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Novel One-Step Synthesis of Random Hyperbranched Polymers from Activated Methylene AB₂ Monomer

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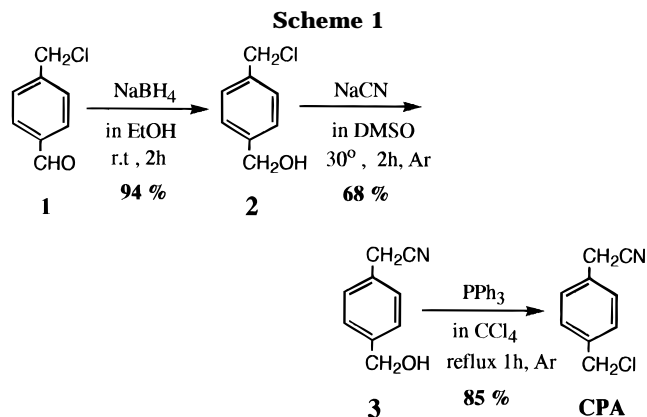
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In recent years, dendrimer architectures with three-dimensional globular shapes and the synthesis of hyperbranched dendritic polymers have attracted the attention of synthetic chemists.¹ Many forms of dendrimers possessing functional surfaces² and functional cores³ were synthesized to give highly controlled macromolecular systems. The synthesis of both dendrimers and hyperbranched polymers usually requires AB_n ($n \geq 2$) type monomers to form branching points, as predicted by Flory 40 years ago.⁴ One of the well-defined structural characteristics of AB₂ patterns may be found in 1,3,5-substituted benzenes. Especially, the successful one-step methods reported recently⁵ in the synthesis of hyperbranched polymers which are obtained from such AB₂ monomers which have A and 2B reactive groups on the benzene ring located at 1,3,5-positions, for examples, 3,5-bis(trimethylsiloxy)benzoyl chloride, 3,5-dihydroxybenzoyl azide, 3,5-dichlorocobonylaniline, 3,5-diaminobenzoyl chloride, etc. However, such AB₂ monomers are not stable to store. Therefore, the selection of chemically stable but reactive AB₂ monomer is of interest and utilizable in the synthesis of hyperbranched dendritic polymers. Our attention in selection of the AB₂ monomer is viewed in the reaction of activated methylene compounds, because the protons on active methylene can be substituted by two alkyl groups using a simple method.⁶ In this paper, *p*-(chloromethyl)phenylacetonitrile (CPA) having reactive groups –CH₂CN and –CH₂Cl at positions 1 and 4 on the benzene ring was synthesized and used as an AB₂ monomer to establish a new one-step route to dendritic polymers.

As shown in Scheme 1, CPA was synthesized from *p*-(chloromethyl)benzaldehyde⁷ via reduction, cyanization, and chlorination processes.⁸ CPA: mp 39–41 °C; IR (cm⁻¹) 2400 for CN; ¹H NMR (250 MHz, in CDCl₃, δ = 0 ppm for TMS) δ 3.7 (s, 2 H, –CH₂CN), 4.6 (s, 2 H, –CH₂Cl), 7.2–7.4 (d & d, 4 H, –C₆H₄–); HR-MS (m/z), obsd 165.0326, calcd 165.0345 for C₉H₉ClN. In general, an activated methylene group (–CH₂CN) is able to react with 2 equiv of halogen compound in an alkali medium with the aid of phase transfer catalysts.⁶ Application of this reaction to polymerize phenylacetonitrile and 1,4-bis(chloromethyl)benzene was reported earlier by Imai et al.⁹ With this in mind, it is apparent that the –CH₂CN group at position 1 and –CH₂Cl at position 4 in CPA



represent B₂ and A in an AB₂ monomer. Thus, a one-step synthesis of hyperbranched polymer from CPA was attempted by using a mixture containing DMSO (or other solvents) and 40% NaOH aqueous solution at ambient temperature. It was found that the reaction of CPA in toluene or chlorobenzene led to precipitation within 1–2 min after adding NaOH solution in the presence of tetra-*n*-butylammonium chloride (TBAC). The precipitates were insoluble in organic solvents. The polymerization of CPA in DMSO also resulted in gelation in the presence of TBAC catalyst when the concentration of CPA was higher (0.072 mol/L in DMSO). In order to overcome the gelation, the polymerization of CPA was performed without catalyst at lower monomer concentrations using smaller amounts of NaOH and shorter reaction times. For example, a mixture containing 0.06 g (0.36 mmol) of CPA dissolved in 20 mL of DMSO and 1 mL of 40% NaOH was stirred at 30 °C for 30 min followed by pouring the mixture into 5% HCl solution to precipitate the polymer. The isolated yield of polymer D-1 (Scheme 2) was 98%. This polymer is orange having the number average molecular weight 2400 with polydispersity of 1.9. But the branching degree could not be determined from the proton NMR spectrum, because the protons due to methylene and methyne resonated as a very broadened singlet within 2.9–3.4 ppm without separating¹⁰ (in the AB₂ systems like 1,3,5-substituted benzenes, the degree of branching determined by proton NMR is usually about 60%^{5a,5d}). Alkali medium also influenced the polymerization of CPA. In NaOH (40% aqueous) medium, the polymerization took place without gelation at the lower monomer concentrations. With KOH(aq) in place of NaOH(aq), however, a polymer bearing carboxylic acid (15 mol % from proton NMR) was produced, indicating that the hydrolysis of cyanide took place in the presence of 40% KOH. Remembering the fact that the CPA is gelled easily in the polymerization reaction and that only half of group B (in our system, B is the activated H) reacts with group A and the other half remains, we examined an analogous copolymerization using AB₂ monomer CPA and chloromethylated aromatics. The selected chloromethyl compounds were benzyl chloride (BC), 4-methoxybenzyl chloride (MC), (chloromethyl)styrene (CS),

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Scheme 2

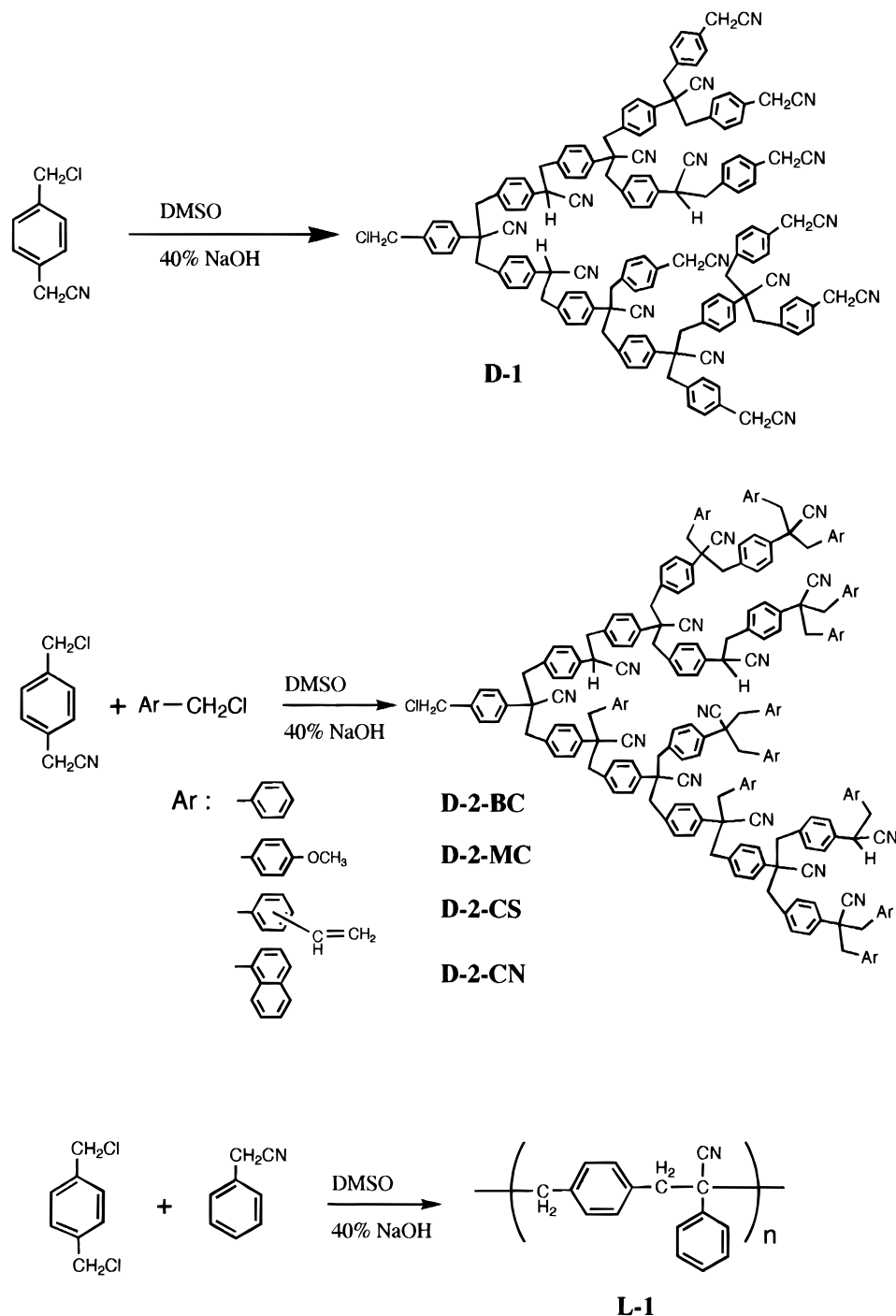


Table 1. Polymers Prepared from the Activated Methylene Monomer

run	reacn conditions ^a			polymers					solubility ^b in			
	monomer (mmol)	40% NaOH (mL)	DMSO (mL)	product	yield (%)	10 ⁻³ M _n	10 ⁻³ M _w	M _w /M _n	DMSO	DMF	CHCl ₃	THF
1	CPA/0.36	1.0	20	D-1	98	2.4 ^c	4.6	1.9	O	O	X	X
2	CPA/BC/0.36	1.0	20	D-2-BC	85	2.7	7.3	2.7	O	O	O	O
3	CPA/MC/0.36	1.0	20	D-2-MC	50	4.2	12.4	2.9	O	O	O	O
4	CPA/CS/0.36	1.0	20	D-2-CS	56	2.6	8.9	3.4	O	O	O	O
5	CPA/CN/0.36	1.0	20	D-2-CN	53	3.6	12.7	3.5	O	O	O	O
6	PAN/BB/0.36	1.0	20	L-1	100				O	O	X	X

^a Reaction was carried out at 30 °C for 30 min. ^b "O" and "X" show soluble and insoluble, respectively. ^c DMF used as a carrier solvent.

1-(chloromethyl)naphthalene (CN), as illustrated in Scheme 2. Stirring the mixture containing CPA (0.36 mmol) and arylmethylenes (0.36 mmol) at the above reaction conditions afforded the corresponding

"copolymers" (D-2 series) in good yields (see Table 1). The number average molecular weights of these copolymers were determined by GPC using THF as a carrier solvent. These molecular weights ranged from 2600 to

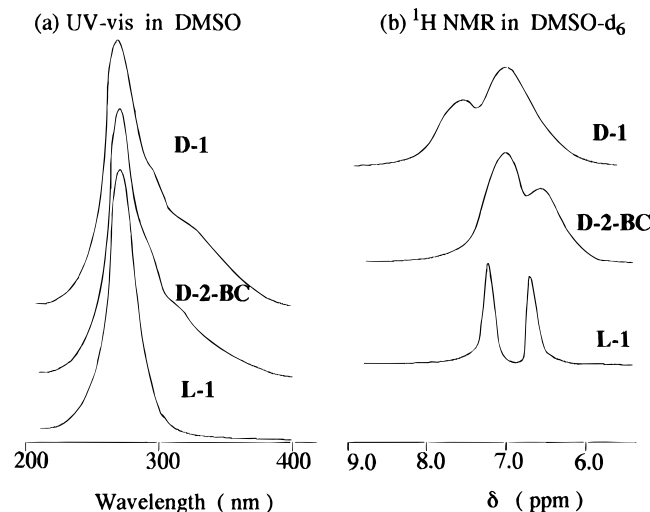
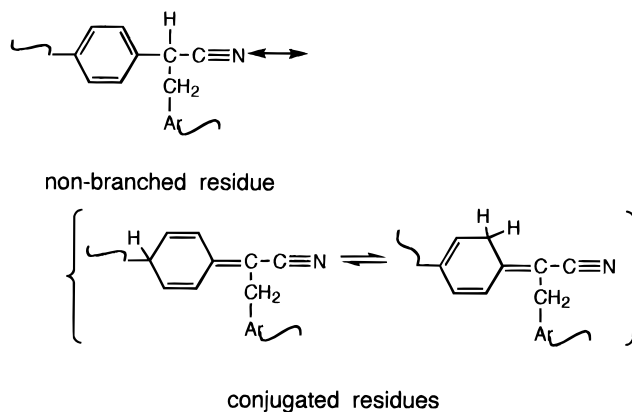


Figure 1. (a) UV-vis spectra of polymers in DMSO with 0.001 g/mL concentration. (b) ¹H NMR (250 MHz, in DMSO-*d*₆) profiles of polymers.

4200 relative to the standard polystyrene (see Table 1) with polydispersities of 2.7–3.5. The ¹H NMR spectra confirmed that the residues of benzene, methoxybenzene, styrene, and naphthalene components were introduced over 35% in the copolymers. It is apparent that addition of chloromethylated aromatics to the reaction of AB₂ monomer of CPA does not prevent the polymerization. As a control experiment, a linear polymer L-1, shown in Scheme 2, was also prepared from phenylacetonitrile (PAN) and 1,4-bis(chloromethyl)benzene (BB) under the same conditions as described above. Different properties were observed for each of the three polymers; nonlinear D-1, D-2s, and linear L-1 (see Table 1 and Figure 1). Polymer D-1 is soluble in DMSO and DMF but insoluble in both CHCl₃ and THF, and the solution was orange in color. The solubility of the linear polymer L-1 is the same as D-1 but exhibits no color in the solution. The copolymers D-2 are soluble not only in DMSO and DMF but also in CHCl₃ and THF. With respect to the copolymer D-2-BC, almost all of the activated protons were converted on the basis of the integration ratio of aromatic protons (Ar-H) to methyl protons (CH₂Ar) on this polymer (obsd ratio 2.35, calcd ratio 2.25 for the [CH₂PhC(CN)CH₂Ph] unit). Thus, it would be concluded that the property of the polymer from CPA can be improved with addition of A' type monomer (chloromethylated aromatics). More importantly, the functional nonlinear polymers (such as D-2-CS, which is a macrostyrene) can be prepared from the copolymerization. In the absorption spectra, interestingly, the polymer D-1 showed a wide band (with a shoulder band) from 250 to 370 nm with λ_{max} = 266 nm in DMSO, but the linear polymer L-1 appeared with a sharp shape (250–305 nm, λ_{max} = 265 nm). In spite of a reduced shoulder, the pattern of the absorption band (λ_{max} = 266 nm) for polymer D-2-BC is similar to that of D-1. Although there is no quantitative data for the degree of branching, it can be deduced from the statistic probability of the reaction that the branching degree of the copolymer D-2s must be lower than that of D-1, because A' type monomer will terminate the activated site. It seems that the wider absorption band of D-1 may be related to the nonbranched residues, because these residues, which are methyne units, may be transformed into isomeric conjugated structures, as shown in Scheme 3. From the results of the solubilities

Scheme 3



of the polymers, it would be considered that the apparent branching degree (including true and pseudo-branching) for D-2 copolymers may be higher than that of D-1, since the residual activated protons in D-1 were substituted by the arylmethylene unit (which are pseudo-branching) in the case of copolymers D-2. This may be the reason that the D-2 copolymers are easily soluble in organic solvents. In the ¹H NMR spectrum of the linear polymer L-1, the protons of aromatic rings resonated with two sharp separated peaks at 6.68 (–C₆H₄–) and 7.22 (–C₆H₅) ppm, which is in agreement with the literature.⁹ However, significantly broadened peaks due to the aromatic rings appeared in the spectra of the polymers D-1 and D-2-BC (see Figure 1B). We also found that the protons due to methoxy (3.5–3.8 ppm, singlet) on D-2-MB and vinyl (5.0–5.3 and 5.4–5.8 ppm, singlet and singlet) on D-2-CS also appeared as very broadened peaks and that the top of the chemical shift (3.65 ppm) of methoxy on D-2-MB resonated upfield (Δδ = –0.15 ppm) relative to the chemical shift (3.80 ppm) of methoxybenzyl chloride. These individual phenomena appeared in the polymers D-1, and D-2s might be also contributed to the branching effect which stacks the aromatic rings in the dendritic structure so that the rotation of the aryl rings becomes slow on the NMR time scale.

In conclusion, we succeeded in demonstrating a one-step synthesis of new dendritic polymers based on AB₂ monomer possessing activated methylene and chloromethylated aromatic components. In our system, the branch juncture for CPA monomer is the activated methylene carbon where two protons will be substituted by two alkyl groups, leading to branched arrays with a benzene ring as a spacer. Additionally, these dendritic polymers have functional cyanide groups in both the inner and outer domain of the dendritic architecture. These groups can allow other functional groups to be introduced with copolymerization strategies. Further polymerizations and property studies concerning dendritic polymers obtained from these activated methylene group AB₂ monomers are in progress.

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