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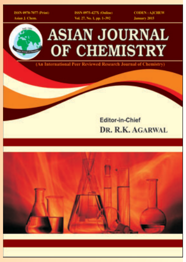

Synthesis of Dendritic Macromolecule with Butane Diamine as Core

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A new 0.5 G dendritic macromolecule is synthesized with butane diamine and ethyl acrylate through Michael addition reaction while a 1 G dendritic macromolecule is synthesized by amidation reaction. The influences of the mole ratio of ester and amine, temperature and time on product are also studied and the optimum conditions are obtained. The products are characterized by IR, GC/MS elemental analyzer and ^{1}H NMR, the relative data testify our expectation.

Keywords: Butane diamine, Dendritic macromolecule, Ethyl acrylate, Synthesis, Characterization.

INTRODUCTION

Dendritic macromolecule is formed by low polymers with repeated unit and it is monodisperse polymer with highly dendrite structure[1-3]. The macromolecule is synthesized generally from the core and grows with repeated units outward. As the increase of generation, the degree of dendritic extends gradually, a closed three-dimensional sphere is presented at last. PAM-AM is synthesized from the core-amine, a macromolecule is constructed through repeated addition reaction. And the surface of molecule has higher density of functional groups. In recent years, further studies on the unique properties on dendritic molecule have attracted much attention[4-6]. It has been reported widely that ethidene diamine or hexane diamine has been adopted as core, methyl acrylate as material to synthesize PAM-AM, while materials of butane diamine and ethyl acrylate are barely reported.

Borrowed the idea of the "divergent synthesis" of PAM-AM[7], new 0.5 and 1 G dendritic macromolecules are synthesized with butane diamine and ethyl acrylate and the suitable conditions are decided.

EXPERIMENTAL

DF-101S thermostat magnetic stirring apparatus; RE-501 rotary evaporator; USA Nicolet FT-IR 750 IR spectrometer. German elemental analyser; Micromass ZQ 4000 mass analyzer (ESI-MS), AVANCE NMR spectrometer.

Butane diamine (analytical grade, Shanghai Ruida fine chemicals limited company); ethyl acrylate (analytical grade, Shenyang Xinxi chemical reagent works); ethyl alcohol (analytical grade, Heilongjiang Acheng chemical reagent works).

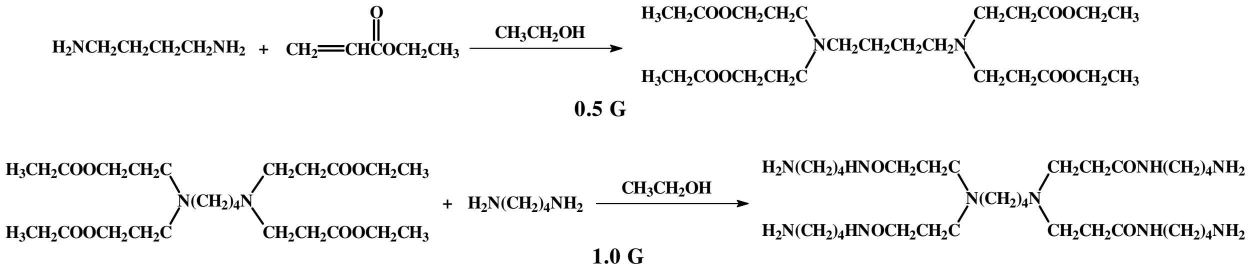
Synthesis of 0.5 G dendritic macromolecule: Amount of butane diamine and ethyl alcohol are added into a 250 mL flask and the reactant is stirred drop by drop with the rate of 1 drop per second for hours. A yellow liquid-0.5 G product is obtained by reduced pressure distillation at the temperature of 70 °C, the pressure of 133Pa, at the same time solvent ethyl alcohol and excessive ethyl acrylate are removed.

Amount of 0.5 G product and moderate ethyl acrylate are added into a 250 mL flask and stirred for 20 min. Ethyl acrylate solution of butanediamine is added drop by drop with the rate of 1 drop per second. A yellow liquid-1G product is obtained by reduced pressure distillation at 70 °C, the pressure of 133Pa and excessive methyl benzene is removed (**Scheme-I**).

RESULTS AND DISCUSSION

Influence of the mole ratio of ester and amine on the productivity: Temperature is controlled at 25 °C, reaction time is 10 h, the influence of the mole ratio of ester and amine on the productivity is shown in Fig. 1. When the ratio is ranging from 4 to 8, the productivity is firstly increasing, then a stable platform emerging. If the ratio is larger than 6, the molecule of product would be wrapped by excess ester. Although the productivity increases, the purity would not increase any more. And therefore the optimum ratio is 6:1. The rate of Michael addition reaction is very fast, there is no need for so much ethyl acrylate. Furthermore, the existence of polar solvent-ethyl alcohol is propitious to the progress of reaction.

At 40 °C, reaction of 16 h, when the amount of butanediamine changes, the productivity is influenced as in Fig. 2. When the mole ratio is in the range from 4:1 to 10:1, the productivity is increasing as the the mole ratio increasing; when



Scheme-I

the mole ratio reaches 8:1, the productivity is 78.6 %; when the mole ratio is higher than 8:1, the productivity remains, therefore the optimum mole ratio is 8:1. The excessive butanediamine would react with the 0.5 G dendritic macromolecule; and it would become the trigger nuclear of another 0.5 G dendritic macromolecule, which would prevent the formation of 1 G dendritic macromolecule.

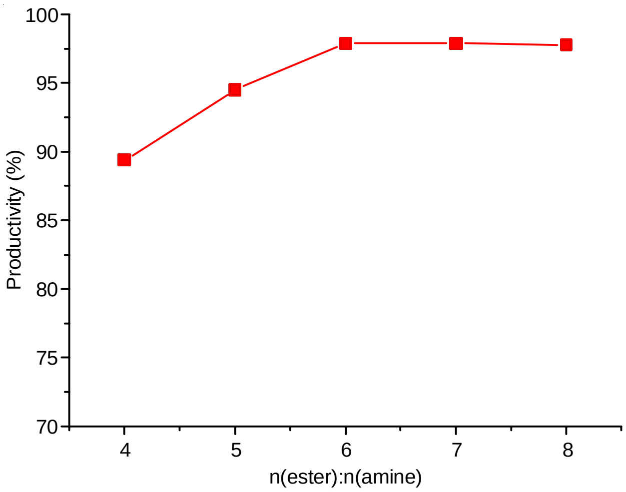


Fig. 1. Influence of the mole ratio of ester and amine on 0.5 G dendritic macromolecule productivity

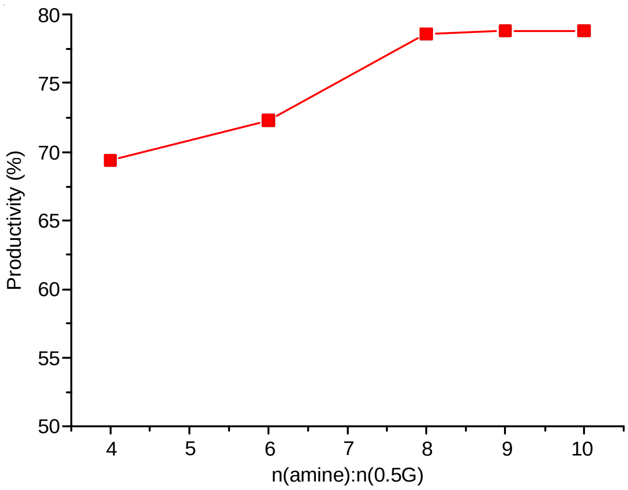


Fig. 2. Influence of the mole ratio of ester and amine on 1 G dendritic macromolecule productivity

Influence of temperature on the productivity: The mole ratio is controlled at 6:1, reaction time is 10 h and the reaction temperature is regulated in the range from 20 to 30 °C. The result in Fig. 3 shows that at the early stage the productivity increases as the temperature increasing. When temperature reaches 30 °C, the color of the product turns light yellow with the productivity of 98.2 %. If temperature exceeds 30 °C, the productivity would decrease, the reason may be the reverse reaction of Michael addition reaction and the oxidation of butane diamine. And the colour of reactants turns darker at the same time. Therefore the optimum temperature is 30 °C.

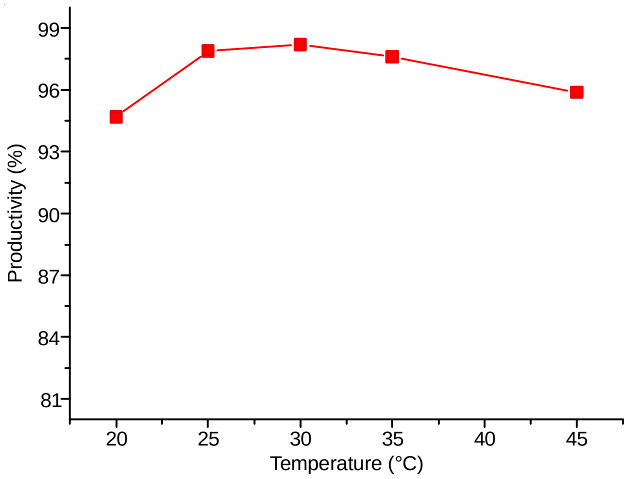


Fig. 3. Influence of temperature on 0.5 G dendritic macromolecule productivity

With the mole ratio of 8:1, reaction of 16 h, when the temperature changes, the productivity is influenced as in Fig. 4. When the mole ratio is in the range from 35 to 45 °C, the productivity is increasing as the temperature increasing; while the increase amplitude is large then small. When the temperature reaches 45 °C, the productivity is the highest but

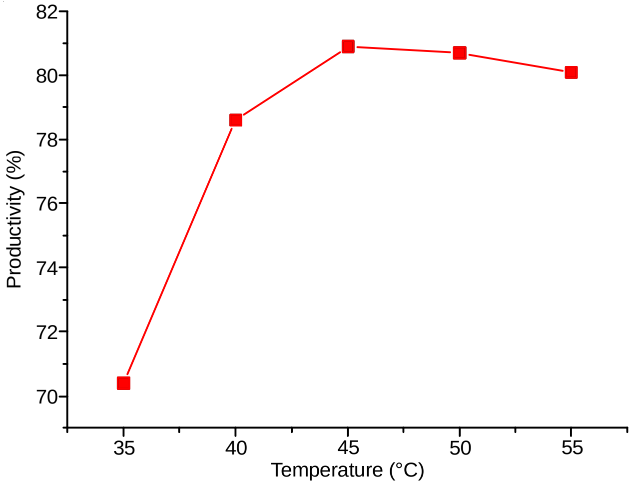


Fig. 4. Influence of temperature on 1 G dendritic macromolecule productivity

when the temperature is in the range from 45 to 55 °C, the productivity decreases. The reason may be that the reaction reacts completely at the temperature of 45 °C, which is higher than the melting point of butane diamine (27-28 °C). However if the temperature is too high, butane diamine would be oxidized and therefore the optimum temperature is 45 °C.

Influence of reaction time on the productivity: The mole ratio is controlled at 6:1, reaction temperature is 30 °C and the reaction time is regulated in the range from 8 to 18 h. The result in Fig. 5 shows that the productivity increases as the reaction time increasing. When the time reaches 12 h, the productivity reaches 98.9 %. When time exceeds 12 h, the productivity remains. The suitable time is optimized as 12 h.

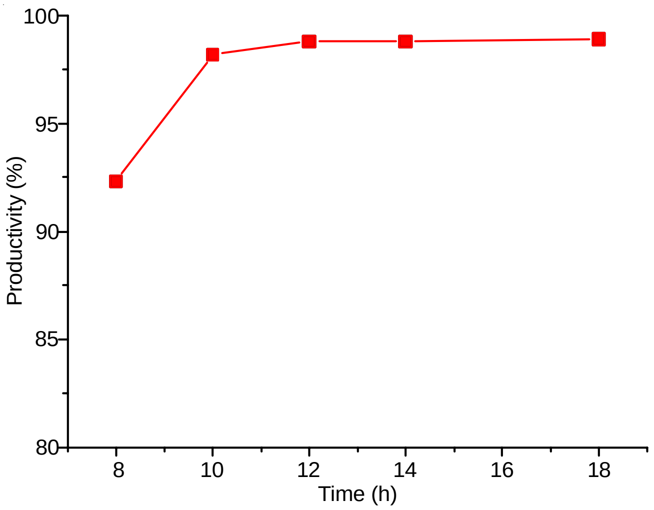


Fig. 5. Influence of reaction time on 0.5 G dendritic macromolecule productivity

With the mole ratio of 8:1, temperature of 45 °C, when the reaction time changes, the productivity is influenced as in Fig. 6. When the reaction time is increasing in the range from 16 to 24 h, the productivity is increasing as the temperature increasing; when the reaction time is increasing in the range from 24 to 32 h, the productivity changes little. Therefore the optimum reaction time is 24 h. Compared with other routine organic reactions, the synthesis of dendritic macromolecule is a long time reaction[8].

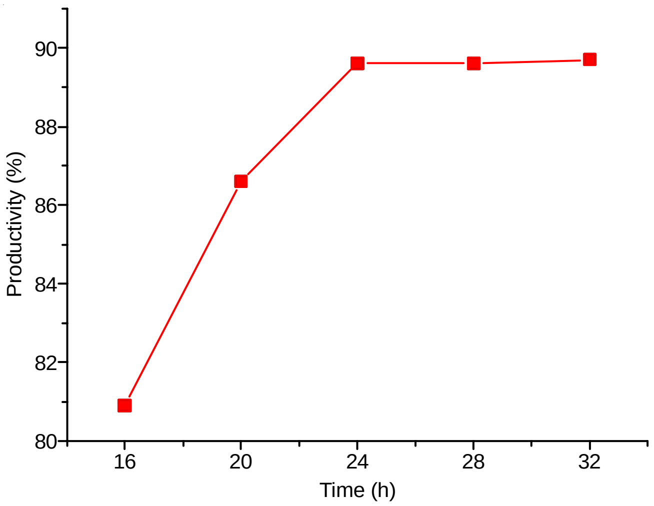


Fig. 6. Influence of temperature on 1 G dendritic macromolecule productivity

Characterization

IR spectrum analysis: The IR spectra of the 0.5 G and 1 G dendritic macromolecules are characterized by USA Nicolet FT-IR 750 Figs. 7 and 8 and the absorption frequency and absorption intensity are attributed in Tables 1 and 2. From the information of Table-1, the strong peaks of 2819, 1465 and 1371 cm^{-1} are attributed to the symmetrical stretch vibration, asymmetric deformation vibration and winding vibration of -CH$_2$-; 1045 cm^{-1} is attributed to the symmetrical stretch vibration of -COO-; 1736 cm^{-1} is attributed to the stretch vibration of -C=O; which testifies the existence of -COO-C. 1355 cm^{-1} is attributed to the weak absorption of N-(R)$_3$, which testifies the bond of N atom and -CH$_2$-.

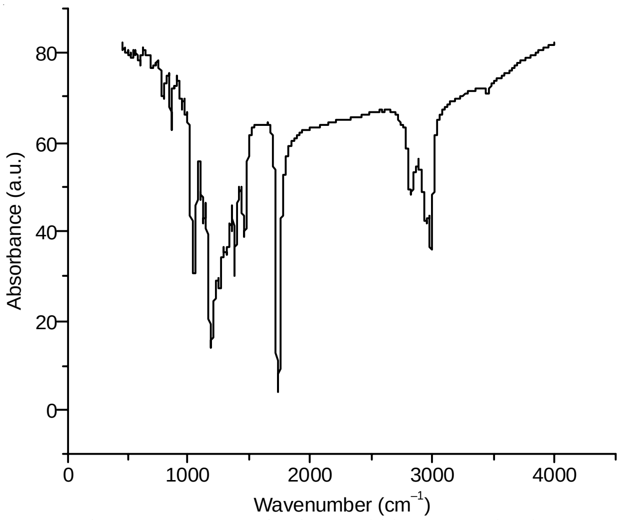


Fig. 7. IR spectrum of 0.5 G dendritic macromolecule

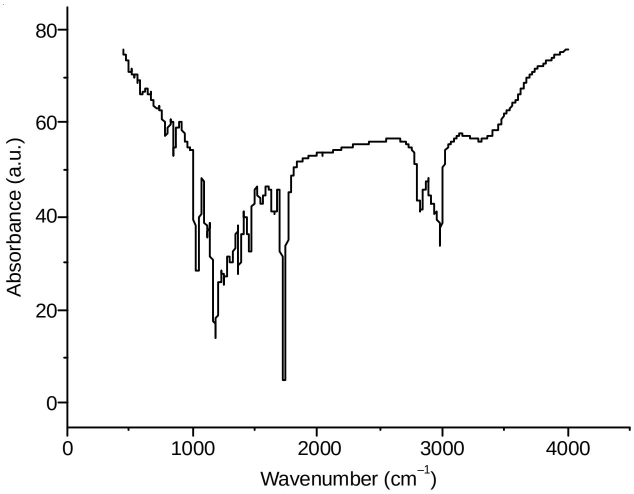


Fig. 8. IR spectrum of 1 G dendritic macromolecule

TABLE-1
IR ANALYSIS OF 0.5 G DENDRITIC MACROMOLECULE

Wave number (cm^{-1})	Functional group	Attribution
2982s	-CH$_3$	Asymmetric stretch vibration
2819s	-CH$_2$-	Symmetrical stretch vibration
1465m	-CH$_2$-	Asymmetric deformation vibration
1371m	-CH$_2$-	Winding vibration
1182w	N-(R)$_3$	Stretch vibration
1045s	-COO-	Symmetrical stretch vibration
1736s	-C=O	Stretch vibration

TABLE-2
IR ANALYSIS OF 1.0 G DENDRITIC MACROMOLECULE

Wave number (cm^{-1})	Functional group	Attribution
2982s	-CH$_2$-	Asymmetric stretch vibration
2828s	-CH$_2$-	Symmetrical stretch vibration
1371m	-CH$_2$-	Asymmetric deformation vibration
1184m	-CH$_2$-	Winding vibration
1042m	C-N	Stretch vibration
1734s	-CONH-	C=O stretch vibration
1465s	-CONH-	N-H deformation vibration
3303w	N-H	Asymmetric stretch vibration

Elemental analysis: The elemental analyses of the 0.5 and 1 G dendritic macromolecules are characterized by a German Heraeus elemental analyzer. The relative data in Table-3 show that there are relative errors of 0.5 G dendritic macromolecule (C = 0.2711 %, H = -0.3326 %, N = -0.6969 %), which may be the existence of excessive ethyl acrylate; there are also relative errors of 1 G dendritic macromolecule (C = 0.3929 %, H = 0.3857 %, N = 1.031 %), which may be because the cavity of macromolecule could accommodate small molecules like excessive butane diamine and ethyl alcohol.

TABLE-3
ELEMENTAL ANALYSIS OF DENDRITIC MACROMOLECULES

Product	C (%)		H (%)		N (%)	
	TV	MV	TV	MV	TV	MV
0.5 G	59.02	59.18	9.02	8.99	5.74	5.70
1.0 G	58.54	58.31	10.37	10.41	21.34	21.56

TV = Theoretical value; MV = Measured value

Mass spectrum analysis: The structure of the 0.5 G dendritic macromolecule is characterized by Micromass ZQ 4000 with ESI technology. From the information in Fig. 9, the maximum abundance appears at the mass to charge ratio (*m/z*) of 488; the relative molecular mass is 488, which is consistent with that of objective molecule. The abundance at *m/z* = 443 (Δm = 45) suggests the destroy of easter. There is characteristic peak of tertiary amine group at *m/z* = 55, the adjacent corresponding peak of Δm = 14 testifies the exaction of the structure. The *m/z* ratio of other impurity is little, that is to say the purity of the product is high. (The molecular mass of 1 G dendritic macromolecule is 656 and fails to be gasified, which could not get MS spectrum)

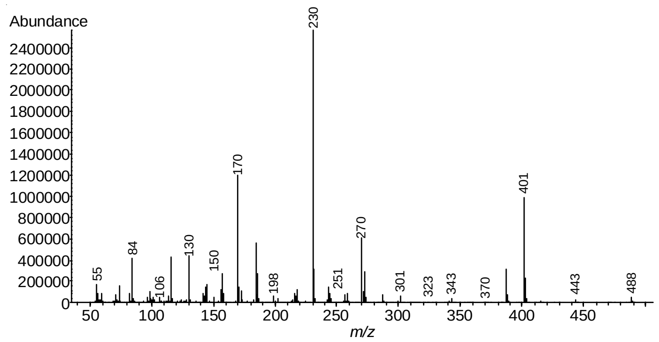


Fig. 9. Mass spectrometric characterization of 0.5 G dendritic macro-molecule

^{1}H NMR analysis: The structure and the purity of the product are characterized by AVANCE NMR spectrometer (CDCl$_3$ as solvent). In ^{1}H NMR spectrum of 0.5 G dedritic macromolecule, there are six groups of peaks, which shows 6 conditions of H atom, δ 1.12-1.26 (4H, H-f), 1.31-1.38 (8H, H-e), 2.33-2.41 (4H, H-d), 2.68-2.76 (8H, H-c), 4.03-4.12 (8H, H-d) 4.18-4.21 (12H, H-a). There is coupling of c-H and d-H, three groups of peaks emerge; the intensity ratio is 1:2:1. All the data show that c-H is near to d-H, there are two c-H and two d-H. There is no fission of d-H and e-H, which shows that there is tertiary amine between d-H and e-H, there is ester group between b-H and c-H. From the calculation of peak area, the 0.5 dendritic macromolecule product has a higher productivity. From the information of 1H NMR spectrum of 1G-dendritic macromolecule, there are six groups of peaks, which fits with the object product. δ 1.97 (8H, H-a, 3.26 (32H, H-b), 2.49 (8H, H-c), 2.76 (8H, H-d), 2.69 (4H, H-e), 2.36 (4H, H-f).

Conclusion

In this paper, a new 0.5 G dendritic macromolecule is synthesized with butane diamine as core, ester as terminal group through Michael addition reaction. The suitable condition is as follows: the mole ratio of ester and amine is 6:1, temperature is controlled at 30 °C, the reaction time is 12 h, with the productivity of 98.8 %, purity higher than 96 %. 1 G dendritic macromolecule is synthesized by amidation reaction. The suitable condition is as follows: the mole ratio of ester and amine is 8:1, temperature is controlled at 45 °C, the reaction time is 24 h, with the productivity of 89.6 %. 0.5 G and 1 G dendritic macromolecules react with ethyl acrylate and butane diamine, higher generation products could be obtained.

The 0.5 G and 1 G dendritic macromolecules are characterized by IR, elemental analyser, ^{1}H NMR and MS and the relative information shows the products are in accordance with our expectation. The purity of 0.5 G dendritic macromolecule is higher than that of 1 G dendritic macromolecule.

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REFERENCES

1. V. Mavrov, I. Dobrevsky, B. Bonev and N. Petkov, *Desalination*, **85**, 335 (1992).
2. J.F.G.A. Jansen, E.W. Meijer and E.M.M. de Brabander-van den Berg, *J. Am. Chem. Soc.*, **117**, 4417 (1995).
3. D.A. Tomalia, M. Herb, H. Brothers and T. Lars, *Polymer Mater. Sci. Eng.*, **73**, 273 (1995).
4. D.A. Tomalia, A.M. Naylor and W.A. Goddard, *Angew. Chem. Int. Ed. Engl.*, **29**, 138 (1990).
5. D.A. Tomalia and H.D. Durst, *Top. Curr. Chem.*, **165**, 193 (1993).
6. O.A. Matthews, A.N. Shipway and J.F. Stoddart, *Prog. Polym. Sci.*, **23**, 1 (1998).
7. D.A. Tomalia, Dense Star Polymers Having Two Dimensional Molecular Diameter, US Patent 4,558,120 (1985).