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"A_2 + CB_n" Approach to Hyperbranched Polymers with Alternating Ureido and Urethano Units

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ABSTRACT: Various hyperbranched polymers with alternating ureido and urethano units in their backbones were synthesized by direct polycondensation of diisocyanates (A_2-type monomers) with compounds containing one amino group and multihydroxyl groups (CB_n-type monomers). Because of the commercial availability of the monomers and the simplicity of the synthesis process, hyperbranched poly(urea−urethane) materials can be large scale accessed. The reaction between an A group and a C group is much faster than that between an A group and a B group, resulting in the formation of AB_n-type intermediates in the initial stage of the reaction. Further self-polycondensation of the intermediates gives hyperbranched macromolecules. The influence of reaction conditions such as temperature and concentration on the polymerization was discussed in detail.

Introduction

Hyperbranched polymers are being paid more and more attention due to their unique features such as three-dimensional architecture, low melting viscosity, good solubility, and large amount of terminal functional groups.[1] This kind of material may be potentially used as coating additives,[2] drug and gene deliveries,[3] electroactive and photochemical molecular devices,[1c] conductive materials,[4] "building blocks" of functional materials,[5] and so forth. It is easier to obtain a hyperbranched polymer than to synthesize its analogue, dendrimer, since the former can be prepared by one-step polycondensation of AB_2-type monomers.[6] However, most of the AB_2 monomers are unavailable commercially and have to be synthesized by the researchers. Therefore, only a few hyperbranched polymeric materials are available in a large scale with relatively low cost. To meet the challenge, it is necessary to develop novel approaches to hyperbranched polymers. Recently, Kakimoto,[7] Fréchet,[8] and Okamoto[9] et al. independently developed the approach to hyperbranched polymers from commercially available A_2- and B_3-type monomers. However, direct polycondensation of A_2 and B_3 monomers would generally result in gelation.[10] To avoid the problems aforementioned, this work represents a novel strategy to prepare hyperbranched polymers by direct polycondensation of commercially available A_2-type monomers and CB_n-type monomers.

The strategy presented here is based on the principle of nonequal reactivity of different functional groups. Figure 1 schematically describes the model of the strategy if the number of group B in CB_n-type monomer is equal to 3 ($n = 3$). A_2 monomer contains two isocyanato functional groups, and CB_n monomer ($n \geq 2$) contains an amino group (C) and n hydroxyl groups (B). Both C and B can react with A, but the reaction between A and C is much faster than that between A and B. So in the initial stage of polymerization, an A group of A_2 reacts fast with a C group of CB_n, generating predominantly an AB_n-type intermediate. On the other hand, the A group of AB_n may further react with the C group of CB_n to form the $B_nC{-}A_2{-}CB_n$ type species with multi B functional groups. Further polymerization of the compounds formed in situ gives a soluble hyperbranched polymer rather than a gel.

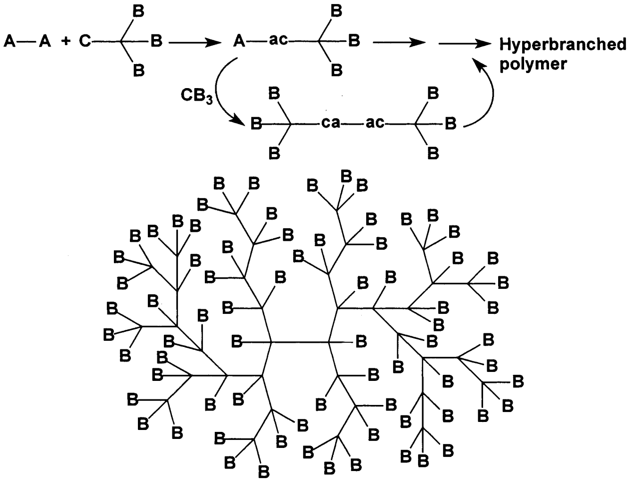

Figure 1. "A_2 + CB_3" approach to hyperbranched polymer.

It is notable that the approach aforementioned is different from the conventional method of polycondensation of AB_2 monomers in the presence of multifunctional core moieties (AB_n + B_n). Compared with the "AB_n + B_n" method published before,[11,12] the "A_2 + CB_n" approach described here shows three characteristics at least: (1) The AB_n and B_n compounds are generated in situ from two or more type monomers which can be commercially available. (2) No clear borderline can be determined between the formation of AB_n and its polymerization. The propagation reaction generally occurs as soon as the formation of an AB_n molecule except it is produced in the given special conditions, so the pure AB_n- or B_n-type compounds formed in situ are hardly separated and then obtained through the route of organic synthesis. (3) The "A_2 + CB_n" approach can be used to design and develop the hyperbranched polymers with new architectures and structures. Via

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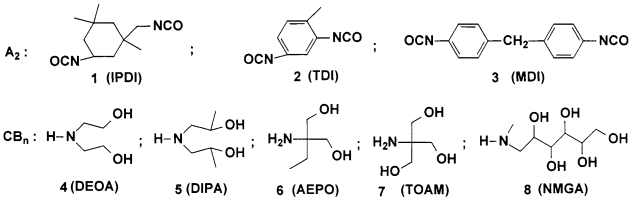
Scheme 1. A$_2$- and CB$_n$-Type Monomers Used in This Paper



this approach, a series of hyperbranched polymers with alternating different units in their frameworks can be easily fabricated. On the contrary, it is very difficult to acquire the hyperbranched polymers with the same structure through the conventional “AB$_2$ + B$_n$” method.

Results and Discussion

As three sorts of very important polymeric materials, line polyurethanes, polyureas, and poly(urea−urethane)s are now widely used in the fields of rubber, plastics, fiber, coating, and so forth. It is well-known that polyurethanes or polyureas can be manufactured from diisocyanates and dihydroxyl compounds or diamines.[13] However, hyperbranched polyurethanes or polyureas cannot be directly synthesized from AB$_2$ monomer with an (or two) isocyanato group ($-N{=}C{=}O$) due to its high reactivity. Several excellent works published first synthesized an AB$_2$ monomer containing a functional group that can be in situ rearranged into the isocyanato group; then further polymerization of the new monomer gives hyperbranched polyurethanes[14] or polyureas.[15] A polymer with alternating ureido and urethano units is very attractive in its application. However, a hyperbranched polymer with alternating ureido and urethano units is very difficult to prepare by a conventional synthesis method. This work aims to obtain the hyperbranched poly(urea−urethane)s and improve their accessibility by direct polymerization of commercially available diisocyanates and multihydroxylamines.

Monomers Selection. Scheme 1 shows the selected monomers in the “A$_2$ + CB$_n$” approach presented. To access the hyperbranched polymers with alternating ureido and urethano units, isocyanato, hydroxyl, and amino groups are selected as A, B, and C groups, respectively. It is known that the nucleophilic reactivity of the amino group is much greater than that of the hydroxyl group.[13b,c] So the intermediate with an isocyanato group and multihydroxyl groups may form in the initial stage of the reaction. Further polymerization of the intermediates would lead to hyperbranched poly(urea−urethane)s without gelation.

FTIR Spectra. FTIR is an efficient technique for the characterization of functional groups of organic molecules.[16] Figure 2 shows the in situ FTIR spectra of the reaction system of IPDI (monomer **1**) and DEOA (monomer **4**). In the initial 40 s, the absorption peak of the isocyanato group at 2261.6 cm^{-1} rapidly decreases, and simultaneously, a new peak assigned to carbonyl groups (C=O) of ureido units (−HN*CO*NH−) appears at 1632 cm^{-1} and significantly increases with the reaction (Figure 2A). Then the peak at 1632 cm^{-1} keeps constant, and the other new peak attributed to carbonyl groups of urethano units (−HN*CO*O−) appears at 1705 cm^{-1} and gradually increases with the decrease of the absorption peak of isocyanato groups, and the absorption band of the isocyanato groups disappears from the spectrum at about 200 h (Figure 2B). These data indicate that one isocyanato group of **1** quickly reacts with the amino group of **4,** leading to the formation of intermediate **9**. Then self-condensation of intermediate **9** results in the branched macromolecules with ureido and urethano units (Scheme 2). The outcome obtained from FTIR spectra is in well agreement with the reaction process predicted.

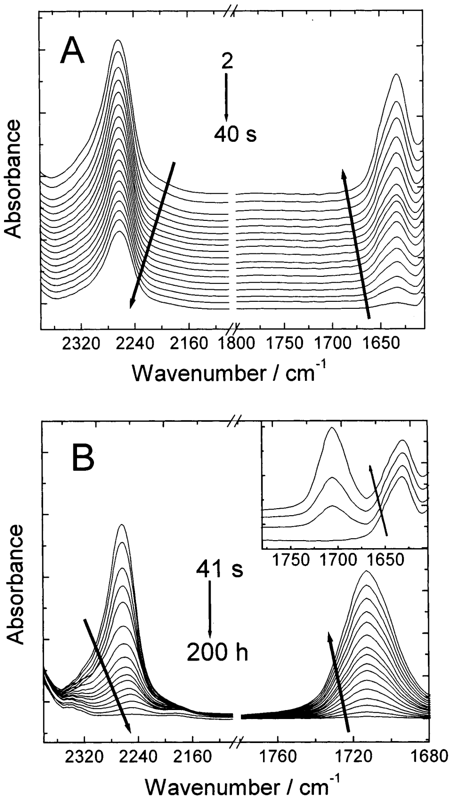
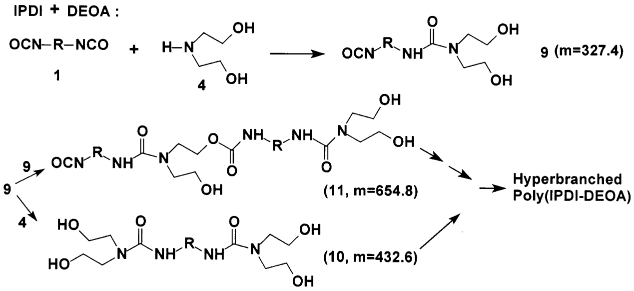


Figure 2. In situ FTIR spectra for the reaction system of IPDI and DEOA with 1/1 feed ratio in chloroform from 2 to 40 s (A) and from 41 s to 200 h (B). The corresponding reaction time of the inserted figure in (B) from bottom to top is 41 s, 10 h, 100 h, and 200 h, respectively.

Scheme 2. Reactions between IPDI and DEOA



Mass Spectrum of Intermediates. In situ FTIR spectra give good evidence of the reaction process. However, the intermediate formed in the initial stage cannot be directly found in the FTIR spectrum. This problem might be solved through the mass spectrum (MS). Figure 3 displays the mass spectrum of the reaction mixture of **1** and **4** at 45 s. The peaks of m/z = 328.3 and 350.3 are assigned to the molecular ion (m + 1) of the AB$_2$-type intermediate **9** (m = 327.4) and AB$_2$ + 23 (m + Na$^+$), respectively. The peak at m/z = 433.4 is attributed to the molecular ion of the multihydroxyl species **10** (B$_2$C−A$_2$−CB$_2$, m = 432.6), and the peak at m/z = 455.4 is attributed to its m + Na$^+$. Species **10**

Table 1. Reaction Conditions and Results of A_2 and CB_n Monomers

code	A_2	CB_n	T/°C[a]	time/h[b]	DB/%	η_{inh}/dL g	T_g	M_w	M_w/M_n
PU-01	IPDI	DEOA	80	100	48.5	0.255	37.1	126 900	6.816
PU-02		DIPA	80	240	45.8	0.188	24.1	28 680	2.550
PU-03		AEPO	60	150	56.5	0.171	41.9	21 970	1.391
PU-04		TOAM	60	120	70.5	0.196	49.3	82 310	3.669
PU-05		NMGA	80	120		0.165	33.4	20 480	1.637
PU-06	TDI	DEOA	60	60	45.5	0.244	42.8	102 800	3.450
PU-07		DIPA	80	120	42.6	0.206	33.5	34 460	3.314
PU-08		AEPO	60	60	43.8	0.178	31.6	19 450	1.749
PU-09		TOAM	60	60	74.2	0.192	48.5	36 780	2.571
PU-10		NMGA	80	100		0.205	39.2	95 850	3.125
PU-11	MDI	DEOA	60	60	48.7	0.236	45.2	60 730	2.675
PU-12		DIPA	80	100	42.5	0.205	34.1	18 250	1.730
PU-13		AEPO	60	60	44.4	0.185	47.9	25 450	1.581
PU-14		TOAM	60	60	71.1	0.198	36.1	55 360	3.158
PU-15		NMGA	80	60		0.212	35.7	130 200	3.320

[a] The reaction temperature during the initial 5−10 h was 0−5 °C. [b] The initial reaction time at low temperature was 5−10 h.

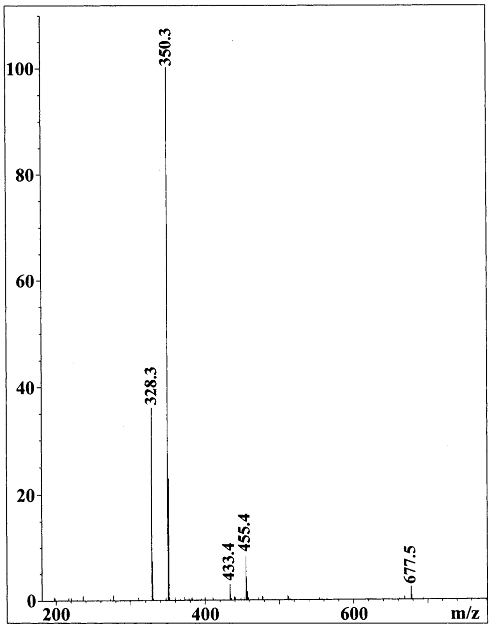


Figure 3. Mass spectrum of the reaction mixture of IPDI and DEOA at initial 45 s.

generated from intermediate **9** and monomer **4** may play the role of “core molecule” in the synthesis of hyperbranched macromolecule, which decreases the possibility of cross-linking,[11] and makes the molecular weight narrower.[12] On the other hand, the existence of AB_n compounds and a small amount of multifunctional moieties may lead to the cyclization in the formation of hyperbranched molecules.[17−19] A detailed investigation is in progress. The molecular ion peak of AB_2’s dimer **11** ($AB_2{-}AB_2$, $m = 654.8$) cannot be effectively detected, and only a small $m + Na^+$ peak is observed at $m/z = 677.5$, which further suggests the reaction between isocyanato and hydroxyl groups is much slower than that between isocyanato and amino groups.

A similar result is obtained from the mass spectrum for the reaction between other A_2 and CB_n monomers at the initial stage.

Polymer Synthesis. Temperature has a great influence on the reaction. The reaction during the initial period must be kept at low temperature (<25 °C); otherwise, gelation would be observed. In our experiments, the temperature in the initial several hours was kept at 0−5 °C. When the feed ratio of A_2 to CB_n monomer is 1/1, the reaction degrees of functional groups were detected by FTIR spectra. Figure 4 describes the reaction degree of the isocyanato group as a function of reaction time at various temperatures (the temperature during the initial 5 h was 0−5 °C). At 60 °C, it only took about 10 h when the reaction degree of the isocyanato group approached 80%, while it took about 120 h at 20 °C. On the other hand, the side reactions such as the reaction between ureido and isocyanato groups will increase with increasing temperature.[13b,c] So the reaction temperature during the second stage was lower than 85 °C.

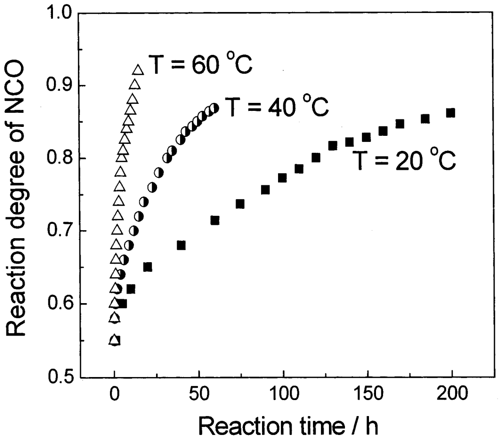


Figure 4. Reaction degree of isocyanato groups as a function of reaction time at various temperatures. The reaction degree of isocyanato groups was determined with FTIR by using carbonyl groups (C=O) of ureido units as internal standard peak.

To test the versatile capability of the strategy presented, monomer **5**, **6**, **7**, or **8**, instead of **4**, is used to react with **1**. Furthermore, any one of the CB_n-type monomers given in Scheme 1 is used to react with monomer **2** or **3** instead of **1**. No cross-linking occurs for all reactions in the given reaction conditions. Significantly, monomer **8** is a kind of chiral glucamine. It is very difficult to obtain a hyperbranched polymer containing similar units by the conventional approaches. The reaction conditions and results are summarized in Table 1. The distribution of molecular weight (DMW) of the resulting hyperbranched poly(urea−urethane)s is general lower than 3.5, and some DMWs are even lower than 2.0. Only one sample’s DMW is relatively high. The possible reasons are being investigated. The resulting poly(urea−urethane)s are well-soluble in the solvents with strong polarity such as DMSO, DMF, DMA, and NMP, while poorly soluble in nonpolar

Table 2. Reaction Conditions and Results of IPDI and DEOA with 3/2 Feed Ratio

code	concn[a]/mol L^{-1}	temp/°C	time/h	gelation
PU-16	0.15	20	1440	no
PU-17	0.15	60	360	no
PU-18	0.30	20	240	yes
PU-19	0.30	40	42	yes
PU-20	0.30	60	10	yes
PU-21	0.30	80	3	yes
PU-22	0.45	60	8	yes
PU-23	0.45	20	180	yes
PU-24	1.0	60	0.15	yes
PU-25	1.0	20	0.5	yes

[a] Mole concentration of IPDI in the mixture solvent of DMSO and DMA.

solvents and those with weak polarity such as tetrahydrofuran (THF), ethyl ether, and acetone.

Because of the commercial availability of raw materials and the simplicity of reaction process, a large amount of hyperbranched poly(urea−urethane) can be easily obtained via the approach presented. The authors successfully synthesized 500−1000 g of hyperbranched poly(urea−urethane) per batch in our laboratory. We think it is not difficult to manufacture this kind of materials on a larger scale without gelation. The improved accessibility of the hyperbranched polymers may open an avenue for the functionalization and application of hyperbranched polymeric materials. A related application work is in progress.

When the feed ratio of A_2 monomer to the CB_n one is equal to 1/1, no gelation was observed in our experiments. If the feed ratio of A_2 monomer to the CB_n one is equal to 3/2, it is not sure whether the cross-linking would occur or not, which depends on the reaction temperature and concentration. Table 2 gives a typical example of the reaction conditions and results when the feed ratio of IPDI to DEOA is 3/2. Gelation would occur within several minutes in the conditions of high concentration (1.0 mol/L) and high temperature (60−80 °C). In contrast, under the conditions of low concentration (0.15 mol/L) and low temperature (20 °C), gelation was not observed even through the reaction had been performed for 60 days (1440 h). The end-capped product was well soluble in polar solvents such as DMSO and DMF. For the reaction between A_2 and B_3, it is very difficult to obtain soluble branched macromolecules when the feed ratio of A_2 to B_3 is equal to 3/2 due to its low critical point of gelation.[7,20] So, the reaction mechanism between A_2 and CB_n is essentially different from that between A_2 and B_3.

The resulting products were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectra. A typical example (poly(IPDI−DEOA)) was illustrated as follows. In the IR spectrum of poly(IPDI−DEOA) with 1/1 or 3/2 feed ratio (Figure 5), the absorption bands at 3600−3200, 1705, and 1632 cm^{-1} are attributed to hydroxyl groups, carbonyl groups of urethano units (NH*CO*O), and carbonyl groups of ureido units (NH*CO*NH), respectively. The peak at 2262 cm^{-1} was not observed in the spectrum of the resulting product with 1/1 feed ratio, which indicated that the isocyanato groups had been reacted completely. In the spectrum of the sample with a 3/2 feed ratio, the peaks of isocyanato and hydroxyl groups were clearly observed. After end-capping, the peak of isocyanato groups vanished from the corresponding spectrum.

Degree of Branching. Fréchet,[21] Müller,[22] and Frey[23] independently defined the degree of branching (DB) of hyperbranched polymers. Considering the molecular weight of the resulting polymer is high, this work calculated DB with Fréchet's[21] equation:

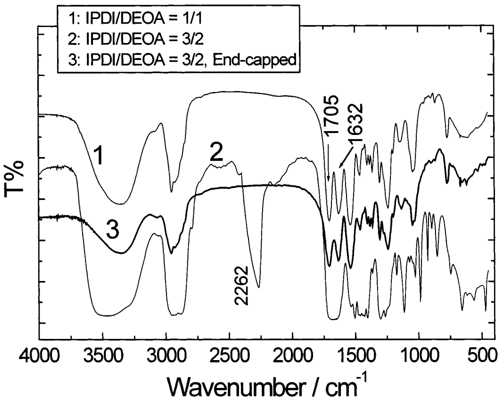


Figure 5. FTIR spectrum of hyperbranched poly(IPDI−DEOA).

$$DB = (N_D + N_T)/(N_D + N_T + N_L) \tag{1}$$

In eq 1, N_D, N_T, and N_L represent the numbers of dendritic or branched units, terminal units, and linear units, respectively. For a hyperbranched polymer made from AB_2 type monomer, $N_D = N_T - 1$. Therefore

$$DB = (N_T - 1 + N_T)/(N_T - 1 + N_T + N_L) = (2N_T - 1)/(2N_T + N_L - 1) \approx 2N_T/(2N_T + N_L) = 1/(1 + N_L/2N_T) \tag{2}$$

For the hyperbranched poly(urea−urethane)s made from A_2 and CB_2 monomers, there are two hydroxyl groups in the terminal units, one hydroxyl group in the linear units, and no hydroxyl group in the branched units. The terminal ((CH$_2$OH)$_2$) and linear (CH$_2$OH) units can be assigned independently in the ^{13}C NMR spectrum. So DB can be calculated with eq 2. Figure 6 displays the ^{13}C NMR spectra of poly(IPDI−AEPO), poly(TDI−AEPO), and poly(MDI−AEPO). DB calculated from the integration of corresponding peaks was summarized in Table 1. The value of DB is higher than 40%.

For the hyperbranched polymers made from A_2 and CB_3, DB was calculated with eq 1. The branched units contain both the units without hydroxyl group and the units with one hydroxyl group, so the DB is higher than that of hyperbranched polymers made from A_2 and CB_2 monomers.

It is not necessary to calculate DB of the poly(urea−urethane)s made from A_2 and CB_5 monomers since the chance that only one hydroxyl group in a unit has been reacted is only a little. Furthermore, DB cannot represent the actual degree of branching of the resulting polymers. Notably, the poly(urea−urethane)s made from A_2 and CB_5 monomers are also highly branched, although the reactivity of primary hydroxyl group is higher than that of secondary hydroxyl group. Figure 7 shows the ^{13}C dept135 NMR spectrum of poly(TDI−NMGA). The ratio of the residual primary hydroxyl group (CH_2OH) in the resulting polymer to the primary hydroxyl group being reacted (CH_2O−) is much greater than 50%. For poly(IPDI−NMGA), similar result with poly(TDI−NMGA) can be observed from the corresponding ^{13}C NMR spectrum (Figure 8). For poly(MDI−NMGA), the residual primary hydroxyl group is lower

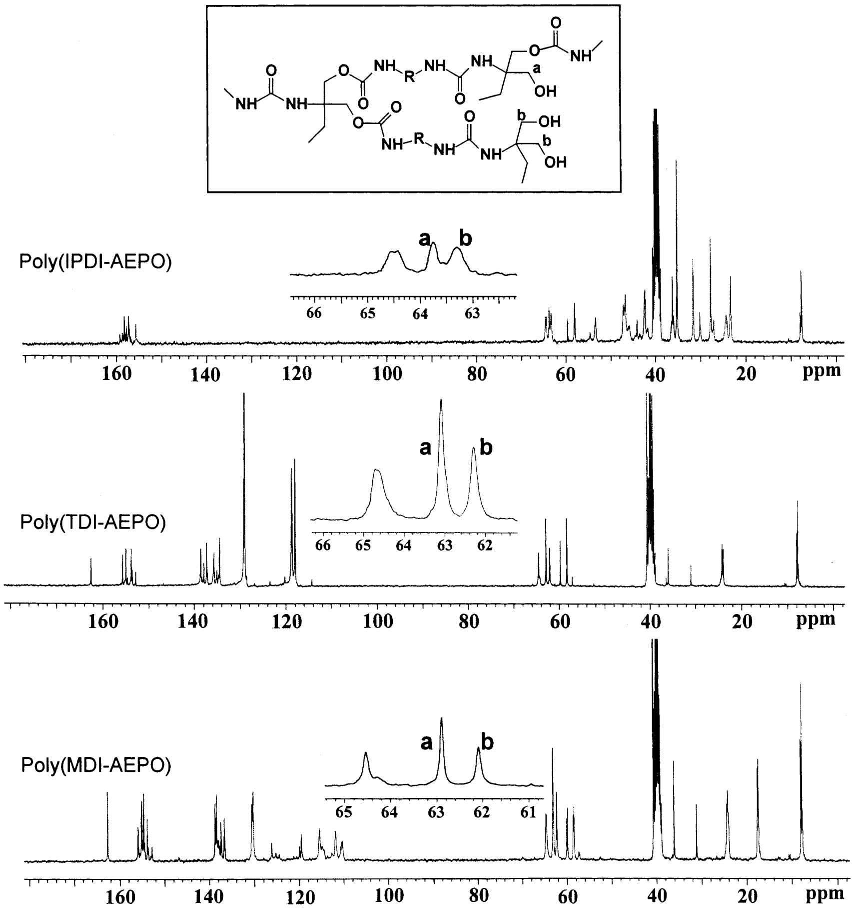


Figure 6. ^{13}C NMR spectra of the resulting hyperbranched poly(IPDI−AEPO), poly(TDI−AEPO), and poly(MDI−AEPO).

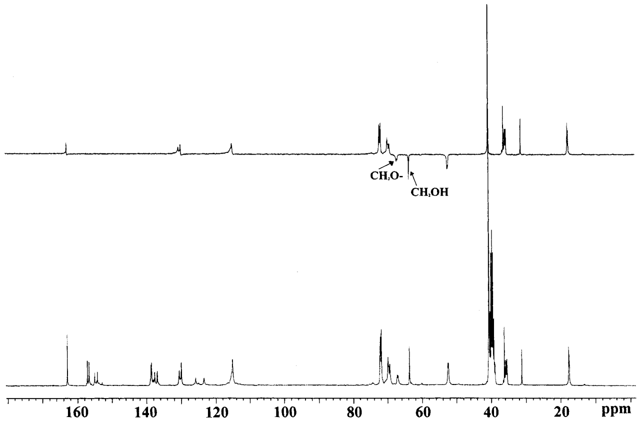


Figure 7. ^{13}C dept135 NMR spectrum of hyperbranched poly(TDI−NMGA).

than that of poly(IPDI−NMGA) or poly(TDI−NMGA) but still higher than the reacted primary hydroxyl group.

Experimental Section

Materials. Isophorone diisocyanate (IPDI), tolylene 2,4-diisocyanate (TDI), 4,4′-methylenebis(phenyl isocyanate) (MDI), diethanolamine (DEOA), diisopropanolamine (DIPA), tris(hydroxymethyl)aminomethane (TOAM), and *N*-methyl-D-glucamine (NMDG) were purchased from Aldrich; 2-amino-2-ethyl-1,3-propanediol (AEPO) was purchased from ACROS. All of the reagents were used as received. The organic solvents such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), and *N*-methyl-2-pyrrolidone (NMP) are purchased from the domestic market and purified by reduced-pressure distillation before use.

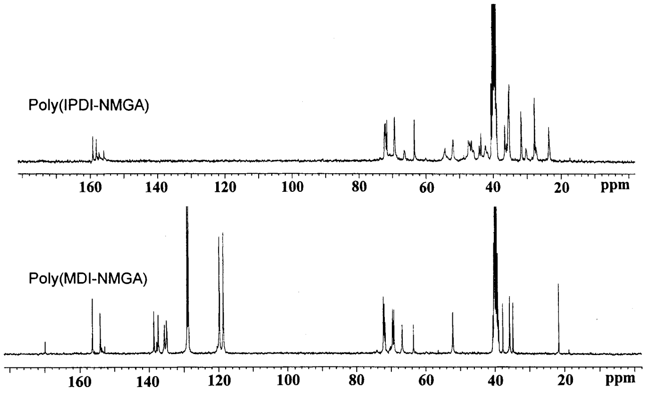


Figure 8. ^{13}C NMR spectra of hyperbranched poly(IPDI−NMGA) and poly(MDI−NMGA).

Characterization. FTIR measurements were performed on a Bruker Equinox 55 spectrometer using Barnes analytical FTIR sealed cell (KBr 0.5 mm). The ^{1}H and ^{13}C NMR studies were conducted on a Bruker 500 MHz NMR spectrometer with DMSO-d_6 as solvent. The inverse-gated spectra were taken when the quantitative analysis of ^{13}C NMR data was done due to the nuclear Overhauser effect. HP 1100 LC/MSD was used to obtain the mass spectrum. The conditions of spray chamber was given as follows: polarity: positive, ionization mode: APCI, fragmentor: 70 v, nebulizer pressure: 60 psig, drying gas flow: 7.0 mL/min, and drying gas temperature: 325 °C. The molecular weight was measured on a GPC with a RI-WAT 150CV+ detector and DMA and 0.05 M LiCl as solvent at 70 °C by using polystyrene as standards. The inherent viscosity (η_{inh}) of the resulting polymer was measured at a concentration of 0.5 g/dL in water at 25 °C.

General Procedure of Polymerization. To a flask placed in an ice−water bath the solution of A_2 and the solution of

CB$_n$ in solvent were added. The mixture was kept at 0−5 °C for 2−10 h and 60−80 °C for 60−150 h and then poured into ethyl ether. The precipitate was collected and dried under vacuum.

Hyperbranched Poly(urea−urethane) Made from A$_2$- and CB$_2$-Type Monomers. Hyperbranched Poly(IPDI−DEOA). To a solution of 10.514 g of DEOA (0.1 mol) in 100 mL of DMA, 22.229 g (0.1 mol) of IPDI in 100 mL of DMA was added with vigorous stirring under nitrogen. The mixture was kept at 0−5 °C for 5 h and 80 °C for 120 h and then poured into ethyl ether. The precipitate was collected and dried under vacuum at 80 °C for 24 h. Yield 27.8 g (85%) of white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1705.9 (NH*CO*O), 1632.4 (NH*CO*NH). ^{1}H NMR (ppm, DMSO-d_6): 7.15, 6.95 (w), 6.3, 5.95, 4.98 (w), 4.9, 4.8 (w), 4.0 (m), 3.75, 3.5, 3.4, 3.3, 2.92, 2.8, 2.55, 1.95 (s), 1.45 (m), 0.9 (vs). ^{13}C NMR (ppm, DMSO-d_6): 170, 159−155 (group), 62.7, 60.63, 60.49, 54.6, 50.7, 50.5, 46.0, 44.3, 42.4, 41.5, 40.6, 37.7, 36.6−34.5, 31.8, 30.2, 27.8, 23.6, 21.6. Calcd for $C_{16}H_{29}N_3O_4$: H, 8.93%; C, 58.69%; N, 12.83%. Found: H, 8.98%; C, 58.61%; N, 12.92%.

Hyperbranched Poly(IPDI−DIPA). Prepared from 22.229 g of IPDI (0.1 mol) and 13.319 g of DIPA (0.1 mol), yielding 28.8 g (81%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1706.1 (NH*CO*O), 1632 (NH*CO*NH). ^{1}H NMR (ppm, DMSO-d_6): 7.05, 6.92, 6.55−6.05 (group), 5.06, 4.75, 3.75, 3.55, 3.18, 2.75, 2.06, 1.5, 1.1, 0.9. ^{13}C NMR (ppm, DMSO-d_6): 158.6, 157.7, 156.5, 155.1, 69.3, 66.2, 66.1, 55.9, 55.8, 46.7, 43.3, 36.4, 35.2, 31.5, 31.4, 30.7, 27.6, 21.2, 18.1. Calcd for $C_{18}H_{33}N_3O_4$: H, 9.36%; C, 60.80%; N, 11.83%. Found: H, 9.42%; C, 60.70; N, 11.88%.

Hyperbranched Poly(IPDI−AEPO). Prepared from 22.229 g of IPDI (0.1 mol) and 11.916 g of AEPO (0.1 mol), yielding 29.7 g (87%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1704.1 (NH*CO*O), 1638 (NH*CO*NH). ^{1}H NMR (ppm, DMSO-d_6): 7.04, 6.95, 6.1−5.42 (group), 5.15, 5.03, 4.01, 3.62, 3.43, 3.02, 2.73, 2.54, 2.08, 1.55, 1.06, 0.9. ^{13}C NMR (ppm, DMSO-d_6): 158.2−155.7 (group), 64.4, 63.7, 63.3, 59.6, 58.0, 54.6, 53.4, 47.2, 46.7, 44.1, 42.3, 41.7, 40.6, 38.9, 36.2, 35.2, 31.7, 30.1, 27.7, 27.0, 24.3, 23.3, 7.9, 7.6. Calcd for $C_{17}H_{21}N_3O_4$: H, 6.39%; C, 61.60%; N, 12.69%. Found: H, 6.44%; C, 61.65%; N, 12.75%.

Hyperbranched Poly(MDI−DEOA). Prepared from 25.026 g of MDI (0.1 mol) and 10.514 g of DEOA (0.1 mol), yielding 29.5 g (83%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1715.4 (NH*CO*O), 1651.8 (NH*CO*NH), 1605.1 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 9.6 (m), 8.53 (m), 8.3 (w), 7.3, 7.05 (vs), 5.25, 5.1 (m), 4.2 (s), 3.8 (s), 3.65 (vs), 3.4 (vs), 2.9, 2.8 (s), 2.1, 2.0 (s). ^{13}C NMR (ppm, DMSO-d_6): 169.6, 155.5 (group), 138 (group), 128, 119 (group), 62.4, 60.3, 60.1, 50.4, 50.3, 39, 37.4, 34.5, 30.7, 21.4. Calcd for $C_{19}H_{21}N_3O_4$: H, 5.96%; C, 64.20%; N, 11.83%. Found: H, 5.91%; C, 64.22%; N, 11.85%.

Hyperbranched Poly(MDI−DIPA). Prepared from 25.026 g of MDI (0.1 mol) and 13.319 g of DIPA (0.1 mol), yielding 30.3 g (79%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1712.1 (NH*CO*O), 1636 (NH*CO*NH), 1602 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 9.6, 8.89−8.52 (group), 8.25, 7.95, 7.34−7.03 (group), 5.39, 5.1, 5.0, 3.9, 3.77, 3.4, 3.28, 2.94, 2.88, 2.78, 2.73, 2.54, 2.50, 1.96, 1.2, 1.06. ^{13}C NMR (ppm, DMSO-d_6): 169.6, 162.3, 156.5−152.5 (group), 138.5−134.6 (group), 128.8, 119.5−118.3 (group), 69.8, 66.2, 65.9, 56.0, 55.7, 52.5, 51.8, 37.4, 34.5, 21.4, 17.9. Calcd for $C_{21}H_{25}N_3O_4$: H, 6.58%; C, 65.76%; N, 10.96%. Found: H, 6.63%; C, 65.80%; N, 10.91%.

Hyperbranched Poly(MDI−AEPO). Prepared from 25.026 g of MDI (0.1 mol) and 11.916 g of AEPO (0.1 mol), yielding 31.4 g (85%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1716 (NH*CO*O), 1645 (NH*CO*NH), 1605 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 9.53, 9.42, 8.6, 8.5, 7.98, 7.33−7.03 (group), 5.85, 5.78, 4.91, 4.82, 4.35, 4.23, 3.78, 3.51, 3.45, 2.85, 2.72, 2.5, 1.8, 1.62, 0.8. ^{13}C NMR (ppm, DMSO-d_6): 162.5, 155.7−152.8 (group), 138.6, 137.9, 137.3, 135.8, 135.1, 134.5, 129.1, 118.6, 117.9, 64.5, 62.9, 62.1, 59.7, 58.3, 39.4, 35.9, 30.9, 24.2, 23.9, 7.9, 7.5. Calcd for $C_{20}H_{23}N_3O_4$: H, 6.28%; C, 65.01%; N, 11.38%. Found: H, 6.35%; C, 65.10%; N, 11.25%.

Hyperbranched Poly(TDI−DEOA). Prepared from 17.416 g of TDI (0.1 mol) and 10.514 g of DEOA (0.1 mol), yielding 22.9 g (82%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1718 (NH*CO*O), 1654.4 (NH*CO*NH), 1601 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 9.57, 8.85, 8.5, 8.23, 8.18, 7.95, 7.48 (group), 7.06 (group), 5.45, 5.2, 5.15, 5.05, 4.2, 3.5, 2.9, 2.76, 2.5, 2.08, 1.75. ^{13}C NMR (ppm, DMSO-d_6): 162.3, 156.5−152.5 (group), 138.5−137.1 (group), 136.4, 136.0, 130.3, 130.1, 129.6, 115.8 (group), 67.1, 62.6, 60.5, 60.4, 60.2, 50.9, 50.4, 46.6, 35.8, 30.8, 25.2, 17.4, 17.2. Calcd for $C_{13}H_{17}N_3O_4$: H, 6.14%; C, 55.89%; N, 15.05%. Found: H, 6.25%; C, 55.98%; N, 14.95%.

Hyperbranched Poly(TDI−DIPA). Prepared from 17.416 g of TDI (0.1 mol) and 13.319 g of DIPA (0.1 mol), yielding 26.1 g (85%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1708 (NH*CO*O), 1652 (NH*CO*NH), 1601 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 9.42, 8.8−8.25 (group), 7.62−6.95 (group), 5.53, 5.38, 5.2, 4.98, 3.91, 3.7, 3.25, 2.92, 2.75, 2.5, 2.06, 1.91, 1.2, 1.06. ^{13}C NMR (ppm, DMSO-d_6): 157.4−153.4 (group), 138.6−136.6 (group), 130.4, 130.1, 129.8, 115.5, 70.2, 66.6, 66.2, 56.3, 56.0, 52.7, 52.0, 39.4, 37.6, 34.6, 21.4, 18.2, 17.7, 17.3. Calcd for $C_{15}H_{21}N_3O_4$: H, 6.89%; C, 58.60%; N, 13.68%. Found: H, 6.95%; C, 58.66%; N, 13.59%.

Hyperbranched Poly(TDI−AEPO). Prepared from 17.416 g of TDI (0.1 mol) and 11.916 g of AEPO (0.1 mol), yielding 23.8 g (81%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1708.4 (NH*CO*O), 1657.1 (NH*CO*NH), 1601 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 9.48, 8.82−8.52 (group), 7.95−6.91 (group), 6.38, 6.25, 5.77, 4.88, 4.21, 3.55, 3.42, 2.86, 2.72, 2.51, 2.08, 1.79, 1.61, 0.85. ^{13}C NMR (ppm, DMSO-d_6): 162.7, 156.0−152.8 (group), 138.7−136.7 (group), 130.6, 126.1, 119.5, 115.3, 111.8, 110.3, 64.7, 63.1, 62.3, 60.0, 59.8, 58.5, 39.4, 36.1, 31.1, 24.2, 17.5, 7.9, 7.7. Calcd for $C_{14}H_{19}N_3O_4$: H, 6.53%; C, 57.31%; N, 14.33%. Found: H, 6.65%; C, 57.35%; N, 14.27%.

Hyperbranched Poly(urea−urethane) Made from A$_2$- and CB$_3$-Type Monomers. **Hyperbranched Poly(IPDI−TOAM).** Prepared from 22.229 g of IPDI (0.1 mol) and 12.114 g of TOAM (0.1 mol), yielding 27.1 g (79%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1703.3 (NH*CO*O), 1647 (NH*CO*NH). ^{1}H NMR (DMSO-d_6): 7.08, 6.95 (w), 6.4, 6.2 (w), 5.85, 5.65 (w), 5.18, 5.03 (m), 4.1 (m), 3.5 (group, s), 2.2 (m), 2.6 (w), 2.5 (vs), 1.47 (m), 0.9 (vs). ^{13}C NMR (ppm, DMSO-d_6): 158 (group), 62.8, 62.6, 62.1, 61.7, 60.7, 59.5, 58.2, 54.7, 53.6, 46 (group), 44.1, 42.6, 41.7, 36.4, 35.2, 31.7, 30.2, 27.8, 27.0, 23.3. Calcd for $C_{16}H_{29}N_3O_5$: H, 8.52%; C, 55.94%; N, 12.24%. Found: H, 8.55%; C 55.88%; N, 12.28%.

Hyperbranched Poly(MDI−TOAM). Prepared from 25.026 g of MDI (0.1 mol) and 12.114 g of TOAM (0.1 mol), yielding 32.7 (88%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1715.8 (NH*CO*O), 1650.4 (NH*CO*NH), 1601.5 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 9.52, 9.48 (w), 8.8, 8.73, 8.5 (w), 7. 35, 7.25, 7.12 (s), 5.95 (m), 4.96 (w), 4.83 (m), 4.4, 4.33 (w), 3.76 (m), 3.62 (w), 3.54 (vs), 3.33 (vs), 2.88, 2.72 (w). ^{13}C NMR (ppm, DMSO-d_6): 162.6, 156.3, 155.6, 153.9, 152.9, 135 (group), 129.1, 118.7, 118.3, 63.2, 61.5, 61.3, 60.9, 59.6, 58.2, 40.4, 38.7, 30.9. Calcd for $C_{19}H_{21}N_3O_5$: H, 5.70%; C, 61.43%; N, 11.32%. Found: H, 5.72%; C, 61.48%; N, 11.28%.

Hyperbranched Poly(TDI−TOAM). Prepared from 17.416 g of MDI (0.1 mol) and 12.114 g of TOAM (0.1 mol), yielding 25.4 g (86%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1715.5 (NH*CO*O), 1650.8 (NH*CO*NH), 1605.1 (Ar). ^{1}H NMR (DMSO-d_6): 9.6, 9.54 (w), 8.78 (m), 7.95−6.95 (group), 6.52, 6.43 (w), 5.95 (w), 4.95, 4.84 (s), 4.3 (s), 3.64, 3.58 (s), 2.9 (s), 2.72 (s), 2.5 (vs), 2.12 (vs). ^{13}C NMR (ppm, DMSO-d_6): 163, 156 (group), 138 (group), 130.8, 121, 115.4, 112.7, 111.5, 63.5, 61.7, 61.4, 61.1, 60.0, 59.9, 40.6, 36.4, 31.3, 17.7. Calcd for $C_{13}H_{17}N_3O_5$: H, 5.81%; C, 52.86%; N, 14.23%. Found: H, 5.88%; C, 52.75%; N, 14.28%.

Hyperbranched Poly(urea−urethane) Made from A$_2$- and CB$_5$-Type Monomers. Hyperbranched Poly(IPDI−NMGA). Prepared from 22.229 g of IPDI (0.1 mol) and 19.521 g of NMGA (0.1 mol), yielding 35.9 g (86%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1708 (NHC*O*O), 1632.4 (NHC*O*NH), 1601 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 7.04, 6.95, 6.13, 5.81, 4.98, 4.66, 4.45, 4.4, 4.31, 4.18, 3.85, 3.65, 3.52, 3.12, 2.78, 2.51, 1.42, 0.9. ^{13}C NMR (ppm, DMSO-d_6): 159.3−153.6 (group), 72.3, 72.1, 71.7, 69.3, 66.5, 63.5, 54.3, 51.9, 47.3−42.3 (group), 36.5, 35.2, 31.7, 30.3, 27.8, 27.3, 23.5. Calcd for $C_{19}H_{35}N_3O_7$: H, 8.45%; C, 54.64%; N, 10.07%. Found: H, 8.41%; C, 54.68%; N, 10.02%.

Hyperbranched Poly(MDI−NMGA). Prepared from 25.026 g of MDI (0.1 mol) and 19.521 g of NMGA (0.1 mol), yielding 37.9 g (85%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1715.3 (NHC*O*O), 1648.8 (NHC*O*NH), 1601 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 9.45 (w), 8.43, 8.37 (w), 7.35, 7.25, 7.06 (s), 5.2 (w), 4.85, 4.6, 4.3, 4.03 (w), 3.75 (m), 3.5 (w), 3.22 (vs), 2.92 (vs), 2.78 (vs), 2.53 (s), 1.95 (vs). ^{13}C NMR (ppm, DMSO-d_6): 169.9, 156.4, 154.1, 138.7, 137.9, 137.4, 135.7, 135.6, 129.0, 128.7, 119.8, 118.6, 72.2, 71.9, 71.7, 69.7, 69.1, 66.8, 63.5, 52.1, 40.5, 37.7, 35.7, 34.7, 21.6. Calcd for $C_{22}H_{27}N_3O_7$: H, 6.11%; C, 59.30%; N, 9.44%. Found: H, 6.15%; C, 59.38%; N, 9.36%.

Hyperbranched Poly(TDI−NMGA). Prepared from 17.416 g of TDI (0.1 mol) and 19.521 g of NMGA (0.1 mol), yielding 31.1 g (84%) of polymer as white powdery solid. IR (cm^{-1}, KBr): 3550−3250 (OH, N−H), 1718 (NHC*O*O), 1650 (NH-C*O*NH), 1601 (Ar). ^{1}H NMR (ppm, DMSO-d_6): 9.48, 8.9, 8.33, 8.01, 7.96, 7.54, 7.43, 7.16, 6.98, 5.45, 5.23, 4.85, 4.61−4.32 (group), 4.03, 3.81−3.48 (group), 2.88, 2.72, 2.05. ^{13}C NMR (ppm, DMSO-d_6): 162.8, 157.1−154.3 (group), 138.7−136.8 (group), 130.6, 129.9, 125.6, 123.5, 115.1, 72.2, 71.9, 70.0, 69.9, 69.7, 67.3, 63.7, 52.6, 52.3, 39.4, 36.2, 35.8, 35.5, 31.2, 17.7, 17.5. Calcd for $C_{16}H_{23}N_3O_7$: H, 6.28%; C, 52.01%; N, 11.38%. Found: H, 6.35%; C, 52.11%; N, 11.30%.

Conclusions

A novel approach for preparation of hyperbranched polymers from commercially available A_2- and CB_n-type monomers is presented in this work. Direct polyaddition of diisocyanates (A_2) to the compounds with one amino group and multihydroxyl groups (CB_n) leads to a series of hyperbranched poly(urea−urethane)s with alternating ureido and urethano units. The analysis of FTIR and MS shows that the AB_n-type intermediates and multihydroxyl molecules generate on line, so no network forms in the polymerization and the molecular weight distribution is relatively narrow. Through this strategy hyperbranched polymers with alternating different units can be easily synthesized. The approach may be used to synthesize other kinds of hyperbranched polymers if other suitable chemicals are selected as A_2- and CB_n-type monomers. The simple technology and the low cost of raw materials would make this approach attractive in the large-scale manufacture of hyperbranched polymeric materials.

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References and Notes

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