 (s, 4H, $Ar\mathbf{CH_2}OCH_2CH_2(CH_2)_7CH_3$).

Diethylene Glycol Ditosylate

Diethylene glycol (5 g, 47.15 mmol) was taken in 20 mL of THF and the contents were cooled to 0 °C. To this solution, 11.32 g (283 mmol) of KOH in 20 mL of water was added and the contents were stirred for 30 min. 27 g (141.5 mmol) of tosyl chloride was taken in 50 mL of THF and added dropwise to the cold reaction mixture; the contents were stirred overnight. After completion, the organic layer was separated, dried, and concentrated under reduced pressure. $CHCl_3$ (50 mL) was added to the concentrated reaction mixture and the precipitated salt was filtered. The concentrated filtrate was used in the next step without any further purification. Crude yield = 90%.

^{1}H NMR (δ, ppm, $CDCl_3$): 3.56 (2H, t, —$O\mathbf{CH_2}CH_2OSOOAr$); 3.70 (2H, t, —$OCH_2\mathbf{CH_2}OSOOAr$); 7.46 (2H, d, —$OCH_2CH_2OSOOAr$-**H**); 7.75 (2H, d, —$OCH_2CH_2OSOOAr$-**H**).

Diethylene Dithioglycol

Twenty grams (48.3 mmol) of the above ditosylate along with 11 g (145 mmol) of thiourea was taken in 100 mL of

ethanol and the contents were refluxed for 6 h. After cooling the solution to room temperature, 4.38 g (120 mmol) of KOH in 20 mL of water was added. The reaction mixture was further refluxed for 6 h under N_2 atmosphere. After completion, the reaction mixture was neutralized with dilute HCl and concentrated under reduced pressure. Twenty milliliters of water was added and the contents were extracted twice with 50 mL of ethyl acetate. The combined organic layer was dried using anhydrous sodium sulfate and concentrated under reduced pressure to yield the pure product in 75% yield.

^{1}H NMR (δ, ppm, $CDCl_3$): 1.7 (1H, t, **SH**CH_2CH_2O—); 2.73 (2H, q, SH**CH_2**CH_2O—); 3.67 (2h, t, $SHCH_2$**CH_2**O—).

Thiol-ene Reaction with Mercaptoethanol (HBP-ME)

A mixture of **HBP-Allyl** (200 mg, 0.46 mmol) and mercaptoethanol (32 mg, 0.41 mmol) were taken in 5 mL $CHCl_3$, along with the photo-initiator, 2,2-dimethoxy 2-phenyl acetophenone (4 mg, 0.015 mmol). The contents were irradiated using a 150 W Hg-vapor lamp for 4 h. The polymer solution was then concentrated under reduced pressure and precipitated in methanol; the polymer was further purified twice by dissolution in $CHCl_3$ and reprecipitation into methanol to yield the partially clicked **HBP-ME**. Yield = 70% (molecular weight: M_w = 72,000).

^{1}H NMR (δ, ppm, $CDCl_3$): 0.87 (3H, t, $ArCH_2OCH_2CH_2(CH_2)_7$**CH_3**); 1.25 (14H, m, $ArCH_2OCH_2CH_2$**$(CH_2)_7$**CH_3); 1.62 (2H, m, $ArCH_2OCH_2$**CH_2**$(CH_2)_7CH_3$); 1.91 (1H, m, —$SCH_2CH_2CH_2$**CH**—); 2.01 (2H, m, —SCH_2CH_2**CH_2**CH—); 2.12 (2H, m, —SCH_2**CH_2**CH_2CH—); 2.25–2.38 (m, 9H, Ar-**CH_3**); 2.59 (t, 2H, —CH_2**CH_2**SCH_2CH_2OH); 2.65 (t, 2H, CH_2CH_2S**CH_2**CH_2OH); 3.59–3.64 (m, 8H, ArO**CH_2**CH_2CH_2**CH_2**OH, $ArCH_2O$**CH_2**—, $ArSCH_2$**CH_2**OH); 4.49 (m, 4H, Ar-**CH_2**O—); 5.034 (2H, m, **CH_2**$CHCH_2CH$—); 5.72 (1H, m, CH_2**CH**CH_2CH—).

Core-crosslinking Using Diethylene Dithioglycol

A mixture of the partially clicked polymer **HBP-ME** (100 mg) along with the photo-initiator, 2,2-dimethoxy 2-phenyl acetophenone (4 mg), was taken in 5 mL of hexane. To this reaction mixture, a stoichiometric amount of the dithiol (with respect to residual allyl groups) was added slowly. The contents were irradiated using a 150 W Hg-vapor lamp for 4 h. The polymer solution was then concentrated under reduced pressure and precipitated in methanol; the polymer was further purified by dissolution in $CHCl_3$ and reprecipitation into methanol to yield the core-crosslinked hyperbranched polymer. Yield = 56% (molecular weight M_w = 50,000).

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