Synthesis of hyperbranched polymers by free radical addition-coupling polymerization with A_3/B_2 and A_2A'/B_2 approaches

Yaobin Liu, Zhiqiang Fan

Department of Polymer Science & Engineering, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Zhejiang University, Hangzhou 310027, China
Correspondence to: Z. Fan (E-mail: fanzq@zju.edu.cn)

ABSTRACT: Two tribromide compounds, 1,3-(propanoic acid, 2-bromo-)-2-(2-bromo-1-oxopropylamino)propyl ester (A1) and trimethylolpropane tris(2-bromopropionate) (A2), were synthesized. By Cu/N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA)-mediated radical addition-coupling polymerization (RACP) of 2-methyl-2-nitrosopropane (MNP) with the tribromide compounds, two types of hyperbranched polymers were synthesized under mild conditions, respectively. Polymerization degrees of the polymers increased with time gradually, which is in line with a step-growth polymerization mechanism. By tracing the polymerization process by gel permeation chromatography and NMR analysis, proper reaction conditions to get hyperbranched polymers was obtained. Based on the results of NMR analysis on the polymer chain structure, mechanism of forming hyperbranched polymer has been proposed, which includes formation of carbon radicals from the tribromo monomer through single electron transfer, their reaction with MNP to form nitroxide radicals, and cross-coupling reaction of the nitroxide radicals with other carbon radicals. The gelation point of the A2-MNP system is larger than that of the A1-MNP system, indicating that probability of intramolecular cyclization in A2-MNP RACP system is higher than the A1-MNP system. The reactivity of —NHCOCH(CH₃)Br group of A1 is lower than its two —OCOCH(CH₃)Br groups, and this resulted in longer distance between two adjacent branch points in the hyperbranched polymer of A1-MNP than the A2-MNP system. It is possible to adjust the chain structure of RACP-based hyperbranched polymer by changing the reactivity of the functional groups in A_3 monomer. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41972.

INTRODUCTION

Research for hyperbranched polymer has continued for a long time.[1] The basic concept of reactions forming hyperbranched polymers was established in the 1940s, under the concept of Three-Dimensional Branch Network proposed by Flory[2] and Stochmayer.[3] In addition to the more matured one step polycondensation reactions leading to hyperbranched polymer, a number of new synthetic methods have been developed. It has been found that hyperbranched polymer can be synthesized from A_3B_2 monomer or a combination of other polyfunctional monomers whenever the polymerization has been stopped before the gelation point. In addition to the traditional polycondensation approach, in recent years some new "living" polymerizations have been applied to preparing hyperbranched polymers, such as self-condensing vinyl polymerization, atom transfer radical polymerization, and proton transfer polymerization. For example, Min and Gao[4] reported an one-pot inimer polymerization method, Kawker et al.[5] reported a living radical polymerization method, Fréchet et al.[6] reported vinyl polycondensation with

cationic polymerization mechanism, and Muller et al.[7] reported a method based on group transfer polymerization.

The radical addition-coupling polymerization (RACP) method used in this work is closely related to metal-catalyzed redox of organic halide, especially atom transfer radical polymerization (ATRP) reported by Sawamoto and Matyjaszewski in 1995.[8–11] In the ATRP, radical is generated by single electron transfer to organic halide and cleavage of the alkyl halide catalyzed by complexes of transition metal halides. This provides a convenient way to generate carbon radical at mild conditions without using peroxide compounds. In addition, radical coupling promoted by transition-metal complex has been widely applied to preparing block polymer and multiblock polymer using mono- or dihalogenated polymer as precursor. The mono- or dihalogenated polymer can be synthesized by ATRP. For example, diblock polymers can be prepared by direct atom transfer radical coupling (ATRC) from two mono-halogenated polymers.[12,13] Both atom transfer nitroxide radical coupling (ATNRC) and single electron transfer nitroxide radical coupling (SET-NRC)

have been reported for synthesizing block polymers, which introduced stable nitroxide radicals to couple with macromolecular chain radicals.[14,15] For example, coupling reaction between radical generated from mono-halogenated polymer and TEMPO end-functionalized polymer has been reported.[16–19] Multiblock polymer has been prepared by ATRC using α,ω-dihalogenated polymer, but the number of blocks in the product is not so large, and multimodal molecular weight distribution is observed, because the coupling efficiency of ATRC normally does not exceed 95%.[13]

In recent years, new kinds of coupling reactions have been realized by comediated radical polymerization (CMRP) in the assistance of small organic reagents like isoprene, and nitrones have been applied in enhanced spin capturing polymerization (ESCP) to improve the efficiency of coupling between polymeric radicals.[20–24] Zhang and Wang[25] reported synthesis of multisegmented polymer by consecutive radical addition-coupling reaction of α,ω-macrobiradical and nitroso compound. Later on, synthesis of high molecular weight linear alternating polymers *via* consecutive radical addition-coupling polymerization with small α,α'-dibromo diester and nitroso type radical scavenger have also been reported.[26,27]

This article explores the feasibility and basic rules of synthesizing hyperbranched polymers using small tribromide compounds with C-nitroso compound via consecutive radical addition and coupling reactions. Two kinds of tribromides as monomers of RACP were prepared, one was 1,3-(propanoic acid, 2-bromo-)-2-(2-bromo-1-oxopropylamino)propyl ester (A1) (a A_2A' type monomer), and the other was trimethylolpropane tris(2-bromopropionate) (A2) (a A_3 type monomer). By using Cu/PMDETA as catalyst, the kinetics of consecutive addition-coupling polymerizations of the two monomers with 2-methyl-2-nitrosopropane (MNP, a B_2 monomer) was investigated, and the synthesized hyperbranched polymers were characterized. This new method allows synthesis of hyperbranched polymers with rather regular chain structure, namely, the chain segments between every two neighboring branch points are identical. This makes it different from most of the conventional approaches. Such hyperbranched polymers are more similar to dendrimers in words of regularity of chain structure, but their synthesis is much simpler and more efficient than that of the dendrimers. Possible applications of these hyperbranched polymers include carriers for drugs, pigments and catalysts, and additive for improving rheological properties of linear polymers like polyesters and polycarbonates.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was dried overnight on solid KOH and further purified by refluxing over sodium before use. Copper powder (3.25–4.75 μm, Alfa Aesar, 99.9%), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, 98%; Alfa Aesar), 2-bromopropiomyl bromide (97%; Aldrich), triethylamine (98%; Aladdin), 2-amino-1,3-propanediol (98%; Aladdin), and trimethylolpropane (98%; Aladdin) were used as received. 2-Methyl-2-nitrosopropane (MNP) and its dimer were prepared according to the literature.[28] The other reagents were used as received.
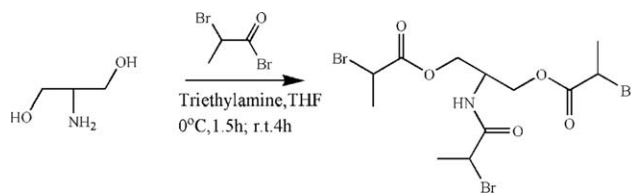

Scheme 1. Synthesis of 1,3-(propanoic acid, 2-bromo-)-2-(2-bromo-1-oxopropylamino) propyl ester.

Synthesis of 1,3-(propanoic acid, 2-bromo-)-2-(2-bromo-1-oxopropylamino)propyl ester (A1)

As shown in Scheme 1, 2-amino-1,3-propanediol (0.015 mol, 1.35 g) and triethylamine (0.067 mol, 9.3 mL) were dissolved in 70 mL of dry THF in a 250-mL three-neck round-bottom flask equipped with a magnetic stirrer. Then, the solution was cooled to 0°C with an ice bath. 2-Bromopropionyl bromide (0.067 mol, 7.2 mL) was added to the solution dropwise during half an hour and maintained at 0°C for an additional hour. The reaction was allowed to warm to room temperature and stirred overnight. The suspension obtained was filtered, THF and residual triethylamine were evaporated. The crude product was dissolved in dichloromethane (30 mL), followed by washing with saturated $NaHCO_3$ (3 × 25 mL) and water (3 × 25 mL). The organic layers were combined and dried over magnesium sulfate, filtered, and then concentrated. The crude product was purified by flash column chromatography (petroleum ether : EtOAc = 10 : 1), which provided 3.30 g of a viscous liquid with red brown color. The bromo functionality measured by ^{1}H-NMR was 100%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.63–4.48 (m, 1H, C**H**NH), 4.48–4.21 (m, 7H, C**H**Br, C**H**$_2$O), 1.87 (ddd, J = 9.7, 7.0, 1.2 Hz, 9H, CHBrC**H**$_3$). ESI-MS: 519.8 [M+Na]$^+$.

Synthesis of trimethylolpropane tris(2-bromopropionate) (A2)

Synthesis of the A_3 type monomer (A2) is shown in Scheme 2. Trimethylolpropane (6.7 g, 0.05 mol), triethylamine (26 mL, 0.18 mol) were dissolved in 150 mL of dry THF in 250 mL three-neck round-bottom flask equipped with a magnetic stirrer. Then, the solution was cooled to 0°C with an ice bath. 2-Bromopropionyl bromide (18.4 mL, 0.17 mol) was added dropwise during half an hour and maintained at 0°C for an additional hour. The reaction was allowed to warm to room temperature and stirred overnight. The suspension obtained was filtered, THF and residual triethylamine were evaporated. The crude product was dissolved in dichloromethane (25 mL), followed by washing with 5% Na_2SO_3 (3 × 25 mL), saturated $NaHCO_3$ (3 × 25 mL), and water (3 × 25 mL). The organic layers were combined and dried over magnesium sulfate, filtered, and then concentrated. The crude product was purified
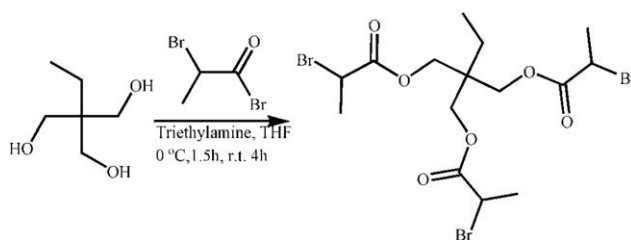
Scheme 2. Synthesis of trimethylolpropane tris(2-bromopropionate).

by flash column chromatography (petroleum ether: EtOAc = 100 : 1), which provided 10.09 g of a yellowish viscous liquid. ^{1}H-NMR (400 MHz, CDCl$_3$) δ 4.40 (q, $J = 6.9$ Hz, 3H, C**H**Br), 4.29–4.06 (m, 6H, OC**H**$_2$), 1.84 (d, $J = 6.9$ Hz, 9H, CHBrC**H**$_3$), 1.64–1.53 (m, 2H, C**H**$_2$CH$_3$), 0.95 (t, $J = 7.6$ Hz, 3H, CH$_2$C**H**$_3$). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 169.75 (**C**(O)O), 65.34–64.25 (C(O)O**C**H$_2$), 41.59 (**C**(CH$_2$)$_4$), 40.25–39.26 (**C**HBr), 22.92 (**C**H$_3$CH$_2$), 21.52 (**C**H$_3$CHBr), 7.34 (**C**H$_3$CH$_2$). HR-ESI-MS: 562.9 [M+Na]$^+$.

Synthesis of Hyperbranched Polymer

In a typical procedure, copper powder (6.38 mg, 1×10^{-4} mol), tribromide A**1** (16.62 mg, 3.35×10^{-5} mol) and MNP (4.35 mg, 5.0×10^{-5} mol) were added to a Schlenk flask equipped with a stirring bar. The Schlenk flask was degassed, backfilled five times with N$_2$ and then left under N$_2$. Deoxygenated PMDETA (21 μL, 1×10^{-4} mol) and 4 mL THF were then injected. The Schlenk flask was kept at 25°C for a given time under stirring. The Schlenk flask was then immersed in liquid nitrogen to stop the reaction, and the mixture was diluted with THF and purified by passing through a neutral alumina column. The concentrated polymer was dissolved in CH$_2$Cl$_2$, then precipitated by an excess of n-hexane for the second purification. The products were dried under vacuum at 55°C overnight to yield a faintly yellow sticky polymer.

Preparation of hyperbranched polymers using A**2** and MNP was conducted in the same procedures.

Characterization of Polymers

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature in a Bruker (400 MHz) spectrometer using tetramethylsilane as the internal standard and CDCl$_3$ as the solvent. Number average molecular weight (Mn) and molecular weight distribution were determined by gel permeation chromatograph (GPC) on a PL GPC220 equipped with two PLgel 5 μm MIXED-C columns using polystyrene standards and THF as the eluent at a flow rate of 1.0 mL/min at 40°C, the sample concentration was 0.3%; K, α values, for polystyrene are 14.1×10^{-3} mL/g and 0.70, respectively. ESI-MS (m/z) were performed using a LCQ Deca XP Max instrument (Thermo Finnigan).

RESULTS AND DISCUSSION

Structure of Hyperbranched Polymer Synthesized by A$_2$A$'$/B$_2$ Type RACP and Detailed Mechanism

A soluble polymer was synthesized by the reaction of A**1** (A$_2$A$'$ monomer) and MNP (BB$'$ monomer) under the catalysis of Cu/PMDETA ($n_{A1} : n_{MNP} : n_{Cu} : n_{PMDETA} = 1 : 1 : 2.2 : 2$, $c_{A1} = 0.5$ M, $V_{THF} = 0.5$ mL, 25°C, 15 min.). Because insoluble gel was formed when the reaction was continued for longer time, the degree of cross-linking in the polymer should grow with time untill a threshold of gelation was reached. It means that after the reaction for enough long time, all the three bromo groups of A**1** could have taken part in coupling reaction with MNP. ^{1}H-NMR analysis of the soluble polymer has been made to elucidate its chain structure.

To accurately characterize the OCOC**H**(Me)–N(t-Bu)O units in the synthesized polymer, a model polymer with linear chain structure was prepared by reacting 2-bromo-propionic acid
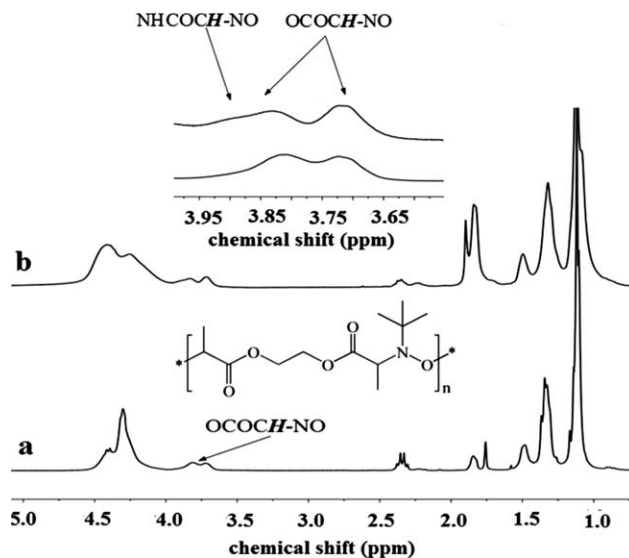
Figure 1. Comparison of ^{1}H-NMR spectra of linear model polymer (a) with the hyperbranched polymer (b). Reaction conditions: (a) $c_{dibromide} = 0.5$ M, $V_{THF} = 0.5$ mL, $n_{dibromide} : n_{MNP} : n_{Cu} : n_{PMDETA} = 1 : 1 : 2.2 : 2$, 25°C, 30 min; (b) $n_{A1} : n_{MNP} : n_{Cu} : n_{PMDETA} = 1 : 1 : 2.2 : 2$, $c_{A1} = 0.5$ M, $V_{THF} = 0.5$ mL, 25°C, 15 min. The insertion is the enlarged spectra of a (lower) and b (upper) in the range of 3.5–4.0ppm.

2-(2-bromo-propionyloxy)ethyl ester (dibromide) with MNP in RACP process. The polymerization condition were $c_{dibromide} = 0.5$ M, $V_{THF} = 0.5$ mL, $n_{dibromide} : n_{MNP} : n_{Cu} : n_{PMDETA} = 1 : 1 : 2.2 : 2$, 25°C, 30 min. In the ^{1}H-NMR spectrum of this linear polymer, the signals of methine proton of OCOC**H**(Me)–N(t-Bu)O appeared at $\delta = 3.65$–3.90 ppm as doublets.[26] By comparing ^{1}H-NMR spectra of the linear model polymer and the soluble polymer synthesized by RACP of A**1** with MNP (see Figure 1), we can find a weak shoulder peak at around 3.90ppm that is overlapped with the doublets at $\delta = 3.65$–3.90 ppm. This peak was assigned to the methine protons in NHCOC**H**(Me)–N(t-Bu)O units. Therefore, both OCOC**H**(Me)–N(t-Bu)O and NHCOC**H**(Me)–N(t-Bu)O units are present in the reaction product of A**1** with MNP. In other words, all the three bromo groups in a A**1** monomer have taken part in the RACP reactions with MNP. Meanwhile, there is a strong peak at $\delta = 1.7$–1.9 ppm, which can be assigned to overlapped peaks of –OCO–CHBr–C**H**$_3$ and –NH–CO–CHBr–C**H**$_3$. It means that many unreacted bromo groups are remained at chain ends of the polymer. Comparing with the linear model polymer, the 1.7–1.9 ppm peak of the polymer formed by A**1** and MNP is much stronger. This is an evidence that this soluble product is a hyperbranched polymer which has much more end groups than the corresponding linear polymer. The other sharp peak appeared at $\delta = 1.7$–1.9 ppm had unfixed chemical shift value, and will be discussed later in this section.

In an attempt to calculate the amount of NHCOC**H**(Me)–N(t-Bu)O and OCOC**H**(Me)–N(t-Bu)O groups in the hyperbranched polymer, it was found that the accuracy of deconvoluting the overlapped peaks between $\delta = 3.55$–4.00 into multiple Lorentz peaks was not high enough. However, it is still possible to estimate that the area of the peak of NHCOC**H**Me–
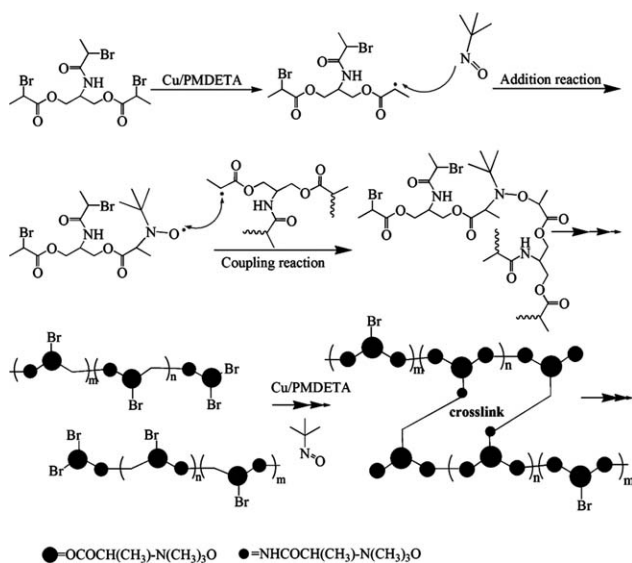
Scheme 3. Mechanism of synthesizing hyperbranched polymer by RACP in A_2A'/B_2 mode.

N(t-Bu)O ($\delta = 3.90$) is smaller than 1/3 of the total area of the signal in $\delta = 3.65$–3.90 ppm. It means that the OCO–CH(CH$_3$)Br groups of A1 are more active than the NHCO–CH(CH$_3$)Br group. In other words, more than 1/3 of the chain ends are NHCO–CH(CH$_3$)Br group.

Since the rate constant of the reaction between nitroxyl radical and carbon radical ($\approx 1 \times 10^8$ L·mol^{-1} s^{-1}) is much larger than that of MNP and carbon radical ($\approx 1 \times 10^6$ L·mol^{-1} s^{-1}), and the self-coupling of nitroxyl radicals ($\approx 1 \times 10^2$ L·mol^{-1} s^{-1}) is rather slow, the coupling reaction between nitroxyl radical and carbon radical becomes the dominant way of forming stable products. Thus the self-coupling of nitroxyl radicals could be neglected.[35–37]

Based on the above results, we proposed the mechanism of the reactions between A1 and MNP (see Scheme 3). As the first step, radical can be generated by single electron transfer from the carbon-bromo bonds of A1 monomer. Because MNP is an active radical scavenger, it can quickly react with the carbon radical to form nitroxide radical. The relatively more stable and long lived nitroxide radicals can then undergo cross-coupling reaction with another carbon radical. This is in principle a kind of RACP between multifunctional monomers. Through many steps of such RACP reactions, hyperbranched or crosslinked polymers can be formed.

In the ^{1}H-NMR spectra of the hyperbranched polymer, there is a sharp singlet in the range of 1.6–1.9 ppm. Because its position is not fixed, it looks like the resonance of an active hydrogen. To prove its nature, deuteroxide exchange experiment was conducted by adding a few drops of deuteroxide into the polymer solution. As shown in Figure 2, the 1.59 ppm peak of the polymer disappeared after the exchange, indicating that it comes from an active hydrogen. Since the polymer does not contain a lot of water, OH groups can be excluded. As the signal of CONHCH in A1 appears at $\delta = 6.6$, NH group can also be excluded. Considering that alkoxy amine radical –NO· can easily
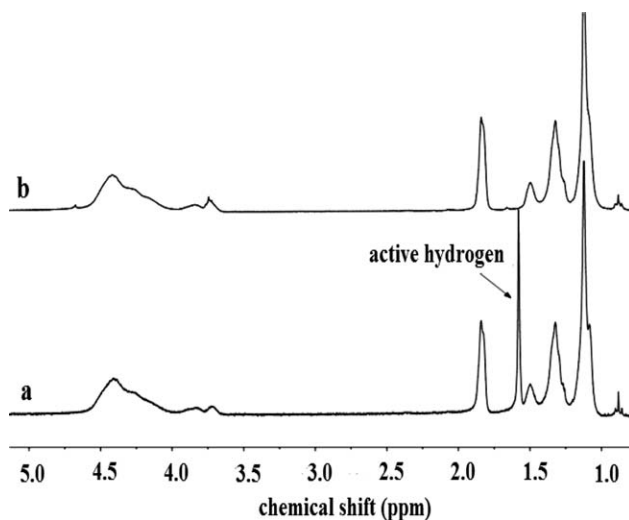

Figure 2. Comparison of ^{1}H-NMR spectra of the polymer prepared by A1 and MNP before (a) and after (b) deuteroxide exchange.

abstract hydrogen from other molecules or groups to generate NOH structure, thus the 1.59 ppm peak was assigned to –NOH.[29–32]

Based on the above experiments, a complete assignment of ^{1}H-NMR spectrum of the hyperbranched polymer was made (see Figure 3).

Kinetics of Radical Addition-Coupling Polymerization of A1 and MNP. As mentioned above, the monomer A1 contains two OCOCHMeBr and one NHCOCHMeBr groups, in which the former has a faster rate to generate carbon radical than the latter when catalyzed by Cu/PMDETA [27]. It is expected that in the initial stage of RACP of A1 with MNP, the two OCOCHBr groups will react preferentially to generate carbon radicals, producing polymer of dominatingly linear structure. With the polymerization reaction proceeding, the concentration of OCOCHBr becomes lower, and the remaining NHCOCHBr groups will start to produce carbon radicals. By reaction of these carbon radicals with MNP and the subsequent coupling reactions, crosslinks between the linear polymer chains will be
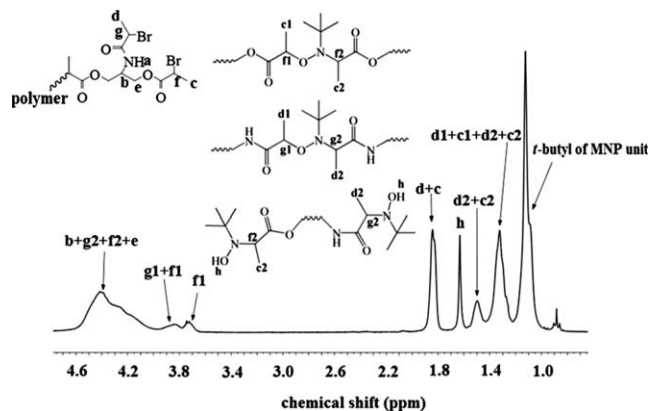
Figure 3. ^{1}H-NMR spectrum of the polymer prepared by 12 min reaction of A1 and MNP.
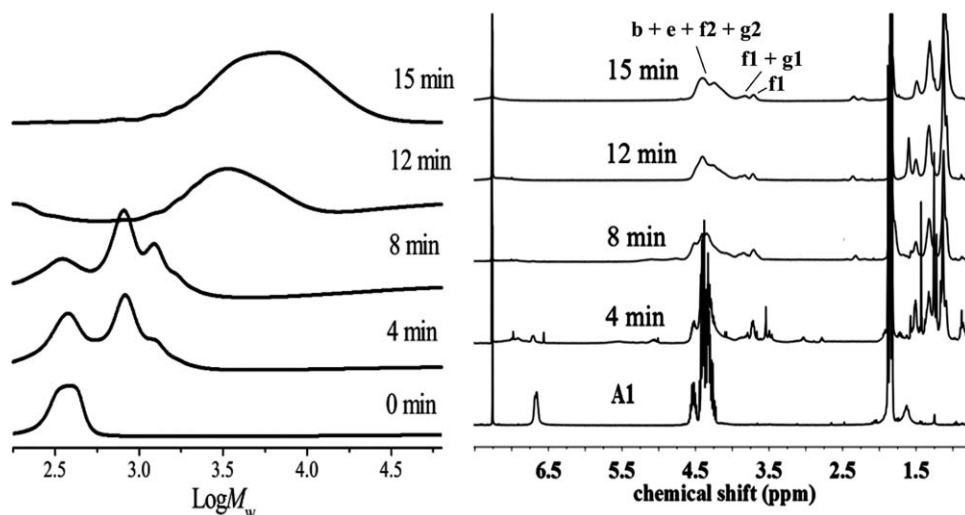
Figure 4. GPC curves (left) and ^{1}H-NMR spectra (right) of polymers prepared by RACP of A1 and MNP promoted by Cu/PMDETA before gelation. Reaction condition: $n_{A1} : n_{MNP} : n_{Cu} : n_{PMDETA} = 1 : 1 : 2.2 : 2$, $c_{A1} = 0.5$ M, $V_{THF} = 0.5$ mL, 25°C.

formed, leading to hyperbranched polymers or three-dimentional structures.

In order to investigate the kinetic laws of RACP of A_2A' monomer and MNP, RACP of A1 and MNP were conducted for different time at $c_{A1} = 0.5$ M, and the polymer was analyzed by gel permeation chromatography and ^{1}H-NMR spectrum. As shown in Figure 4, with the polymerization reaction proceeding, the molecular weight of polymers increased, and the molecular weight distributions were rather broad. The gradual incr molecular weight with time is in keeping with a step-growth polymerization mechanism, but the rather broad molecular weight distribution means that its mechanism is different from the typical step-growth polymerization. Under the conditions of Figure 4, the reaction degree reached 0.68 after 12 min of reaction according to calculation on the Br-containing groups in ^{1}H-NMR spectrum. Gelation point was reached at nearly 16 min under this condition. Comparison of ^{1}H-NMR spectra of polymers formed at different reaction time shows that the peak of C**H**(CH$_3$) of A1 at $\delta = 1.7–1.9$ ppm was weakened as the polymerization proceeded, meanwhile the *tert*-butyl group of

MNP at $\delta = 1.0–1.2$ was gradually enhansed, indicating that more MNP was incorporated in the polymer.

By resolution of the peak at $\delta = 1.7–1.9$ ppm into multiple Lorentz peaks (see Figure 5), the reaction degrees of NHCOCHBrC**H**$_3$ and OCOCHBrC**H**$_3$ groups were calculated. These two groups have different rates of generating carbon radical under the same condition. The rate of the latter is about five times of that of the former at 8 min (see Table I).

Ratios of the two monomers in the polymers were calculated by comparing the integrated areas of the peaks at $\delta = 3.6–4.7$ (methine and methylene protons of A1 units) and $\delta = 1.1$ (*tert*-butyl group of MNP units) using the equation $n_{MNP}/n_{A1} = (S_{MNP}/9)/(S_{A1 \; \delta = 3.6–4.7}/8) = (S_{\delta = 0.96–1.20}/9)/(S_{A1 \; \delta = 3.6–4.6}/8)$. Degree of polymerization $X_{n,GPC}$ of the polymer was calculated by $M_{n,GPC}$. The reaction degree, P was quantified by two methods, which were named as $P_{A,MNP}$ and P_A, respectively. $P_{A,MNP}$ is calculated by molar ratio of the two monomer units in the polymer using the equation $P_{A,MNP} = 2n_{MNP}/(3n_A)$; P_A is calculated based on the degree of reduction of integrated area of
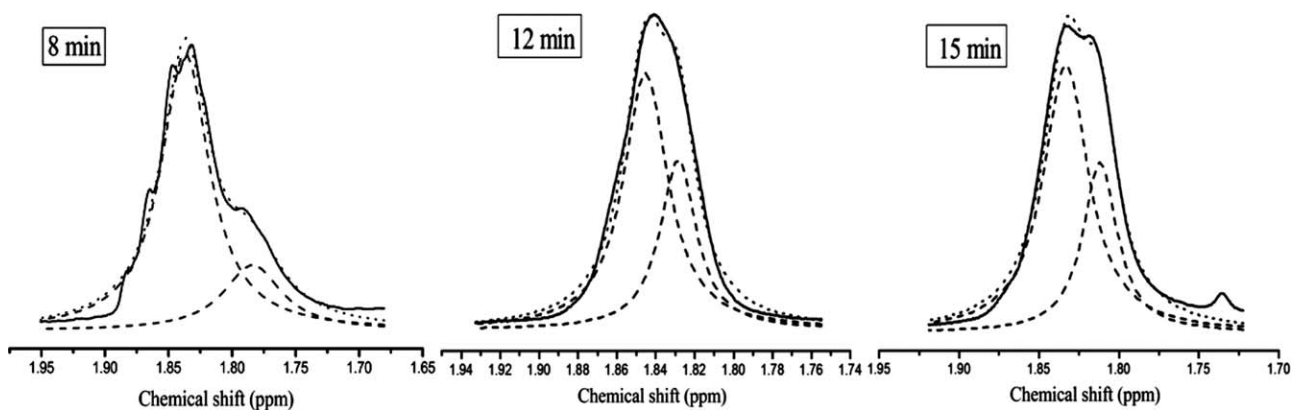
Figure 5. Deconvolution of the ^{1}H-NMR peak at 1.70–1.93 ppm into two Lorentz peaks. The polymer samples were synthesized by RACP of A1/MNP for different time. The Lorentz peak at 1.84–1.85 ppm was assigned to NHCOCH(C**H**$_3$)Br, and the one at 1.79–1.82 ppm was assigned to OCOCH(C**H**$_3$)Br.

Table I. Comparison of Hyperbranched Polymers Synthesized by RACP of A1-MNP and A2-MNP

Monomers	Time (min)	P_A	n_{MNP}/n_A	$P_{A,a}$	$P_{A,b}$	$P_{A,MNP}$	Br (%)	NOH (%)[a]	$X_{n,GPC}$[b]	PDI
A1 + MNP[c]	4	0.36	0.35	–	–	0.23	64	12.7	1.1	1.36
	8	0.50	0.44	0.83	0.17	0.29	50	20.7	1.4	1.35
	12	0.68	0.87	0.84	0.39	0.58	32	10	7.3	1.34
	15	0.71	1.02	0.86	0.40	0.68	29	3	10.5	1.70
A2 + MNP[d]	10	0.73	1.06	–	–	0.71	27	2.3	45.6	1.67
	13	0.77	1.12	–	–	0.75	23	2.3	90.6	6.81

[a] Assuming 1 mole A unit in polymer had x mole NOH structure, thus, $(3 \times P_A - x)/2 = n_{MNP}/n_A$, NOH (%) $= 100 \times (x/3)$.
[b] $X_{n,GPC} = M_{n,GPC}/M_{unit}$, M_{unit} is the molecular weight of the repeating unit in two kinds of polymers, $M_{unit} = 3 \times Br \% \times M_{Br} + (M_A - 3M_{Br}) + 3 \times (1 - Br \%) \times M_{MNP}/2$.
[c] General conditions: $n_{A1} : n_{MNP} : n_{Cu} : n_{PMDETA} = 1 : 1 : 2.2 : 2$, [A1] $= 0.5$ M, $m_{A1} = 74.4$ mg, $V_{PMDETA} = 62.4$ μL, $V_{THF} = 0.4$ mL, 25°C.
[d] General conditions: $n_{A2} : n_{MNP} : n_{Cu} : n_{PMDETA} = 2 : 3 : 6 : 6$, [A2] $= 0.3$ M, $V_{THF} = 0.5$ mL, 25°C.

CH(C$\boldsymbol{H_3}$)Br in A1 with reaction time, using the equation $P_A = 1 - S_{d+c}/[(S_{A1 \ \delta = 3.6-4.7}) \times (9/8)]$. $P_{A,a}$ is reaction degree of OCOCHBr structure, calculated based on the area of the 1.79–1.82 ppm peak (the deconvoluted peak on the right side) in the overlapped (d+c) peaks with the equation $P_{A,a} = 1 - (S_{right}/S_{total}) \times S_{d+c}/6$. $P_{A,b}$ is reaction degree of NHCOCHBr structure, which is also calculated based on the area of the 1.84–1.85 ppm peak (the deconvoluted peak on the left side) in the overlapped (d+c) peaks with the equation $P_{A,b} = 1 - (S_{left}/S_{total}) \times S_{d+c}/3$. All these results have been listed in Table I.

Comparison between A_2A'/B_2 and A_3/B_2 RACP Systems

Kinetics of the reaction of A2 and MNP under catalysis of Cu/PMDETA has been investigated before, and the detailed results have been presented in our another works.[33,34] By reacting A2 that has three equivalent bromo groups (an A_3 type monomer) with MNP in the catalysis of Cu/PMDETA, another hyperbranched polymer has also been synthesized. The RACP mechanism shown in Scheme 3 should also be applicable to this reaction, as the OCOCH(Me)Br groups of A2 should have similar activity as those in A1 in the RACP process.

As shown in Table I, $X_{n,GPC}$ of polymers prepared by A_2A'/B_2 system were lower than that of polymers obtained by A_3/B_2 system, particularly the polymerization degree close to the gelation point was much lower than the latter. This may be caused by different activities of OCOCH(Me)Br and NHCOCH(Me)Br groups in the polymerization process.

Table I shows that two polymerizations were so fast that the reaction degrees reached 0.68 at 12 min and 0.73 at 10 min for A_2A'/B_2 and A_3/B_2 systems, respectively. The gelation point was reached at about 16 min and 14 min, respectively. Thus, P_A of A_2A'/B_2 at 15 min and P_A of A_3/B_2 at 13 min are approximately close to their gelation points P_c. By calculations based on ^{1}H-NMR spectra, it was found that P_c of A_2A'/B_2 and A_3/B_2 systems were approximately equal to 0.71 and 0.77, respectively. Changes in $X_{n,GPC}$ and P_A of the two systems with time before the gelation point are shown in Figure 6. It is seen that in the A_2A'/B_2 system, P_A increased with time gradually, but in the A_3/B_2 system P_A quickly increased in the first 7 minutes and then leveled off, indicating that A_3 reacts with MNP faster than A_2A', and the OCOCHBr(CH$_3$) group has a faster rate to produce radicals than the NHCOCHBr(CH$_3$) group. This is also
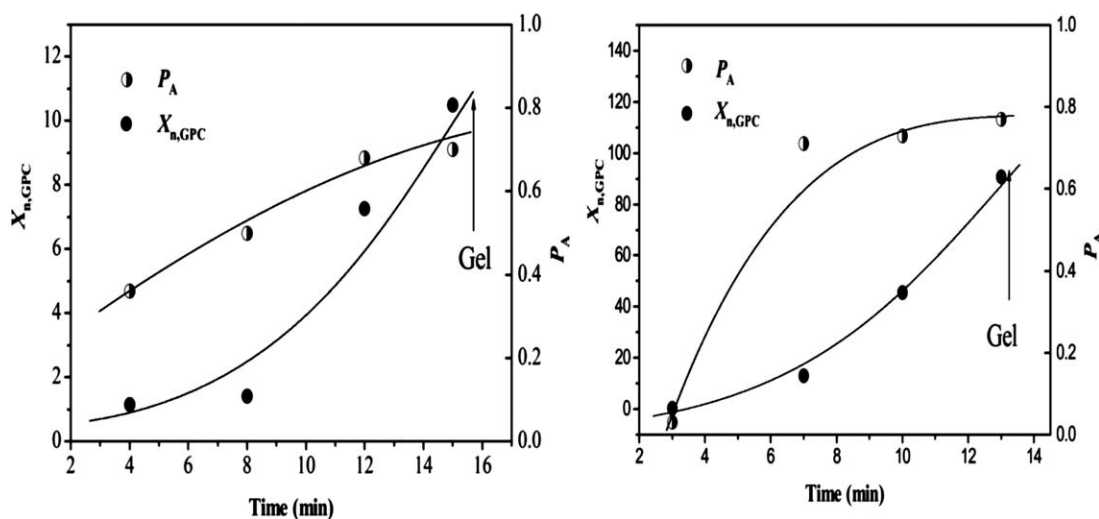
Figure 6. Changes in $X_{n,GPC}$ and P_A with time for A_2A'/B_2 (left) and A_3/B_2 (right) systems.

the reason that it took longer time to reach gelation point in the A_2A'/B_2 system than in the A_3/B_2 system.

For the A_2A'/B_2 system, $P_{A,a}$ was 0.83, 0.84, and 0.86 after 8, 12, and 15 min reaction, but the corresponding $P_{A,b}$ was only 0.17, 0.39, and 0.40. $P_{A,b}$ was much smaller than $P_{A,a}$ at short reaction time, but it grew faster than $P_{A,a}$ as the polymerization proceeded. This means that in the initial stage of polymerization, coupling reactions originated from $OCOCH(Me)Br$ were dominant, and linear polymer chains were the main product. As the polymerization proceeded, more $NHCOCH(Me)Br$ groups took part in the reactions, leading to formation of hyperbranched and crosslinked structure.

Strictly speaking, because the two functional groups of MNP participating in RACP reaction are N=O and N–O•, respectively, they will show different reactivities. Therefore, $A_2A'/B(B')$ and $A_3/B(B')$ models should be used to describe the two systems studied in this work.[38] However, because both functional groups are highly active in the reactions with carbon radicals ($1 \times 10^6 - 1 \times 10^8$ L·mol^{-1} s^{-1}), this difference of reactivities can be neglected. Thus A_2A'/B_2 and A_3/B_2 polycondensation models are actually used to predict the gelation points. As seen in Table I, the observed gelation point (P_c) of the A_3/B_2 system (about 0.77) is much higher than the theoretical value $P_{c,th} = 0.707$ predicted by the Carothers equation. This evident deviation may be explained by the possible competition between intramolecular and intermolecular coupling reactions in the system. Because both the A1 and A2 monomers have rather flexible structure, the possiblity of intramolecular cyclization reaction cannot be neglected. Intermolecular reactions lead to continuous incr polymer molecuar weight and formation of three-dimentional structure, while intramolecular reactions do not contribute to incr molecular weight and reduce the probability of gel formation. Therefore, the presence of intramolecular cyclization reaction will inevitably delay the formation of gel. It has been proved that increasing the degree of cyclization will enlarge the difference between the theoretical and the experimental gelation point.[38,39]

For A_a/B_b type polycondensation reactions with intramolecular cyclization, the overall reaction degree P should be divided into two parts, the reaction degrees P_{A1} and P_{A2} for intramolecular and intermolecular reactions, respectively. A general formula for intramolecular cyclization reaction of an A_aB_b system is shown below.[40]

$$P_{A1} = \left(\frac{3}{2\pi v l^2}\right)^{3/2} \frac{V \sum_{n=1}^{\infty}[P_{A2}P_{B2}(a-1)(b-1)] \times n^{-5/2}}{2aN_A} \quad (1)$$

where v is the number of atoms in the repeating units of polymer main chains, l is the effective chain length (length between two adjacent branch points), and $P_{B2} = rP_{A2}$. According to the repeating structures of A1-MNP and A2-MNP polymers,

$$v_1 = 11 \times [(P_{A2,a} \times 2)/3]/([(P_{A2,a} \times 2)/3] + [(P_{A2,b} \times 1)/3]) + 9$$
$$\times [(P_{A2,b} \times 1)/3]/([(P_{A2,a} \times 2)/3] + [(P_{A2,b} \times 1)/3]) v_2 = 11$$

Using material conservation equation,

$$P_B = rP_A, \quad r = aN_A/bN_B \quad (2)$$

when $a = 3$, $b = 2$, and $r = 1$, eq. (1) can be written as

$$P_{A1} = \left(\frac{3}{2\pi v l^2}\right)^{3/2} \frac{V \sum_{n=1}^{\infty} 2P^{2n}_{A2} \times n^{-5/2}}{6N_A} \quad (3)$$

when P_{A2} is known, $\sum_{n=1}^{\infty} 2P^{2n}_{A2} \times n^{-5/2}$ can be found in Truesdell function table.[41]

Let $P_{A1(1)}$ and l_1 be intramolecular cyclization degree and effective chain length for the A1-MNP polymer, $P_{A1(2)}$ and l_2 be intramolecular cyclization degree and effective chain length for the A2-MNP polymer, we have

$$\frac{P_{A1(1)}}{P_{A1(2)}} = \frac{\left(\frac{3}{2\pi v_1 l_1^2}\right)^{3/2}}{\left(\frac{3}{2\pi v_2 l_2^2}\right)^{3/2}} \times \frac{V_1/N_{A1}}{V_2/N_{A2}} \quad (4)$$

where $l_1 = 2.37 l_2$.

So the effective chain length of A1-MNP is longer than that of A2-MNP. This means that the former system forms a looser three-dimensional network structure. Comparing the active hydrogen peaks in ^{1}H-NMR spectra of two kinds of polymers, it can be found that the A1-MNP polymer contained more —NOH structures than the A2-MNP polymer, indicating that there is a greater obstruction to the coupling reaction in the former. This is also a proof for large difference in the arrangement of polymeric segments between the two polymers. The larger gelation point of A2-MNP system ($P_c = 0.77$) than the A1-MNP system ($P_c = 0.71$) means that probability of cyclization reaction in the A_3/B_2 system is larger than the A_2A'/B_2 system. It is understandable that the three $OCO–CH(CH_3)Br$ groups of the A_3/B_2 system form three pairs of ABA cyclization reactions (here the two A groups come from the same A_3 monomer), whereas in A_2A'/B_2 system, because the reactivity of two A groups ($OCO–CH(CH_3)Br$) is significantly higher than the A' group ($NHCO–CH(CH_3)Br$), there is only one pair of ABA cyclization reaction. This difference can lead to much lower probability of intramolecular reaction in the A_2A'/B_2 system. The high rate of cyclization reaction in A_3/B_2 system postponed the gelation and make the polymer coil more compact. In summary, it is possible to adjust the chain structure of RACP-based hyperbranched polymer by changing the reactivity of the three A groups of the A_3 monomer.

CONCLUSIONS

Two tribromides with functonal groups of unequal activity (A_2A') and equal activity (A_3) were synthesized. They reacted with MNP to form hyperbranched polymers through a radical addition-coupling polymerization (RACP) mechanism. Polymerization degrees of the polymers all gradually increased with time, which is in line with a step-growth polymerization mechanism. The gelation point was found to be in accordance with the value predicted by a A_3B_2 polycondensation model, rather than a $A_3B(B')$ model. P_c for the A2-MNP (A_3/B_2) system is larger than that of the A1-MNP (A_2A'/B_2) system, meaning that the latter system has lower probability of intramolecular cyclization.

In summary, this article reports a novel method of synthesizing hyperbranched polymers by radical addition-coupling polymerization. By changing the reactivity of the three functional

groups of the A$_3$ monomer, it is possible to adjust the chain structure of hyperbranched polymers, especially the effective chain length between the branch points.

REFERENCES

1. Voit, B. I.; Lederer, A. *Chem. Rev.* **2009**, *109*, 5924.

2. Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083.

3. Stochmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45.

4. Min, K.; Gao, H. F. *J. Am. Chem. Soc.* **2012**, *134*, 15680.

5. Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763.

6. Fréchet, J. M. J.; Hemmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *259*, 1080.

7. Muller, A. H. E.; Simon, P. F. W.; Radke, W. *Abstr. Am. Chem. Soc.* **1997**, *214*, 254-PMSE.

8. Curran, D. P. *Synthesis-Stuttgart* **1988**, *1988*, 489.

9. Bamford, C. H. In Comprehensive Polymer Science; Eastmond, G. C.; Ledwith, A.; Russo, S.; Sigwalt, P., Eds.; Pergamon: London, **1989**; p 127.

10. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.

11. Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.

12. Otazaghine, B.; David, G.; Boutevin, B.; Robin, J. J.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2004**, *205*, 154.

13. Sarbu, T.; Lin, K. Y.; Ell, J.; Siegwart, D. J.; Spanswick, J.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 3120.

14. Fu, Q.; Zhang, Z. N.; Lin, W. C.; Huang, J. L. *Macromolecules* **2009**, *42*, 4381.

15. Kulis, J.; Bell, C. A.; Micallef, A. S.; Monteiro, M. J. *Aust. J. Chem.* **2010**, *63*, 1227.

16. Fu, Q.; Zhang, Z. N.; Lin, W. C.; Huang, J. L. *Macromolecules* **2009**, *42*, 4381.

17. Wang, G.; Zhang, Y.; Huang, J. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 1633.

18. Li, Y. G.; Zhang, Y. Q.; Zhai, S. J.; Deng, Y.; Xiong, H. M.; Lu, G. L.; Huang, X. Y. *J. Polym. Sci. Polym. Chem.* **2011**, *49*, 23.

19. Kulis, J.; Bell, C. A.; Micallef, A. S.; Jia, Z. F.; Monteiro, M. J. *Macromolecules* **2009**, *42*, 8218.

20. Debuigne, A.; Jerome, C.; Detrembleur, C. *Angew. Chem. Int. Edit.* **2009**, *48*, 1422.

21. Debuigne, A.; Poli, R.; De Winter, J.; Laurent, P.; Gerbaux, P.; Wathelet, J. P.; Jerome, C.; Detrembleur, C. *Macromolecules* **2010**, *43*, 2801.

22. Debuigne, A.; Poli, R.; De Winter, J.; Laurent, P.; Gerbaux, P.; Dubois, P.; Wathelet, J. P.; Jerome, C.; Detrembleur, C. *Chem. Eur. J.* **2010**, *16*, 1799.

23. Wong, E. H. H.; Junkers, T.; Barner-Kowollik, C. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 7273.

24. Wong, E. H. H.; Stenzel, M. H.; Junkers, T. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2118.

25. Zhang, C. Y.; Wang, Q. *J. Polym. Sci. Polym. Chem.* **2011**, *49*, 612.

26. Zhang, C. Y.; Wang, Q. *Macromol. Rapid Commun.* **2011**, *32*, 1180.

27. Zhang, C.; Ling, J.; Wang, Q. *Macromolecules* **2011**, *44*, 8739.

28. Stowell, J. C. *J. Org. Chem.* **1971**, *6*, 3055.

29. Stefan, A. F. B.; Grégory, C.; Anton, L. G. *Macromolecules* **1999**, *32*, 8269.

30. Drockenmuller, E.; Catala, J. M. *Macromolecules* **2002**, *35*, 2461.

31. Hoffmann, A. K.; Henderson, A. T. *J. Am. Chem. Soc.* **1961**, *83*, 4671.

32. Li, L.; Hamer, G. K.; Georges, M. K. *Macromolecules* **2006**, *39*, 9201.

33. Liu, Y. B.; Fan, Z. Q. *J. Polym. Sci. Part A: Polym. Chem.* **2015**, DOI: 10.1002/pola.27518.

34. Liu, Y. B.; Fan, Z. Q. *Des. Monomers Polym.* **2015**, DOI: 10.1080/15685551.2014.999465.

35. Doba, T.; Ichikawa, T.; Yoshida, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3158.

36. Schmid, P.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 6434.

37. Brandrup, J.; Immergut, E. H.; Grulke, E. A. Polymer Handbook, 4th ed.; John Wiley & Sons: New York, **1999**.

38. Flory, P. J. Principles of Polymer Chemistry, Cornell Univ. Press: Ithaca, NY, **1953**; p 354.

39. Price, F. P. *J. Phys. Chem.* **1958**, *62*, 977.

40. Zheng, F. A.; Liu, F. Q.; Zhao, D. H.; Tang, X. J. *Chem. J. Chin. Univ.* **1986**, *7*, 372.

41. Truesdell, C. *Ann. Math.* **1945**, *46*, 144.