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Hyperbranched polymers from divinylbenzene and 1,3-diisopropenylbenzene through anionic self-condensing vinyl polymerization

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Abstract

Hyperbranched polymers were synthesized using anionic self-condensing vinyl polymerization (ASCVP) by forming 'inimer' (initiator within a monomer) in situ from divinylbenzene (DVB) and 1,3-diisopropenylbenzene (DIPB) using anionic initiators in THF at − 40 °C. The reaction of equimolar amounts of DVB and *n* BuLi results in the formation of hyperbranched poly(divinylbenzene) through self-condensing vinyl polymerization (SCVP). The hyperbranched polymers were invariably contaminated with small amount of gel ($<15\%$). No gelation was observed when using DIBP with anionic initiators. The presence of monomer–polymer equilibrium in the SCVP of DIPB restricts the growth of hyperbranched poly(DIPB). The inimer synthesized from DIPB at 35 °C undergoes intermolecular self-condensation to different extent depending on the nature of anionic initiator at − 40 °C. The molecular weight of the hyperbranched polymers was higher when DPHLi was used as initiator. A small amount of styrene ($[\text{styrene}]/[\text{Li}^+] = 1$) was used to promote the chain growth by inducing cross-over reaction with styrene, and subsequent reaction of styryl anion with isopropenyl groups of inimer/hyperbranched oligomer. The hyperbranched polymers were soluble in organic solvents and exhibited broad molecular weight distribution ($2 < M_w/M_n < 17$).

Keywords: Anionic polymerization; Self-condensing vinyl polymerization; Hyperbranched polymers

1. Introduction

Synthesis of branched polymers using vinyl addition polymerization has attracted significant interest in recent years [1–3]. Fréchet and coworkers [1] elegantly demonstrated a novel 'self-condensing' vinyl polymerization (SCVP) for the synthesis of hyperbranched polymers using specialty vinyl monomers possessing a dormant functional group capable of initiating addition polymerization. Upon activation, initiation occurs intermolecularly with vinyl groups of other molecules, which also possess a dormant initiating group. Subsequent intermolecular reactions lead to the formation of hyperbranched polymer.

Recently, Müller and coworkers [4,5] calculated the molecular weights, its distribution moments and the degree of branching for SCVP. They showed that the SCVP follows different kinetics than the conventional polycondensation of AB_2 type monomer. Recently, Mülhaupt [6] as well as Fréchet [7] and coworkers synthesized hyperbranched polymers using glycidol and 4-(2-hydroxyethyl)-ε-caprolactone by ring-opening anionic polymerization.

A vinyl monomer capable of undergoing SCVP can be called 'inimer' as it contains both initiator as well as monomer in it. Several vinyl monomers such as *p*-(chloromethyl)styrene [8], 2-((2-bromopropionyl)oxy)ethyl acrylate [9], and styrene possessing a nitroxide (TEMPO) group [2] are used for SCVP. Depending on the nature of inimer, suitable polymerization methods have been adopted for SCVP, i.e. cationic [8], TEMPO-mediated radical [3], atom transfer radical [9], and group transfer polymerization (GTP) [10]. In all these processes, the propagating centers exist as dormant species in the absence of a catalyst. Hence, it is possible to synthesize a monomer containing potential initiating group. However, monomer containing anionic initiating moiety is difficult to synthesis due to its higher reactivity. Recently, Baskaran [11] demonstrated anionic

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SCVP of 1,3-diisopropenylbenzene with *n*-butyllithium as initiator. This paper describes the synthesis of hyperbranched polymers by in situ formation of inimer from different anionic initiators with divinylbenzene and diisopropenylbenzene.

2. Experimental

Divinylbenzene (mixture of 1,3 and 1,4 isomers and 35% ethylstyrene, DVB, Aldrich), 1,3-diisopropenylbenzene (DIPB, Aldrich) and styrene (Aldrich) were distilled over calcium hydride and stored under nitrogen in a refrigerator. They were further distilled over fluorenyllithium just prior to polymerization. *n* Butyllithium (*n* BuLi) was prepared using *n*-butylchloride and lithium metal in cyclohexane. The concentration of *n* BuLi was determined by the double titration method. 1,1-Diphenylethylene (DPE, Aldrich) was distilled in presence of a small amount of *n* BuLi under high vacuum. 1,1-Diphenylhexyllithium (DPHLi) initiator was synthesized by reacting *n* BuLi with an equimolar amount of DPE in THF. Fractionated THF was purified by refluxing over K metal and stored over fresh Na–K alloy in a vacuum line. N_2 gas (Industrial Oxygen, Pune) was purified by passing through a heated column containing Cu (200 °C) (2 × 1 m), and column containing A4 molecular sieves (2 × 1 m), and finally was bubbled through a toluene solution of oligostyryllithium.

2.1. Synthesis of hyperbranched polymer using DVB and *n* BuLi

Polymerization was carried out in a flame-dried glass reactor under pure nitrogen atmosphere. The solvent and monomer were transferred by capillary technique or syringe. In a typical reaction, 40 ml of THF was transferred into a two-necked round bottom flask connected with an ampoule containing a required amount of *n* BuLi in cyclohexane. DVB of 1.2 ml (35% ethylstyrene) was added into the polymerization flask and the temperature was brought to -40 °C. The initiator was added into the monomer solution very rapidly (<2 s) under vacuum by opening a Teflon valve of initiator ampoule. The reaction solution turned into dark red color immediately. The reaction was terminated after 10 min, in some cases immediately after the initiator addition, with degassed methanol. The reaction mixture was filtered to remove the presence of a small amount of gel. The polymer was recovered by precipitation in excess methanol and dried under vacuum at 60 °C for 12 h.

2.2. Synthesis of hyperbranched polymer using DIPB and anionic initiators

Into a dry 250 ml round bottom flask equipped with magnetic needle, nitrogen/vacuum three-way adapter with rubber septum was added 50 ml of dry tetrahydrofuran. To this, 5.84×10^{-3} mol of DPE and 3.4 ml of *n* BuLi (1.4 M) were reacted at 30 °C for 10 min to form DPHLi. Then, 1.0 ml, 5.84×10^{-3} mol of diisopropenylbenzene was added into the initiator solution under vigorous stirring. The reaction solution turned into dark red color and no gelation was observed. In the case of *n* BuLi as initiator, DIPB was taken first into the reaction flask and subsequently equimolar amount of initiator was added quickly (<2 s). The reaction was stirred for 15 min and a small amount of sample was withdrawn to characterize the reaction product, if necessary. Then, the reaction temperature was brought down to -40 °C and stirred for 15 min before withdrawing a second sample to characterize the intermolecular self-condensate. After 15 min, 0.7 ml (6.1×10^{-3} mol) of styrene was added to enhance self-condensation of the preformed hyperbranched oligo(DIPB). The reaction was terminated with 2 ml of degassed methanol after 20 min. The polymer was recovered by precipitation in excess methanol and dried at 60 °C for 12 h under vacuum giving 2 gm of hyperbranched poly(DIPB-*co*-styrene) (~100% yield).

2.3. Characterization

Size exclusion chromatography (SEC) was carried out using a GPC system consisting of ThermoSeparation's Spectra System P100 pump, AS 300 autosampler, UV-100 detector and RI-150 refractive index detector connected with 5 μm PSS-SDV gel, 10^2–10^5 linear Å 60 cm and 100 Å 60 cm columns. The data were processed using Polymer Standards Service software (PSS WinGPC). THF was used as the mobile phase at a flow rate of 1 ml/min at 30 °C. Standard monodisperse poly(styrene) samples (PL, UK) were used for calibration. In some cases, the molecular weight of the hyperbranched polymers were determined by SEC coupled with a multi-angle laser light scattering (MALLS) detector. MALLS detector used was a Wyatt Technology Dawn F with 'Astra' software. The specific refractive index increment, d*n*/d*c* of the synthesized hyperbranched polymers were determined using integrated refractive index peak of a calibrated RI detector. The d*n*/d*c* for the hyperbranched poly(diisoprophenylbenzene-*co*-styrene) samples were found to be dependent on the composition of styrene. The values are 0.155 ± 0.002 and 0.165 ± 0.002 ml/g for hyperbranched polymers prepared with $[\text{styrene}]/[\text{DIPB}] = 1$ and $[\text{styrene}]/[\text{DIPB}] > 1$, respectively.

The intrinsic viscosity of the polymers was measured in chloroform at 30 °C using single point specific viscosity method [12]. The glass transition temperature (T_g) of the polymers was determined by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC 7 at a heating rate of 10 °C/min. The ^{1}H NMR spectrum was obtained in $CDCl_3$ using a Bruker SE-300 MHz spectrometer.

3. Results and discussion

3.1. Synthesis of hyperbranched polymers using DVB and *n* BuLi

The synthesis of hyperbranched polymer using SCVP requires an inimer possessing both initiator and monomer in a same molecule. Divinlybenzene(DVB) was selected as a precursor monomer for the generation of inimer. It is known that the synthesis of star molecules either by core-first or arm-first method using DVB results into a monoaddition leading to a short linear chain at the beginning of the reaction which subsequently undergoes cross-linking [13]. This is due to high reactivity of vinyl groups in the unreacted monomer compared to pendant vinyl groups of the polymeric chain. Hence, it was thought that it would be possible to form monoadduct (inimer) by reacting equimolar amounts of initiator and divinylbenzene in polar solvent.

Experiments were performed to form inimer from divinylbenzene and *n* BuLi (Scheme 1) by reacting 1:1 moles of *n* BuLi and divinylbenzene under rapid mixing (<2 s) conditions. Results of SCVP of the inimer generated in situ in THF at -40 °C are given in Table 1. The reactions were terminated after few minutes and it was found that the reaction mixture contains some insoluble gel (1–15%). However, the polymer recovered after filtration of reaction mixture and precipitation in excess methanol is soluble in common organic solvents. The formation of a small amount of insoluble gel indicates the presence of cross-linking reaction, which probably occurred due to inadequate mixing of reagents. Apparent number-average molecular weight ($M_{\mathrm{n(app)}}$) of the polymers was determined using standard polystyrene as celebrants in SEC. The polymers obtained have higher molecular weights with broad molecular weight distributions ($3 < M_{\mathrm{w}}/M_{\mathrm{n}} < 17$) indicating the formation of hyperbranched poly(divinylbenzene) through self-condensation of inimers.

It is known that the intrinsic viscosity and $M_{\mathrm{n(app)}}$ of microgels prepared from DVB using radical or anionic polymerization does not increase with conversion during polymerization, though $M_{\mathrm{w(app)}}$ increases [14]. For comparison, soluble microgel was synthesized using high ratio of $[\mathrm{DVB}]/[n\mathrm{BuLi}] = 2.8$ in high dilution. The soluble microgel obtained had low viscosity though the apparent molecular weight was very high ($M_{\mathrm{w(app)}} = 707.3 \times 10^3$ g/mol, Table 1, run 7). However, the viscosity of the hyperbranched polymers obtained using in situ inimerization increases linearly with increase of apparent $M_{\mathrm{n(app)}}$ (Table 1) which indicates that they are topologically different from cross-linked soluble microgel. Reaction of divinyl compounds with living precursors has been theoretically studied by Yan and Zhou [17]. According to their calculation, the critical condition for phase transition during double conversion is $[1/2r]^{1/2}$ where $r = [\mathrm{DVB}]/[\mathrm{I}]$. In the present system, it is 0.7 which also supports the reaction of DVB with BuLi and the formation of hyperbranched poly(divinylbenzene). The commercial divinylbenzene contains 20–35% of 3- or 4-ethylstyrene that can enter into the reaction as a comonomer or in forming an ordinary initiator, but this does not affect the formation of hyperbranched polymer. However, in some cases, additional initiator equivalent to the presence of this comonomer was taken which also gave high molecular weight hyperbranched polymer within 2 s. It is also noted that the molecular weight and polydispersity of the hyperbranched polymer increases with increasing reaction time (Table 1, runs 5 and 6).

Mark-Houwink coefficient determined for the hyperbranched poly(divinylbenzene) (run 6, Table 1, Fig. 1) using SEC coupled with on-line viscosity detector and light-scattering detector is 0.39.[1] The lower value of Mark-Houwink coefficient ($\alpha = 0.39$) compare to linear polystyrene ($\alpha = 0.70$) indicates a densely packed three-dimensional structure resulting from the hyperbranched topology. ^{1}H NMR of the hyperbranched polymer shows an approximately 1:1 ratio for butyl and aromatic groups, which also agrees with the proposed mechanism. Viscosity of the hyperbranched polymers is slightly higher than that of microgel considering the amount of monomer taken for the synthesis. The higher viscosity found for the branched polymer suggests that they are topologically different from soluble microgel.

The formation of inimer requires that the rate of monoadduct formation between *n* BuLi and divinylmonomer should be higher than that of the subsequent propagation reaction. However, difficulties associated with homogeneous mixing of the reagents using vacuum/or N_2 pressure in a batch reactor led to a stoichiometric imbalance. In such a situation, the possibility of the formation of diadduct cannot be ruled out. The formation of diadduct was not considered in a statistical way due to the fact that the delocalization of monoadduct anion would decrease the reactivity of second vinyl group in DVB. Linear propagation and diadduct formation in inimer synthesis would give rise to residual unreacted divinylbenzene and difunctional initiator. The presence of such side reactions leading to cross-linking was evident as a small amount ($<15\%$) of insoluble macrogel was recovered during SCVP of DVB.

3.2. Synthesis of hyperbranched polymers using DIPB with anionic initiators

The use of DVB in the synthesis of hyperbranched polymer has disadvantages such as (a) the inimer formation and the subsequent self-condensation is very fast and hence uncontrollable especially in THF and (b) hyperbranched poly(divinylbenzene) is contaminated with small amount of

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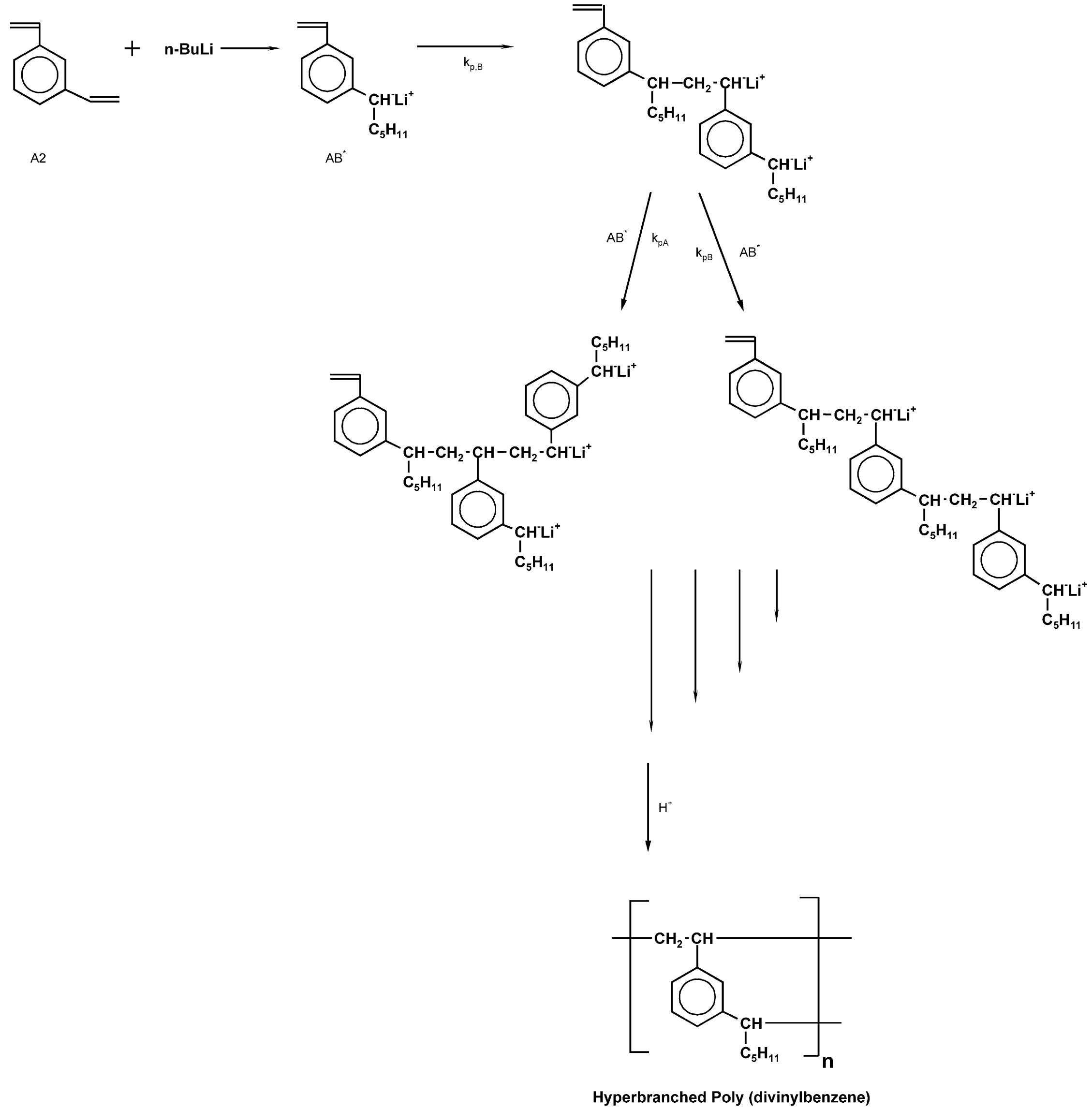
[1] Mark-Houwink coefficient for the hyperbranched poly(divinylbenzene) was determined by A.H.E. Müller and P. Simon at the Insititute for Physical Chemistry, University of Mainz, Germany.



Scheme 1. Synthesis of hyperbranched poly(divinylbenzene) from in situ reaction of equimolar amount of *n*BuLi and DVB in THF at −40 °C.

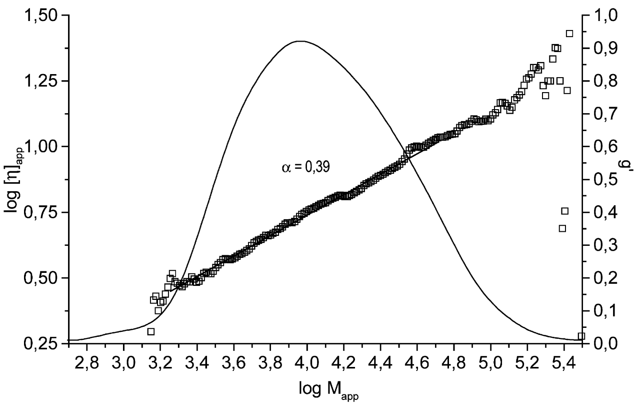


Fig. 1. Mark-Houwink exponent determined by online GPC/viscosity measurement for hyperbranched poly(divinylbenzene) in THF at −40 °C. [DVB]/[*n*BuLi] = 0.4, $M_{\mathrm{n(app),GPC}} = 16,900$, $M_{\mathrm{w(app),GPC}} = 249,000$ and $M_w/M_n = 14.68$ (Table 1, run 6).

gel. In order to synthesis pure inimer containing anionic active center from commercially available divinyl monomers, 1,3-diisopropenylbenzene (DIPB) was selected. It is known that the DIPB has a low ceiling temperature ($T_c \sim 50$ °C) and it undergoes linear propagation leaving one double bond as pendent groups [15,16]. Hence, its reaction with equimolar amount of anionic initiators near ceiling temperature would give only inimer. The synthesis of inimer from 1,3-diisopropenylbenzene and *n*BuLi and its SCVP in the presence of a small amount of styrene was reported recently by Baskaran [11]. Herein we examine the effect of various anionic initiators with respect to the formation of inimer using DIPB (Scheme 2).

Synthesis of self-condensing vinyl monomer with anionic center was performed by rapid mixing of an equimolar amount of DIPB and anionic initiators such as *n*BuLi, *sec*-BuLi and *tert*-BuLi and DPHLi in THF at 30 °C.

Table 1
Results of ASCVP of inimer prepared from the reaction of DVB and DIPB with *n* BuLi in THF at −40 °C

No.	[DVB][M] (m/l)	[*n* BuLi][I] (m/l)	[M]/[I]	*t* (min)	$M_{n,GPC}$[a] ($\times 10^{-3}$)	$M_{w,GPC}$[a] ($\times 10^{-3}$)	M_w/M_n	$[\eta]$[b] (dl/g)	Gel[c] (%)
Hyperbranched polymer									
1	0.160	0.160	1.0	60	83.50	476.40	5.70	3.770	10
2	0.070	0.064	1.1	10	37.20	118.50	3.20	0.770	<2
3	0.056	0.050	1.1	10	8.70	155.40	17.80	0.086	<1
4[d]	0.072	0.075	0.96	300	1.60	10.30	6.40	0.053	5
5	0.050	0.125	0.4	0.03	4.30	15.40	3.50	0.087	15
6	0.050	0.125	0.4	0.17	16.90	249.00	14.70	0.850	15
Microgel									
7[e]	0.027	0.009	2.8	10	215.30	707.30	3.20	0.130	5

Inimerization was done by fast addition of *n* BuLi into DVB solution.

[a] Molecular weights correspond to PMMA calibration.

[b] Single point viscosity in $CHCl_3$ at 30 °C.

[c] Wt% of insoluble materials present in the reaction mixture.

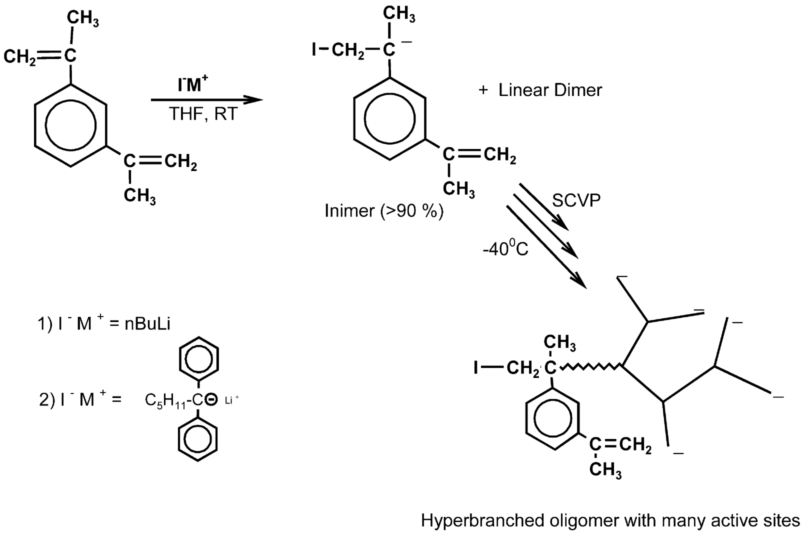
[d] Reaction was done in cyclohexane using *s* BuLi as initiator for 5 h at rt.

[e] Soluble microgel was synthesized at high dilution.

The reaction mixture turned instantly dark red indicating the formation of isopropenyl-α-methyl styryl anion. No gelation was observed. ^{1}H NMR of the protonated reaction product shows the presence of 50% vinyl groups. The integral ratios corresponding to one initiator methyl and one vinyl group per aromatic ring are 0.84 and 1.9 which are close to the theoretical value of 0.75 and 2, respectively. Thus, the reaction of equimolar amount of anionic initiator with DIPB at 30 °C in THF gives inimer with anionic active site and insignificant side products such as linear dimer or gel formation. The inimer can add intermolecularly to the isopropenyl group of another molecule to form a dimer, which is now an AB_2 type monomer with one polymerizable double bond and two initiating or propagating centers (Scheme 2).

It is known that DIPB has low heats of polymerization similar to α-methylstyrene and the monomer is in equilibrium with the growing polymer chain. To promote the self-condensing propagation of inimer, the temperature was reduced to −40 °C and the reaction was terminated with degassed methanol after 3 h. The SEC eluogram of the crude reaction mixture shows the presence of hyperbranched oligo(diisopropenylbenzene) with apparent weight average molecular weight of 1770 g/mol (Table 2). The molecular weight did not grow further indicating the presence of limiting equilibrium monomer concentration, $[M_e]$ for the inimer at −40 °C in THF ($k_p[M_e] < k_{dp}$). The polymerization proceeds initially when the monomer concentration is higher than $[M_e]$ and chain growth is restricted at later stage due to the presence of monomer–polymer equilibrium.

Interestingly, when DPHLi was used to form inimer with DIPB, it did not react with DIPB in THF at 25 °C. ^{1}H NMR of the methanol terminated reaction product showed the presence of 1,1′-diphenylhexane (protonated anion as a triplet at 3.8 ppm) and DIPB. Recovery of the protonated



Scheme 2. Synthesis of inimer from diisopropenylbenzene using anionic initiators.

Table 2
SCVP of 1,3-diisopropenylbenzene using *n*BuLi as initiator in THF at −40 °C

No.	[DIPB] (m/l)	[Styrene]/[I] (m/l)	t^a (min)	$M_{n,GPC}{}^b$ ($\times 10^{-3}$)	$M_{w,GPC}{}^b$ ($\times 10^{-3}$)	$M_w{}^c$ ($\times 10^{-3}$) (SEC–MALLS)	$M_w/M_n{}^b$
1[d,e]	0.034	0	30	0.08	0.22	–	2.58
2[e]	0.078	0	180	0.23	1.77	–	7.86
3[e]	0.106	0	120	0.36	1.50	–	4.16
4[f]	0.145	0.2	120	3.00	5.10	–	1.60
5	0.089	1	60	4.70	13.90	25.70	2.95
6	0.097	1	30	3.82	7.90	12.90	2.07

Equimolar amounts of DIPB and *n*BuLi were reacted at 35 °C for 15 min and then at −40 °C for 30 min. Styrene dose was added at −40 °C. In all cases, the yields were above >90%.

[a] Total reaction time at −40 °C.

[b] Apparent molecular weight and molecular weight distribution determined using SEC calibrated using PS standards.

[c] Molecular weight determined using SEC coupled with MALLS detector.

[d] *t*BuLi was used as initiator.

[e] Crude reaction products were analyzed by SEC.

[f] Monomer solution contains 20% of styrene.

DPHLi suggests that either the initiator is not reactive towards DIPB or the equilibrium position of the initiation is by far shifted towards initiator at room temperature. However, at −40 °C well below the ceiling temperature of the monomer, DPHLi initiates DIPB. It appears that the ceiling temperature of DIPB is dependent on the nature of initiator and solvent. The inimer formation and its subsequent self-condensation were evident when the temperature was lowered to −40 as hyperbranched poly(diisopropenylbenzene) exhibiting higher molecular weight ($M_{w(SEC)} = 17,300$ g/mol) was obtained after 15 min (Table 3, run 1). The apparent weight average molecular weight of the polymer increases with increasing time (Table 3, run 1 and 2). The weight average molecular weight of the hyperbranched polymer(diisopropenylbenzene) determined by SEC coupled with light scattering detector, $M_{w(SEC-MALLS)}$ increases with increasing concentration of the inimer. After 150 h, the molecular weight did not increase further (Table 3, run 3). This suggests the presence of monomer–polymer equilibrium for the SCVP of inimer synthesized from DPHLi and DIPB (Scheme 3).

It is important to note that the inimer synthesized from DIPB with various anionic initiators at 35 °C in THF undergo intermolecular self-condensation to different extent. Higher molecular weight hyperbranched polymers were obtained when DPHLi was used as initiator in contrast to *t*BuLi where only a small amount of oligomer was obtained (Table 2, run 1). This implies that the limiting equilibrium monomer concentration, [M_e] of inimers is dependent on the nature of initiator group present on the

Table 3
SCVP of 1,3-diisopropenyl benzene using diphenylhexyllithium as initiator in THF at −40 °C

No.	[DIPB] (m/l)	[Styrene]/[I] (m/l)	t^a (min)	$M_{n,GPC}{}^b$ ($\times 10^{-3}$)	$M_{w,GPC}{}^b$ ($\times 10^{-3}$)	$M_w{}^c$ ($\times 10^{-3}$) (SEC–MALLS)	$M_w/M_n{}^b$	Yield[d] (%)	T_g
1	0.165	0	15	3.70	17.90	–	4.76	16	–
			30	15.80	30.00	96.50	1.90	37	120
2	0.064	0	15	2.20	10.40	–	4.70	8	–
			30	11.70	20.00	36.50	3.42	34	110
3	0.105	0	150	9.50	17.90	35.60	1.88	43	97
4	0.117	0	10	3.10	17.30	–	5.57	14	–
		1	15	9.70	26.30	69.96	2.71	80	
5	0.129	0	15	4.20	16.90	–	4.03	15	–
		1	15	5.30	17.90	49.40	3.35	79	–
		1	15	9.85	40.80	146.76	4.14	78	–
6	0.116	0	15	1.50	13.20	–	9.01	10	–
		5	15	7.20	52.00	527.95	7.19	95	95

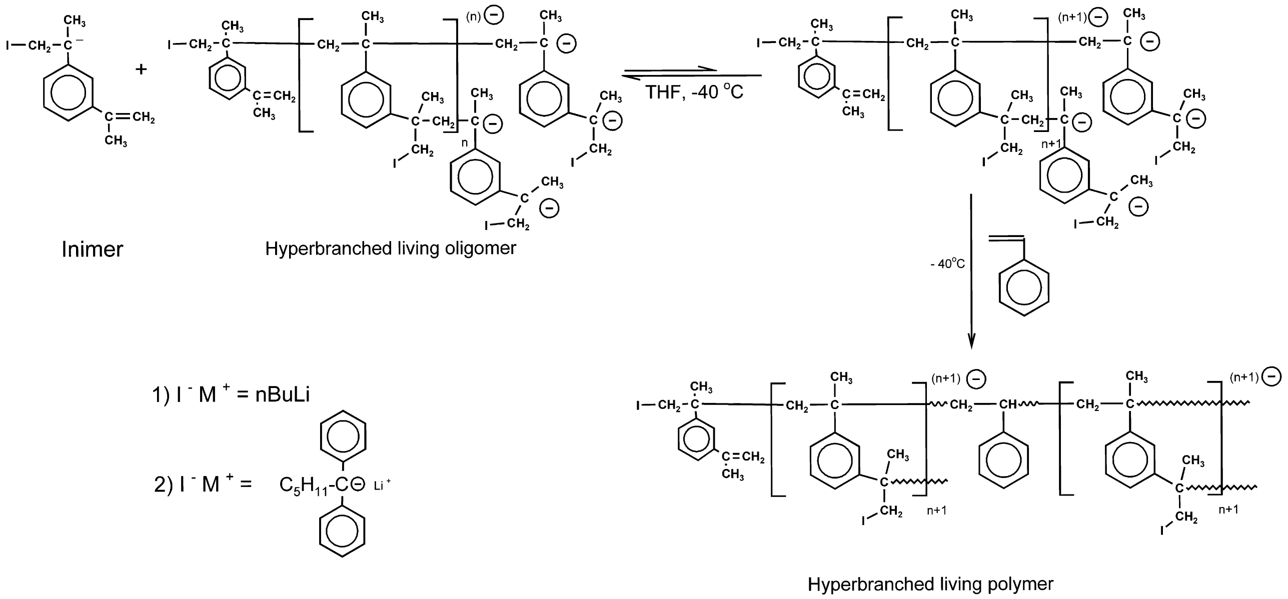
Equimolar amounts of DIPB and *n*BuLi were reacted at 35 °C for 15 min and then at −40 °C for 30 min. Styrene dose was added at −40 °C. In all cases, the yields were above >90%.

[a] Total reaction time at −40 °C.

[b] Apparent molecular weight and molecular weight distribution determined using SEC calibrated using PS standards.

[c] Molecular weight determined using SEC coupled with MALLS detector.

[d] Recovered polymer precipitated in excess methanol with respect to the total weight of DPE and DIPB.



Scheme 3. Schematic representation of monomer–polymer equilibrium in the synthesis of hyperbranched living oligo(1,3-diisopropenylbenzene) and its chain growth using styrene as promoter.

inimer/propagating active species and the $[M_e]$ of the inimer derived from DIPB and DPHLi is lower than the inimer derived from BuLi due to inductive effect of the aromatic substitution. However, the difference in apparent molecular weights can also result from higher molecular weight of DIPB–DPH repeat unit which is twice as high as the molecular weight of DIPB-Bu unit and relative higher hydrodynamic volume of the hyperbranched polymer derived from DIPB–DPH inimer. Hence, the dependent of $[M_e]$ on the initiator cannot be authenticated without comparing absolute molecular weights of the polymers and determining the polymer yields at equilibrium.

The presence of styrene in a small amount, either as a comonomer or added to the reaction mixture after 30 min at −40 °C, gave high molecular weight hyperbranched poly(diisopropenylbenzene-*co*-styrene) in good yields (Table 2, run 4–6 and Table 3, run 4–6). This suggests that the existence of monomer–polymer equilibrium can be disturbed and the chain growth can be promoted by cross-over reaction with styrene ($[\text{styrene}]/[\text{Li}^+] = 1$). Addition of styrene into the dark red colored reaction mixture (substituted α-methylstyryl anion) containing oligomers converts the active chain ends into styryl anion (orange), which further adds intermolecularly to the isopropenyl group of inimer/hyperbranched oligomer. This leads to the formation of higher molecular weight hyperbranched copolymer consisting of DIPB and styrene repeat units (Scheme 3).

SEC eluogram of the quenched reaction product of the equimolar amount of DPHLi and DIPB in THF at −40 °C show the hyperbranched polymer with $M_{w(SEC)} = 17,300$ g/mol with $M_w/M_n = 5.57$. Addition of equimolar amount of styrene with respect to Li^+ concentration increases the molecular weight of hyperbranched polymer to $M_{w(SEC)} = 26,300$ g/mol ($M_{w(SEC-MALLS)} = 69,950$ g/mol) with $M_w/M_n = 2.3$ (Fig. 2, Table 3, run 4). The obtained broad MWD of the hyperbranched copolymer supports the reported theoretical calculation of molecular weight distribution function in SCVP system [18]. Moreover, the increase in the molecular weight is not proportional to the amount of styrene added indicating the self-condensation of molecules through vinyl addition polymerization.

Once all the styryl chain ends undergo an intermolecular cross-over reaction with the isopropenyl group of hyperbranched oligomer or polymer; the resulting tertiary carbanion would re-establish its equilibrium with the isopropenyl group of another hyperbranched molecule.

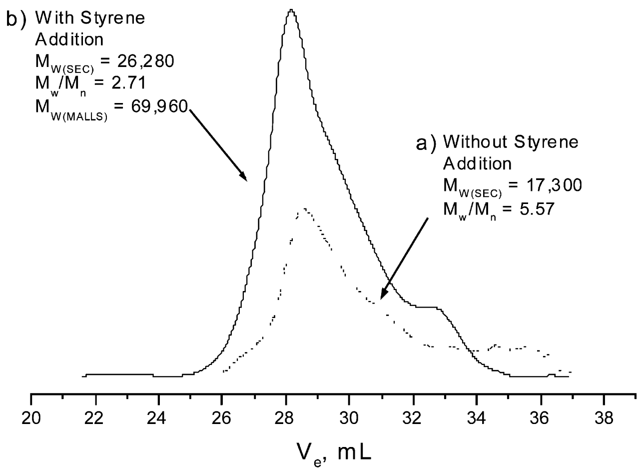


Fig. 2. SEC eluograms of hyperbranched poly(DIPB) synthesized from DIPB using DPHLi as initiator in THF at −40 °C (Table 3, run 4); (a) before the addition of styrene, $[\text{DIPB}]/[\text{Li}^+] = 1$ and (b) after the addition of styrene, $[\text{styrene}]/[\text{Li}^+] = 1$.

This enables one to further grow new generation of branching by simple addition of equimolar amount of styrene with respect to initial initiator concentration, ([styrene]/[Li^+] = 1). Each dose of styrene increases the molecular weight of the hyperbranched polymer that is not proportional to the amount of styrene added as determined by SEC (Table 3, run 5). The substantial increase of molecular weight confirms the presence of intermolecular self-condensation of hyperbranched molecules.

If more amount of styrene is added, it is possible to control interchain-length between two branch-points. The polymer obtained in this manner possesses very high molecular weight as determined by light scattering and can be called as hybrid linear-hyperbranched polymer (Table 3, run 6). The ^{1}H NMR of the hyperbranched polymers indicates the presence of signals at 5–5.5 δ corresponding to the residual double bond. DSC analysis of the hyperbranched polymer synthesized using DPHLi as initiator showed a small, broad transition. However, the hybrid linear-hyperbranched polymer synthesized in the presence of styrene shows T_g at 95 °C.

4. Conclusions

The synthesis of hyperbranched polymers by anionic self-condensing vinyl polymerization (ASCVP) offers great advantages that (1) one can use readily available divinylbenzene monomers such as DVB and DIPB, (2) the monomer group present in the polymer chain exists in equilibrium with propagating anion. This allows the synthesis of higher 'generations' of hyperbranched polymer by the addition of several repetitive doses of styrene, (3) initiating group becomes a part of the repeat unit in the polymer, thus facilitates tailoring physical properties and (4) the living chain-ends of the hyperbranched polymer can be manipulated for functionalization, block copolymerization toward the synthesis of unique molecular architectures.

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