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Dendritic Macroinitiator for the Ring-Opening Polymerization of γ-Benzyl L-Glutamate N-Carboxyanhydride

You Liang ZHAO, Chuan Fu CHEN, Fu XI*

State Key Laboratory of Polymer Physics and Chemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

Abstract: By using OH-terminated polyarylether dendrimer and N-Fmoc-glycine as raw materials, the dendritic polyarylether 2-aminoacetate (G3-NH_2) was synthesized *via* two step reactions. G3-NH_2 as a macroinitiator for the ring-opening polymerization of γ-benzyl L-glutamate N-carboxyanhydride was investigated. It is found that the resulting copolymers possessed relatively high molecular weight and narrow molecular weight distribution ($1.12< M_w/M_n<1.28$).

Keywords: Dendrimer, macroinitiator, ring-opening polymerization, polypeptide.

Much effort has been dedicated to the molecular design and synthesis of model proteins to define protein folding interactions and to develop protein-based materials. Among them, the ring-opening polymerization of α-amino acid-N-carboxyanhydrides (NCAs) has drawn much attention because the resulting artificial polypeptides have wide applications in biotechnology, biomineralization and diagnostics[1, 2].

It is well known that dendrimers are hyperbranched macromolecules possessing a very high concentration of surface groups. So far, a variety of dendrimers have been developed by introducing functionalities into these terminal groups. For instance, PAMAM dendrimers modified with oligo-L-glutamate display greatly enhanced helicity due to the assembling effect of peptide segments at the dendrimer surface[3].

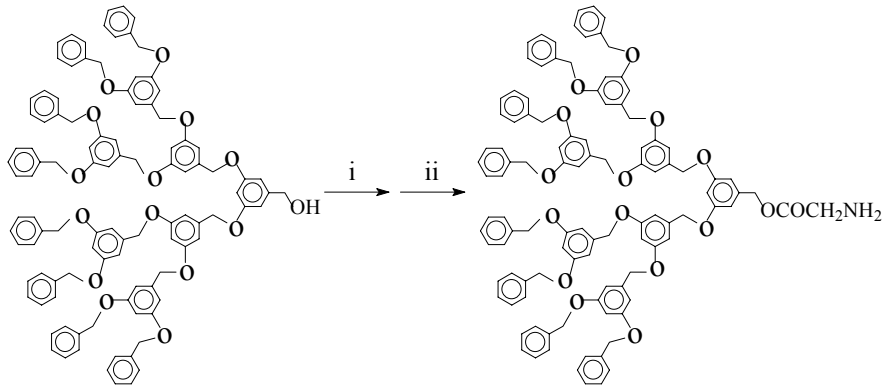
In this letter, the dendritic polyarylether 2-aminoacetate (G3-NH_2) derived from the third-generation Fréchet-type dendrimer (G3-OH) was synthesized by two step reactions. The novel macroinitiator was obtained according to the route as shown in **Scheme 1**.

Ring-opening polymerization of γ-benzyl L-glutamate N-carboxyanhydride (BLG-NCA) with G3-NH_2 as a macroinitiator was carried out at 30°C in a bottle under nitrogen atmosphere. As a comparison, the polymerization was conducted in DMF, dioxane and chloroform, respectively. The block copolymer G3-PBLG was purified by repeated reprecipitations from the reaction solvent into ethanol. The resulting product was a light-yellow or white solid. The DP of the poly(γ-benzyl L-glutamate) (PBLG) block was determined by ^{1}H NMR spectroscopy, using average signal intensity ratios of ArH of Dendron (6.5-6.7 ppm) to methylene protons of PBLG (1.5-3.0 ppm). As shown in **Table 1**, the GPC analysis revealed that the

*E-mail: xifu@infoc3.icas.ac.cn.

copolymer had well-defined molecular weight and narrow molecular distribution ($1.12<M_w/M_n<1.28$). Meanwhile, it is found that the molecular weight determined by NMR was much closer to calculated

Scheme 1



G3-OH **G3-NH_2**

Reagents and conditions: (i) N-Fmoc-glycine, DPTS, DCC, CH_2Cl_2, 30°C, 36 h, 93.2%; (ii) piperidine, DMF, 30°C, 8 h, 89.6%.

value. The result is obviously correspondent to the character of anionic living polymerization.

Table 1 G3-NH_2 as a macroinitiator for the ring-opening polymerization of BLG-NCA at 30°C

Run	solvent	time (days)	yield (%)	M_n(calc.)	DP	M_n(NMR)	M_n(GPC)	M_w/M_n
1	DMF	2	48.6	22940	109	25520	38400	1.19
2	DMF	4	73.5	33840	154	35380	42870	1.28
3	DMF	6	88.3	40330	176	40200	45640	1.12
4	Chloroform	6	80.4	36870	172	39320	45920	1.20
5	Dioxane	6	77.2	35460	160	36690	42250	1.16

Reaction conditions: [M]/[I] = 200.

References and Notes

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2. T. J. Deming, *J. Polym. Sci., Part A: Polym. Chem.*, **2000**, *38*, 3011.
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4. Specrra data of **G3-NH_2**: ^{1}H NMR ($CDCl_3$, δ_{ppm}): 7.27-7.45 (m, 40 H, PhH), 6.57-6.71 (m, 21 H, ArH), 5.03 (s, 16 H, $PhCH_2O$), 4.97 (s, 12 H, $ArCH_2O$), 4.88 (s, 2 H, CH_2), 4.57 (d, 2 H, $ArCH_2O$), 3.50 (m, 2 H, NH_2); IR (NaCl, cm^{-1}): 3325, 3063, 3032, 1722, 1596, 1497, 1450, 1374, 1157, 1051, 833, 737, 697. MS: 1672.81 $[M+Na]^+$. Anal. Calcd for $C_{107}H_{95}NO_{16}$: C 77.85, H 5.80; Found: C 77.84, H 5.82.
5. Spectra data of **G3-PBLG** block copolymer: ^{1}H NMR ($CDCl_3$, δ_{ppm}): 6.9-7.5 (m, PhH), 6.67 (m, ArH), 6.58 (m, ArH), 5.02 (s, $PhCH_2O$), 4.97 (s, $ArCH_2O$), 4.70 (s, CH_2), 4.59 (d, $ArCH_2O$), 3.6-4.5 (m, CH), 2.46 (s, CH_2), 2.27 (s, CH_2); IR (NaCl, cm^{-1}): 3294, 3065, 3035, 2951, 1735, 1656, 1628, 1544, 1452, 1389, 1168, 1083, 828, 748, 699.

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