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ARTICLE

Synthesis of Hyperbranched Polymers with Pendent Norbornene Functionalities via RAFT Polymerization of a Novel Asymmetrical Divinyl Monomer

Zhong-min Dong,[†,‡] Xiao-hui Liu,[†] Xiu-lan Tang,[§] and Yue-sheng Li*[,†,§]

[†]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China,* [‡]*Graduate School of the Chinese Academy of Sciences, Changchun Branch and* [§]*College of Environment & Chemical Engineering, Yanshan University, Qinhuangdao 066004, China*

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ABSTRACT: Hyperbranched polymers with numerous pendent norbornene functionalities have been synthesized via the radical polymerization of a novel asymmetrical divinyl monomer bearing a higher reactivity methacrylate group and a lower reactivity norbornene group. Mediated by a rapid reversible addition−fragmentation chain transfer (RAFT) equilibrium, the concentration of polymeric chain radicals is decreased, and thus the gelation did not occur until higher monomer conversions (ca. 90%). An increase in reaction temperature can also significantly promote the formation of the hyperbranched structure owing to the decreased stability of the intermediate radicals derived from the norbornene group, which was confirmed by a model copolymerization system of two single vinyl monomers with similar structures to the vinyl groups in the asymmetrical divinyl monomer. Furthermore, Tri-SEC and conventional Sin-SEC as well as ^{1}H NMR analyses show that hyperbranched structures and higher molecular weights were formed at moderate-to-high monomer conversion stage, whereas the early polymerization stage only afforded linear polymers with a relatively narrower molecular weight distribution.

Introduction

Asymmetrical divinyl monomers (ADMs) containing two vinyl groups with different reactivities can proceed regioselective polymerization. Accordingly, the tailored polymers bearing multiple vinyl-functionalized pendants are afforded. The resultant polymers can be applied widely, such as further functionalization, cross-linking, and postpolymerization.[1−6] Employing appropriate polymerization strategies and reaction conditions, the linear polymers with pendent vinyl groups were successfully synthesized from the polymerizations of ADMs. For example, the well-defined linear polymers containing alkene-functionalized pendants were synthesized by anionic polymerizations of 4-(vinylphenyl)-1-butene, allyl methacrylate (AMA), and *trans, trans*-1-methacryloyloxy-2,4-hexadiene.[7−9] Recently, Kamigaito and co-workers succeeded in extending this route to conventional radical polymerization, and linear polymers were obtained by regiospecifically polymerizing vinyl methacrylate in the presence of Lewis acids.[10] Recently, Wooley's group also announced a facile approach to synthesize well-defined linear polymers bearing pendent vinyl functionalities via selective reversible addition−fragmentation chain transfer (RAFT) polymerization.[11,12] Using asymmetrical divinyl monomers with a fluorinated styrene group, preferential polymerizations toward high selectivity styrene group were achieved, and the well-defined linear polymers with multiple pendent alkene or cycloalkenyl groups were obtained.

Polymerization of ADMs can also be used to synthesize hyperbranched polymers by optimizing monomer molecular structure and reaction conditions. AMA is one of the most widely studied ADMs. Unfortunately, its radical homopolymerization will easily lead to cross-linking at an early stage of the polymerization reaction.[13−16] Atom transfer radical polymerization and RAFT polymerization techniques were also accessed to AMA but failed to yield the expected results[17−21] because the reactivity difference between methacrylate and allyl groups is not sufficient enough to prevent the gelation. Recently, we detailed a novel strategy to synthesize hyperbranched polymers via RAFT-mediated living radical polymerization of an ADM.[21,22] Adjusting the reactivity difference of two vinyl groups toward the polymerization, hyperbranched polymers with numerous pendent vinyl groups were generated until higher monomer conversions (ca. 80%).

As proposed by Wooley et al., homopolymerization of an ADM can be viewed as a copolymerization system of two different vinyl monomers.[11] The reactive difference between the two vinyl groups can be quantatively compared by the reactivity ratios (r_1, r_2) calculated on the basis of the (Q, e) values from Alfrey−Price theory, i.e., $r_1 = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)]$ and $r_2 = (Q_2/Q_1)\exp[-e_2(e_2 - e_1)]$, where the ($Q$, e) values are cited from polymer handbook if not especially mentioned.[23,24] For this treatment, vinyl group 1 corresponds to a higher reactivity toward polymerization, whereas vinyl group 2 corresponds to a lower reactivity. Thus, an ADM with a lower ratio (r_1/r_2) trends to result in cross-linking, while an ADM with a higher ratio can produce soluble polymers. Taking AMA as an example, it can be viewed as the copolymerization of methyl methacrylate (MMA) and allyl acetate, which possesses a very low reactivity ratio ($r_1/r_2 = 28$). Consequently, gelation does easily occur during the polymerization. Conversely, RAFT homopolymerization of undecenyl methacrylate (UMA, based on MMA and 1-hexene) with a higher reactivity ratio value ($r_1/r_2 = 987$) efficiently produced hyperbranched polymers with high monomer conversions (75%).[21] However, the resultant polymers possess low degrees of branching (DBs, ca. 0.1), and the

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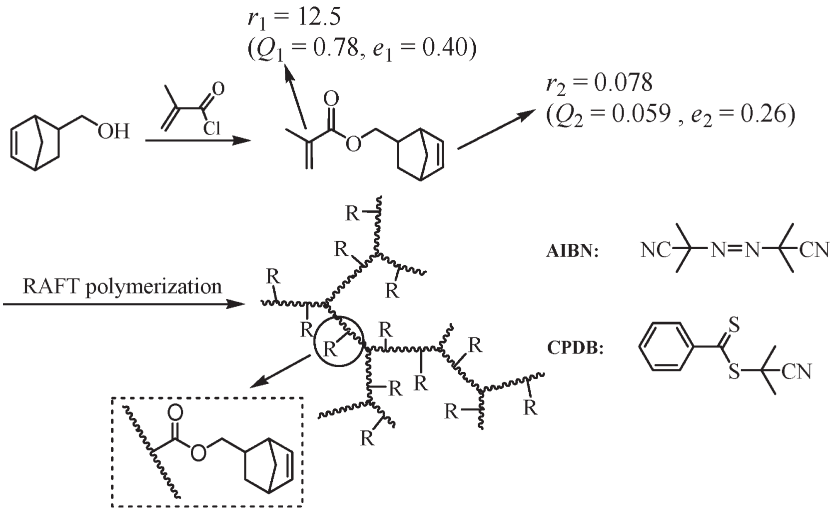
*Corresponding author. E-mail: ysli@ciac.jl.cn.

Scheme 1. Synthesis of Hyperbranched Polymers with Pendent Norbornene Groups from an Asymmetrical Divinyl Monomer



polymerizations inevitably gelled at a further increased monomer conversions.

Herein, we design a novel ADM with a lower reactivity ratio (r_1/r_2 = 159) relative to UMA, consisting of a higher reactivity methacrylate group ($Q_1 = 0.78$, $e_1 = 0.40$, based on MMA) and a lower reactivity norbornene group ($Q_2 = 0.059$, $e_2 = 0.26$, based on norbornene derivative),[25,26] with the purpose to synthesize hyperbranched polymers exhibiting higher DBs (Scheme 1). The hyperbranched architectures and their evolutions were confirmed by the model copolymerization system and the combination of a triple detection size exclusion chromatography (Tri-SEC), a conventional single detection SEC (Sin-SEC), and ^{1}H NMR analyses.

Experimental Section

Materials. 5-Norbornene-2-methanol (NB-CH_2OH) was purchased from Aldrich and purified by distillation before use. Triethylamine was refluxed over CaH_2 for 24 h and distilled before use. Acetone was dried over anhydrous magnesium sulfate. Toluene was purified by a Mbraun solvent purification system (M. Braun Co. Ltd., Germany). 2,2-Azodiisobutyronitrile (AIBN) was recrystallized prior to use. 2-(2-Cyanopropyl) dithiobenzoate (CPDB) was synthesized according to the literature procedures.[27] All other materials without specially mentioned were used as received.

Synthesis of 2-(5-Norbornene)methyl Methacrylate (NBMMA). The asymmetrical methacrylate-type divinyl monomer was prepared via esterification reaction. NB-CH_2OH (28.0 g, 0.23 mol), triethylamine (47 mL, 0.34 mol), and acetone (60 mL) were mixed in a predried 500 mL flask with a mechanical stirrer. Methacryloyl chloride (50 mL, 0.34 mol) in 20 mL of acetone were added dropwise to the mixture with stirring at room temperature over 2 h. The resultant white suspension was maintained at 50 °C for a further 4 h to ensure a complete reaction. After filtration and removal of acetone, the liquid mixture was dissolved in ethyl acetate and washed by 10% NaOH solution and then distilled water to remove residual reactants. The organic layer was dried over anhydrous calcium chloride. Vacuum distillation of the residue yielded NBMMA as a colorless liquid. Yield: 37.6 g (85.2%). The exo/endo molar ratio is 18.3:81.7. ^{1}H NMR ($CDCl_3$): δ 0.50−0.56 (qd, 1H, J = 5.85 Hz, 2.25 and 1.35 Hz, endo-H of $-CH_2-$ in norbornene ring), 1.24−1.41 (m, 2H, bridge head $-CH_2-$), 1.79−1.83 (m, 1H, exo-H of $-CH_2-$ in norbornene ring), 1.89 (s, 3H, $-CH_3$), 2.38 (m, 1H, $-CH-CH_2O-$ in norbornene ring), 2.75 (s, 1H, $-CH-$ in norbornene ring), 2.83 (s, 1H, $-CH-$ in norbornene ring), 3.62−3.69 (dd, 1H, J = 5.4 Hz, 4.8 Hz, $-CH_2OCO-$), 3.85−3.91 (dd, 1H, J = 5.4 Hz, 3.3 Hz, $-CH_2OCO-$), 5.48 (t, 1H, J = 4.5 Hz, $=CH_2$ in methacrylate group), 6.04 (t, 1H, J = 4.5 Hz, $=CH_2$ in methacrylate group), 5.88−5.90 (dd, 1H, J = 1.35 Hz, 2.85 Hz, $-CH{=}CH-$ in norbornene ring), 6.08−6.11 (dd, 1H, J = 1.5 Hz, 2.85 Hz, $-CH{=}CH-$ in norbornene ring). ^{13}C NMR ($CDCl_3$): δ 18.59 ($-CH_3$), 29.25 ($-CH_2-$ in norbornene ring), 38.17 ($-CH-CH_2O-$ in norbornene ring), 42.53 ($-CH-$ in norbornene ring), 44.26 ($-CH-$ in norbornene ring), 49.68 (bridge head $-CH_2-$), 68.26 ($-CH_2OCO-$), 125.30 ($=CH_2$ in methacrylate group), 132.49 ($-CH{=}CH-$ in norbornene), 137.82 ($-C{=}CH_2$ in methacrylate group), 167.54 ($-COO-$).

Synthesis of 2-(5-Norbornene)methyl Acetate (NBMAc). The synthetic route of NBMAc was as follows. NB-CH_2OH (20.0 g, 0.16 mol) and diethyl ether (5 mL) were added dropwise to the mixture of anhydrous $AlCl_3$ (0.5 g) and Ac_2O (60 mL) at 30 °C with stirring overnight to ensure the complete reacting of NBCH_2OH. Diethyl ether (50 mL) was added to dissolve the product, and 10% $NaHCO_3$ aqueous solution was used to wash off the residual reactants. After being washed to neutrality with distilled water, the organic layer was dried over anhydrous $CaCO_3$. Diethyl ether was evaporated off, and the residual liquid was distilled under reduced pressure. The distillate at 75 °C (6 mmHg) was collected to yield 25.3 g (92.8%) of product as a colorless liquid. The exo/endo molar ratio is 18.3:81.7. ^{1}H NMR ($CDCl_3$): δ 0.47−0.51 (qd, 1H, J = 5.85 Hz, 2.25 and 1.35 Hz, endo-H of $-CH_2-$ in norbornene ring), 1.16−1.39 (m, 2H, bridge head $-CH_2-$), 1.72−1.81 (m, 1H, exo-H of $-CH_2-$ in norbornene ring), 2.00 (s, 3H, $-CH_3$), 2.30 (m, 1H, $-CH-CH_2O-$ in norbornene ring), 2.74 (s, 1H, $-CH-$ in norbornene ring), 2.80 (s, 1H, $-CH-$ in norbornene ring), 3.54−3.60 (dd, 1H, J = 4.65 Hz, 5.4 Hz, $-CH_2OCO-$), 3.74−3.80 (dd, 1H, J = 3.45 Hz, 5.4 Hz, $-CH_2OCO-$), 5.85−5.88 (dd, 1H, J = 1.5 Hz, 2.85 Hz, $-CH{=}CH-$ in norbornene ring), 6.09 (dd, 1H, J = 1.5 Hz, 2.85 Hz, $-CH{=}CH-$ in norbornene ring).

Homopolymerization of NBMMA. A typical homopolymerization of NBMMA is as follows. NBMMA (1.0 g, 5.2 mmol), CPDB (12.5 mg, 0.052 mmol), AIBN (8.5 mg, 0.052 mmol), and toluene (1 mL) with the predetermined ratio ([NBMMA]/[CPDB]/[AIBN] = 100:1:1, entry 2 in Table 1) were mixed in a Schlenk polymerization tube. The mixture was degassed by conventional freezing−thawing technique to remove residual oxygen and charged with nitrogen before sealed. The system was then maintained at 60 °C for the desired reaction time. The polymerization was ceased by liquid nitrogen. The produced viscous mixture was diluted with ethyl acetate, and methanol was added to sedimentate the product. The resultant polymer was dried in vacuo at room temperature. The monomer conversions were determined gravimetrically. Yield: 0.73 g (72%). M_n(Sin-SEC) = 34.5 kDa, PDI(Sin-SEC) = 1.70,

M_n(Tri-SEC) = 23.9 kDa, PDI(Tri-SEC) = 6.56, [IV] = 0.21 dL/g, Mark−Houwink $\alpha = 0.49$. ^{1}H NMR ($CDCl_3$): δ 0.45−0.72 (br, endo-H of $-CH_2-$ in the ring), 0.87 (s, $-CH_3$ in the backbone), 1.03−1.44 (br, $-CH-$ in the ring and $-CH_2-$ in bridge head), 1.62−1.75 (br, $-CH-$ and exo-H of $-CH_2-$ in the ring), 1.83 (br, $-CH_2-$ in the backbone), 2.05−2.47 (m, $-CH-$), 2.81, 2.88 (d, $-CH-$ in norbornene ring), 3.41−4.15 (br, $-CH_2OCO-$), 5.27 (s, $=CH_2$ in methacrylate group), 5.88−6.13 (br, $-CH{=}CH-$ in norbornene ring). ^{13}C NMR ($CDCl_3$): δ 16.9, 18.7 ($-CH_3$ in the backbone), 29.5 ($-CH_2-$ in the ring), 30.2 ($-CH-$ in norbornene ring), 37.8 ($-CH-CH_2OCO-$), 42.0 ($-CH-$ in the backbone), 42.6 ($-CH-$ in norbornene ring), 44.4 (quaternary *C* in the backbone), 49.9 (bridge head $-CH_2-$), 54.7 ($-CH_2-$ in the backbone), 68.7 and 69.6 ($-CH_2-OCO-$), 132.4 ($-CH{=}CH-$ in norbornene ring), 177.1 and 178.1 ($-COO-$). FTIR (cm^{-1}, CH_2Cl_2 solution): 3058 ($\nu_{=CH}$), 2967 (ν_{CH3}), 2869 (ν_{CH_2}), 1728 ($\nu_{OC=O}$), 1640 ($\nu_{C=C}$), 1265 and 1240 (ν_{C-O-C}), 989 ($\delta_{=CH}$), 720 ($\delta_{=CH}$).

Model Copolymerization of MMA and NBMAc. A typical model copolymerization of MMA and NBMAc is as follows. MMA (1.56 g, 15.6 mmol), NBMAc (2.60 g, 15.6 mmol), CPDB (69.0 mg, 31.2 mmol), AIBN (25.5 mg, 15.6 mmol), and toluene (3 mL) with the predetermined ratio ([MMA]/[NBMAc]/[AIBN]/[CPDB] = 100:100:1:2, entry 1 in Table 2) were mixed in a Schlenk polymerization tube. The mixture was degassed by conventional freezing−thawing technique to remove residual oxygen and charged with nitrogen before sealed. The system was then maintained at 80 °C for the desired reaction time. The polymerization was ceased by liquid nitrogen. The produced viscous mixture was diluted with ethyl acetate, and methanol was added to sedimentate the product. The resultant polymer was dried in vacuo at room temperature. The monomer conversions were determined gravimetrically. Yield: 2.38 g (56%). M_n(Sin-SEC) = 13.9 kDa, PDI(Sin-SEC) = 1.28, M_n(Tri-SEC) = 14.5 kDa, PDI(Tri-SEC) = 1.39, [IV] = 0.09 dL/g, Mark−Houwink $\alpha = 0.71$. ^{1}H NMR ($CDCl_3$): δ 0.69−1.11 (d, $-CH_3$ in the backbone and endo-H of $-CH_2-$ in the norbornane ring), 1.13−1.48 (m, $-CH-$ in norbornane ring and bridge head $-CH_2-$), 1.56 (br, exo-H of $-CH_2-$ in norbornane ring), 1.78 (s, CH_3COO- and $-CH-$ in the norbornane ring), 1.82−2.04 (br, $-CH_2-$ and $-CH-$ in the backbone), 3.56 (br, $-CH_2O-CO-$). ^{13}C NMR ($CDCl_3$): δ 16.7, 19.0 ($-CH_3$ in the backbone), 21.3 ($-OCO-CH_3$), 29.3 ($-CH_2-$ in norbornane ring), 30.5 ($-CH-$ in norbornane ring), 37.8 ($-CH-CH_2OCO-$), 42.5 ($-CH-$ in the backbone), 44.8 ($-C-$ in the backbone), 49.6 (bridge head $-CH_2-$), 52.0 ($-COO-CH_3$), 54.7 ($-CH_2-$ in the backbone), 68.2 ($-CH_2-OCO-$), 177.2, 178.3 ($-COO-$). FTIR (cm^{-1}, CH_2Cl_2 solution): 2996 (ν_{CH3}), 2951, 2842 (ν_{CH2}), 1731 ($\nu_{OC=O}$), 1486 (δ_{CH_2}), 1387 (δ_{CH_3}), 1272 and 1242 (ν_{C-O-C}), 1063 ($\nu_{O=C-CH_3}$).

Table 1. Hyperbranched Polymers Synthesized via RAFT Polymerization[a]

no.	*T* (°C)	[M]/[CPDB]	time (h)	conv (%)	M_n[b] (kDa)	PDI[b]	NB %[c]	DB[d]
1[e]	60	100:0	0.5	17	gel			
2		100:1	12	72	34.5	1.70	69	0.31
3		100:2	22	68	29.9	1.68	67	0.33
4		100:3	49	80	13.1	1.91	68	0.32
5		100:4	49	68	10.9	1.60	83	0.17
6	70	100:1	3	72	25.3	1.98	69	0.31
7		100:2	11	73	14.2	1.76	72	0.28
8		100:3	27	71	14.6	1.98	77	0.23
9		100:4	100	79	17.2	2.30	67	0.33
10	80	100:2	10	91	26. 5	3.58	69	0.31
11		100:3	12	92	20.1	2.60	69	0.31
12		100:4	100	75	17.1	2.31	67	0.33

[a] [M] = 5.2 mol/L, [M]:[AIBN] = 100:1, solvent: toluene. [b] M_ns and PDIs were measured by Sin-SEC. [c] The content of pendent norbornene group (NB%) was calculated from ^{1}H NMR data. [d] Degree of branching determined from ^{1}H NMR data. [e] Conventional radical polymerization under the same reaction conditions.

Characterization. ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer. ^{13}C NMR spectra were recorded with a Varin Unity 400 spectrometer operating at 100.0 MHz. In all spectra, $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) was used as the internal standard. FTIR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Number-average molecular weights (M_n) and polydispersity indices (PDIs) of the hyperbranched polymers were determined by single detection size exclusion chromatography (Sin-SEC), which was performed with a Waters 1525 fitted with two columns (Styragel HT3 and HT4 THF 7.8 × 300 mm column). Additional measurements of weight-average molecular weights (M_w) and Mark−Houwink exponent α values were performed on a triple detection size exclusion chromatograph (Tri-SEC) containing a Waters 1525 separation module (Waters Corp.) connected with M302 triple detector array (Viscotek Corp., Houston, TX), a combination of refractive index (RI), light scattering [LS angle, 7° (LALS) and 90° (RALS), laser wavelength, $\lambda = 670$ nm), and viscosity detector (IV-DP). Two mixed bed SEC columns (GMH_{HR}-M, GMH_{HR}-H, Viscotek Corp.) were employed. For all SEC analyses, HPLC grade THF was used as the mobile phase.

Results and Discussion

Synthesis of Hyperbranched Polymers with Abundant Norbornene Pendants. As accepted, the success of RAFT polymerization for a given monomer depends on the structure of both Z and R groups of the chain transfer agent (CTA).[28−33] CPDB was reported to be one of the most efficient CTAs for controlling the polymerization of MMA and its derivatives.[31−35] Therefore, this dithiobenzoate RAFT agent was employed to mediate the radical polymerization of an asymmetrical divinyl monomer, 2-(5-norbornene)methyl methacrylate (NBMMA), in order to synthesize hyperbranched polymers. All polymerizations were performed under varied reaction conditions with AIBN as a source of radicals. The polymerizations were terminated before the occurrence of gelation, and the representative results are summarized in Tables 1 and 2.

For a comparison's sake, a blank polymerization experiment was first performed in the absence of CPDB under the same reaction conditions at 60 °C. As expected, the polymerization gelled at a low monomer conversion of 17% only after 0.5 h, and the product is insoluble in any solvent (entry 1 in Table 1). In contrast, the radical polymerization in the presence of CPDB did not cross-link after a much longer reaction time, and a moderate-to-high monomer conversion

Table 2. Comparison of Typical Samples under Varied Reaction Temperatures[a]

no.	*T* (°C)	time (h)	conv (%)	M_n[b] (kDa)	M_w[b] (kDa)	PDI[b]	[IV][b] (dL/g)	M-H α[b]
1[c]	80	10	56	14.5	20.0	1.39	0.09	0.71
2	60	22	68	28.0	149	5.32	0.12	0.50
3	70	11	73	30.4	334	11.0	0.19	0.44
4	80	10	91	28.9	402	13.9	0.22	0.39

[a] Reaction conditions: [M] = 5.2 mol/L, [M]:[AIBN]:[CPDB] = 100:1:2, solvent: toluene. [b] M_n, M_w, PDI, intrinsic viscosity ([IV]), and Mark−Houwink exponent α were measured by Tri-SEC. [c] RAFT copolymerization of MMA and NBMAc at 80 °C. Reaction conditions: [MMA] = [NBMAc] = 5.2 mol/L, [MMA]:[NBMAc]:[AIBN]:[CPDB] = 100:100:1:2, solvent: toluene.

(68−80%) were easily obtained (entries 2−5 in Table 1). These experiments can also be repeated at elevated reaction temperatures (70−80 °C), producing the similar or even better results (entries 6−12 in Table 1). As entries 10 and 11 show, cross-linking did not occur until high monomer conversions (ca. 90%) at the low molar ratios of monomer to CPDB. Importantly, the polymerizations mediated by CPDB yielded the soluble hyperbranched polymers with a broader number-average molecular weight (M_n) range from 10.9 to 34.5 kDa and a higher PDIs (1.60−3.58) measured by a single detection SEC (Sin-SEC).

The hyperbranched structure can be confirmed by Tri-SEC analyses with triple detectors including RI, light scattering [two angles, 7° (LALS) and 90° (RALS)], and viscosity detector (IV-DP), as shown in Figure 1. Clearly, the chromatograms of all detectors are shoulder modal consisting of multiple peaks corresponding to the different generation. LALS and RALS detectors show higher weight-average molecular weights (M_ws) than RI detector, possibly indicating the formation of hyperbranched architecture, which is typically encountered with SEC characterization of hyperbranched polymers.[36,37]

Molecular weights vs retention volume curves were plotted and are shown in Figure 2. Generally, hyperbranched polymers display longer retention times because of their less hydrodynamic volumes than linear poly(NBMMA) counterparts with M_n(Tri-SEC) = 9.07 kDa and PDI(Tri-SEC) = 1.20. Thus, the molecular weights of hyperbranched polymers should be higher than those of linear polymers at a given retention volume.[37,38] The profiles corresponding to the hyperbranched polymers obtained by RAFT polymerization of the asymmetrical divinyl monomer perfectly match this rule, as they usually lie above the linear PNBMMA sample by RAFT polymerization of NBMMA under the same conditions.

The hyperbranched structure for the obtained samples can also be supported by lower intrinsic viscosities (IVs) compared to linear samples, which is a unique characteristic of hyperbranched structure (Figure 3).[39−42] More accurately, a lower slope obtained from the plot of log IV vs log M, i.e., Mark−Houwink exponent α (Table 2), is observed in the hyperbranched polymer in comparison with the linear PNBMMA. The α values are usually less than 0.5, indicating a more compact hyperbranched structure.[37,40−44] Particularly, the α value is only 0.39 for entry 4 in Table 2. Such a low α value is typically reflected in hyperbranched macromolecule. These results powerfully proved that the hyperbranched structure successfully formed during RAFT polymerization of NBMMA.

Finally, more information about hyperbranched structure can be acquired from ^{1}H NMR analyses (Figure 4). Peaks i′ and j′ represent the reacted methacrylate groups contributing to the formation of primary chain. Peaks e at 5.8 ppm and f at 6.2 ppm correspond to the $-CH{=}CH-$ protons in unreacted norbornene groups. The integral comparisons of peaks e and f with peaks e′ and f′ was used to evaluate the content of residual norbornene groups in the hyperbranched polymers, as listed in Table 1. The high residual norbornene contents (67−83%) endow the hyperbranched polymers potential with further chemical modifications and postpolymerization. In addition, the unreacted $CH_2{=}C-$ protons in methacrylate group can also be found in the spectra, assigning to peak i at 5.25 and 5.90 ppm. The remained methacrylate vinyl content was less than 3%, and it decreased to zero with the increase of reaction temperature. Possessing few high reactivity vinyl groups, the resultant hyperbranched polymers are more stable compared with those obtained in our previous works. Therefore, the results indicate that ^{1}H NMR data does support a hyperbranched polymer or pregel structure.

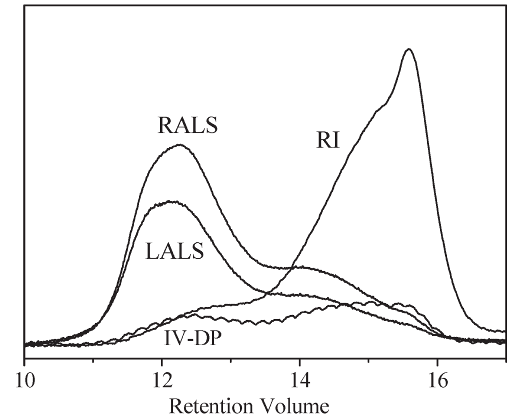


Figure 1. Tri-SEC curve for typical hyperbranched polymer obtained in entry 10 of Table 1.

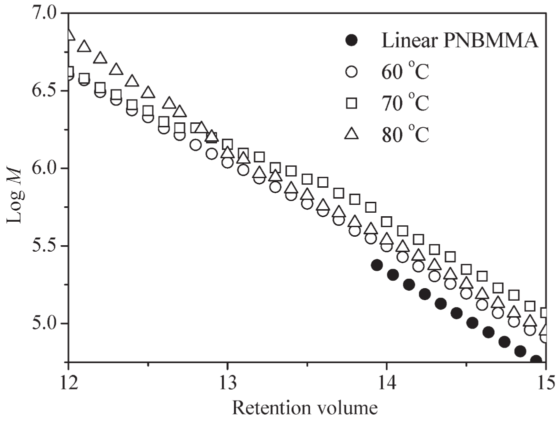


Figure 2. Molecular weight vs retention volume curves for linear PNBMMA and hyperbranched polymers under various reaction temperatures in entries 2−4 of Table 2.

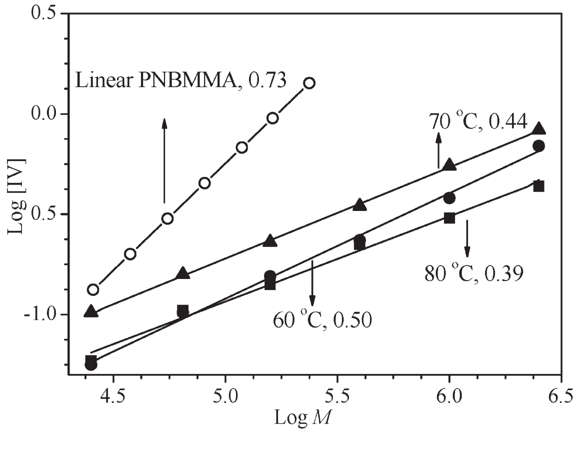


Figure 3. Mark−Houwink plot of hyperbranched polymers synthesized at 60 °C (●), 70 °C (▲), and 80 °C (■) and linear PNBMMA (○). Reaction conditions: [M] = 5.2 mol/L, [M]:[AIBN]:[CPDB] = 100:1:2, solvent: toluene. The values beside the curves correspond to their Mark−Houwink exponent α values.

Considering that the degree of branching (DB) defined by Fréchet[45] and Frey[46] are not applicable to this system, we qualitatively compare the DBs by determining the content of

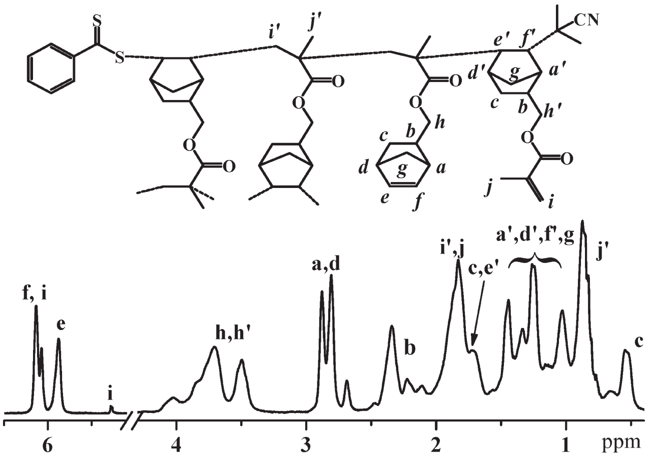


Figure 4. ^{1}H NMR spectrum of hyperbranched polymer. Comparisons of peaks e and f with peaks h and h′ were used as the evaluation of DB. Reaction conditions: [M] = 5.2 mol/L, [M]:[AIBN]:[CPDB] = 100:1:1, T = 60 °C, solvent: toluene.

reacted pendent norbornene groups.[21,22]

$$\mathrm{DB} = \frac{I_{3.4-4.1} - I_{5.8-6.2}}{I_{3.4-4.1}}$$

where $I_{5.8-6.2}$ refers to the integration of peaks e and f and $I_{3.4-4.1}$ refers to that of peaks h and h′ corresponding to the $-\mathrm{COOC}H_2-$ protons. Noticeably, the DB values (0.17−0.35, Table 1) are much higher than those produced by the polymerizations of undecenyl methacrylate (DBs around 0.10) or 1-(3-butenyloxymethyl)-4- vinylbenzene (DBs around 0.16),[21,22] indicating a more highly branched structure. The significant improvement in DB originates from a lower reactivity difference between methacrylate and norbornene vinyl groups.

Effect of Reaction Temperature on Hyperbranched Architecture. The earlier results indicate that the hyperbranched polymers with pendent norbornene functionalities were generated from RAFT polymerization of novel asymmetrical divinyl monomer at three reaction temperatures (60, 70, and 80 °C). To further investigate the effect of reaction temperature on hyperbranched architecture, the typical samples (entries 3, 7, and 10 in Table 1) obtained at the varied reaction temperatures were emphasizedly characterized by Tri-SEC, and the analysis results are presented in Table 2.

The data in Table 2 show that M_ws and PDIs measured by Tri-SEC enhance with the increase of reaction temperature, indicating that more highly branched structure was formed at higher reaction temperature. Furthermore, the decrease tendency of M-H α value is more convincing, as the polymers with higher branched structures exhibit lower α values compared with those possessing less branched structures. This rule can also be clearly observed from the plots of log [IV] vs log M (Figure 3). As expected, with the increase of reaction temperature, the slope of log [IV] vs log M decreases gradually. This result suggests that reaction temperature significantly influenced the proceeding of branched structure, and a higher reaction temperature favors the formation of hyperbranched polymers.

The improvement in hyperbranched structure with reaction temperature may be ascribed to the reactivity increase of norbornene double bond. To validate this assumption, a model monomer pair, MMA and 2-(5-norbornene)methyl acetate (NBMAc), which have similar reactivity ratios compared with two vinyl groups of asymmetrical divinyl monomer (NBMMA), were copolymerized at 60 and 80 °C under the same reaction conditions. The copolymerization at 80 °C can yield the polymers with monomer conversion close to 99%, and a sample terminated after the same reaction period (10 h) with entry 4 was used as the linear reference (entry 1 in Table 2). However, the copolymerization at 60 °C only obtained trace product even after a longer reaction time. ^{1}H NMR spectra of the resultant copolymers are illustrated in Figure 5. The incorporation of the norbornene moiety can be evaluated by the integral ratio of norbornene protons to that assigned to MMA unit. The results show that NBMAc incorporation is 0.17 mol % at 60 °C, whereas NBMAc incorporation raises to 0.21 mol % at 80 °C. Despite the drastic improvement of monomer conversion, the incorporation values do not vary greatly. Therefore, a branching mechanism is proposed to explain the obvious discrepancy of hyperbranched structures produced at various reaction temperatures.

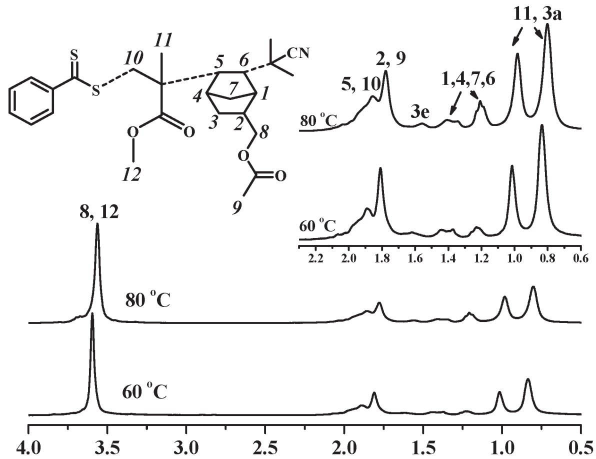


Figure 5. ^{1}H NMR spectra of linear P(MMA-*co*-NBMAc) under different reaction temperatures. 3e and 3a refer to equatorial and axial bonds of H3, respectively. Reaction conditions: [MMA] = [NBMAc] = 5.2 mol/L, [MMA]:[NBMAc]:[AIBN]:[CPDB] = 100:100:1:2, solvent: toluene.

As illustrated in Scheme 2, two intermediate radicals originating from methacrylic (2) and norbornene (5) units were generated during RAFT copolymerization of MMA and NBMAc. The stability of intermediate radicals 2 or 5 could significantly influence the addition−fragmentation equilibrium.[31−33] Intermediate radicals formed from the initiated methacrylate group (2) are less stable, and the transformation between active species (1) and dormant species (3) is more ready to occur, as reported in other works.[33,50] In the case of norbornene unit, the corresponding intermediate radicals (5) are difficult to fragmentize, especially at low reaction temperature, so that they should be more stable and have a longer lifetime.[32,33,51,52] Therefore, they would go through more termination reactions.[30,50,53−58] Consequently, it leads to the active propagation radicals successive to the termination reactions onto these stable intermediate radicals (5), which directly induces a reduction in the concentration of propagation chain radicals. This result would accounts for the reduction of both the rate of copolymerization and molecular weights of the copolymer for the copolymerization of MMA and NBMAc at 60 °C. With the increase of reaction temperature, intermediate radicals 5 become less stable, and the transformation between active species (4) and dormant species (6) is easy to occur, which brings their concentration to decrease. As a result, though the content of initiated norbornene groups does not significantly increase, the lower concentration of less stable intermediate radical (5) and a rapid RAFT process involving 5 will make the copolymerization more controlled, and the copolymers with higher molecular weight and monomer conversion can be produced.

As for the homopolymerization of NBMMA, the higher stability of intermediate radicals (5′) will make propagation less likely to occur from the initiated norbornene group, which usually acts as the branching site in the resultant polymer as reported in our previous works.[21,22] Thus, the polymers obtained at lower temperature would exhibit less branched structure than those obtained at higher temperature. Likewisely, at higher reaction temperature, the stability of intermediate radicals (5′) decreased greatly, which cause rapid reversible addition−fragmentation equilibriums. Therefore, termination reactions involving these stable intermediate radicals (5′) are effectively eliminated, and polymers with a higher level of molecular weights and monomer conversions were obtained.

Evolution of Molecular Dimension and Hyperbranched Structure. The earlier results show a prominently hyperbranched structure produced by entry 4 in Table 2 at a higher temperature (80 °C). Therefore, this reaction proceeding was investigated detailedly (Figures 6 and 7) to follow the evolution of molecular dimension including molecular weights and molecular weight distributions as well as corresponding hyperbranched structures during the polymerization process.

As shown in Figure 6, M_ns increase linearly up to a monomer conversion of 50% at the early stage of the polymerization, and they are in perfect accord with theoretical values. Concerning PDIs, they remain less than 1.4 during this stage, which can be confirmed from obviously monomodal Sin-SEC curves for the resultant polymers at low monomer conversions (24% and 50%, Figure 7). These results indicate that the initial polymerization can be controlled well and show controlled/living radical polymeriza-

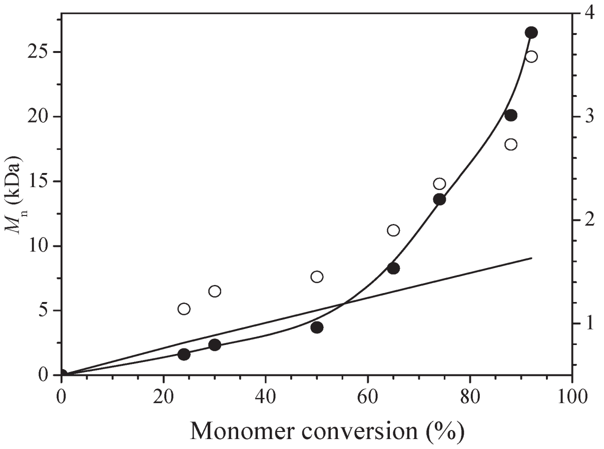
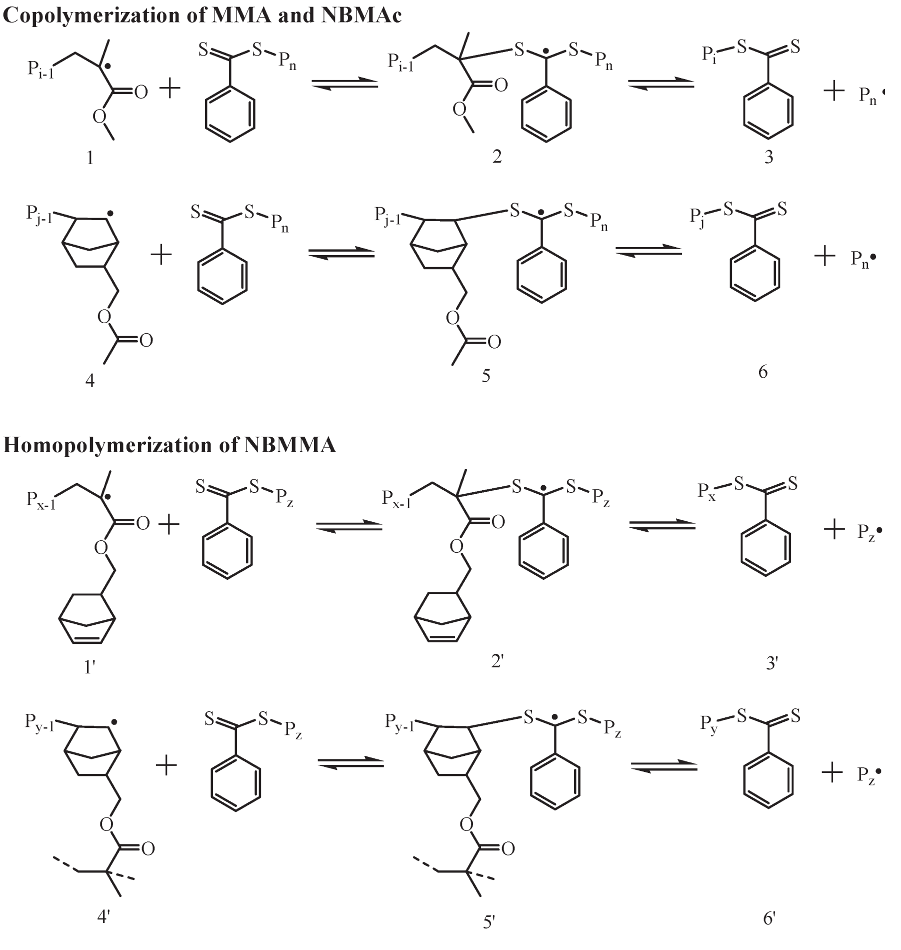


Figure 6. Plots of M_n (●, — theoretical) and PDI (○) of resultant polymers with monomer conversion. [M] = 5.2 mol/L, [M]:[AIBN]:[CPDB] = 100:1:2, T = 80 °C, solvent: toluene.

Scheme 2. Reversible Addition−Fragmentation Equilibriums Occurring in Homopolymerization of Asymmetrical Divinyl Monomer (NBMMA) and Copolymerization of MMA and NBMAc



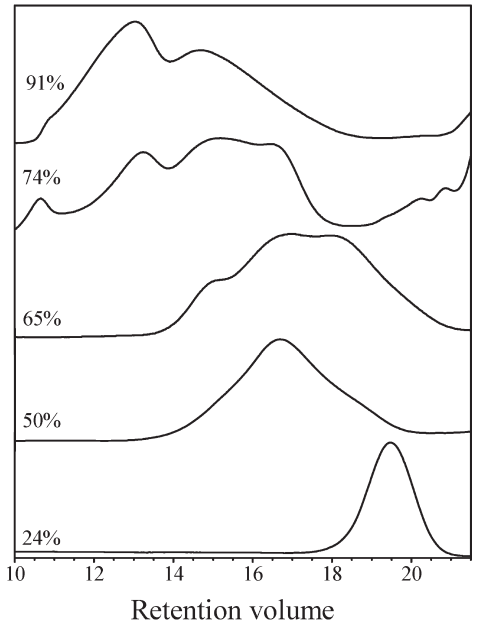


Figure 7. Sin-SEC curves for the resultant polymers at different monomer conversions: 24%, 50%, 65%, 74%, and 91%. Reaction conditions: [M] = 5.2 mol/L, [M]:[AIBN]:[CPDB] = 100:1:2, T = 80 °C, solvent: toluene.

tion characteristics,[37,59] and the obtained polymers possess linear structures. In addition, Sin-SEC curves also indicate that loss of control is observed for these polymerizations. As an asymmetrical divinyl monomer, NBMMA contains quite higher reactivity methacrylate double bond relative to norbornene double bond. Therefore, due to higher initial concentration of methacrylate groups, the preferential free-radical polymerization occurs in the methacrylate units to form a linear macromolecular main chain with norbornene-functionalized side chains. This can be confirmed by ^{1}H NMR analyses which reveal that norbornene vinyl groups in the polymer backbone remained intact at the early polymerization stage (Figure 8).

With the further increase of monomer conversion, the concentration of methacrylate groups gradually decreased, whereas the norbornene number in the side chains reached a high level. Therefore, the newly formed macroradicals may have a great tendency to react with some of the norbornene groups despite their low reactivities, which usually generate the branching sites. The continuous propagation reactions in these branching sites eventually result in the formation of hyperbranched structure. As a result, the norbornene contents gradually decreased to ca. 70% at the end of the polymerization (Figure 8). In accord with this analysis, M_ns increase considerably and are far higher than the theoretical values in the high monomer conversion region (Figure 6). PDIs also show a sharp increase from a living/controlled polymerization product criterion (<1.5) to a hyperbranched polymer range (ca. 3.5). Moreover, Sin-SEC curves almost shift cleanly and completely to higher molecular weights (Figure 7). Importantly, there is a shoulder at the high molecular weight in all case. It gradually changed into a higher molecular weight peak at a monomer conversion of 91% and molecular weight distribution correspondingly broadened. In a word, the latter polymerization stage contributes to generating hyperbranched structures and higher molecular weights, whereas the early stage only contributes to increasing monomer conversions.

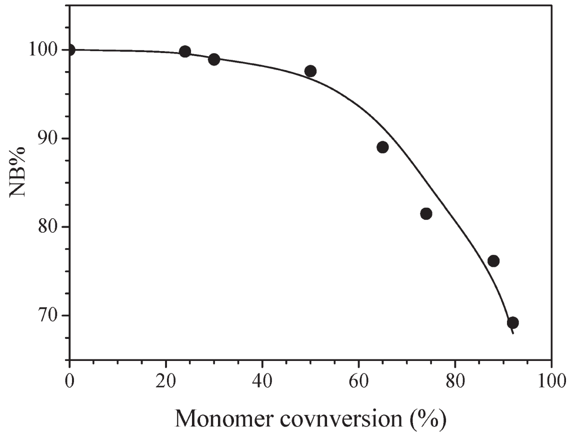


Figure 8. Evolution of residual norbornene contents in the resultant polymers (NB%) with monomer conversions. [M] = 5.2 mol/L, [M]:[AIBN]:[CPDB] = 100:1:2, T = 80 °C, solvent: toluene.

Conclusions

The hyperbranched polymers with pendent multiple norbornene functionalities were prepared via RAFT polymerization of a novel asymmetrical divinyl monomer, 2-(5-norbornene)methyl methacrylate. The DBs have been obviously enhanced compared with our previous reports due to a decreased reactivity difference between methacrylate and norbornene groups. The gelation did not occur until a higher level of monomers conversions (ca. 90%) by employing the RAFT technique to keep a low propagation chain concentration via a fast reversible chain transfer equilibrium. The model copolymerization studies confirmed that reaction temperature significantly influenced the stability of the intermediate radicals from norbornene and hyperbranched structure; i.e., an increase in reaction temperature favored the formation of a more highly branched structure, as evidenced by high molecular weights and low Mark−Houwink exponent α values. Furthermore, Tri-SEC and conventional Sin-SEC as well as ^{1}H NMR analyses confirm that hyperbranched structures and high molecular weights were gradually formed at the latter polymerization stage, whereas the early stage only yield linear polymers with controlled molecular weights and lower PDIs. Finally, the abundant norbornene functional groups (ca. 70%) in the side chains can be directly performed chemical modifications, post-polymerization, etc.

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