

Synthesis and Characterization of Novel Dendritic Poly(ester-amine) with Peripheral Hydroxyl

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ABSTRACT: Dendritic poly(ester-amine) with a peripheral hydroxyl [PEA(OH)] was synthesized from dendritic PEA terminated with acrylic double bonds [PEA(=)] and diethanolamine (DEA) by a Michael addition reaction. The effects of the reaction temperature, time, and solvent on the purities of PEA(OH) were studied. It was found that when the mole ratio of PEA(=) to DEA was 1:8 and the reaction was carried out in methanol at 25°C for 22 h, the purity of

PEA(OH) was 94.6%. The structure of PEA(OH) was identified by IR, ¹H-NMR, and elemental analysis. PEA(OH) is a surfactant and its aqueous form exhibits cloud points between the mass concentrations of 0.1 and 50 mass %. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 60–64, 2005

Key words: dendrimers; synthesis; solution properties; surfactants

INTRODUCTION

Dendrimers are a relatively new class of macromolecule. Compared to traditional linear polymers, dendrimers are highly branched, monodisperse, and terminated with multiple functional groups. Their perfect and well-defined structure leads to a number of interesting characteristics and features, including globular, void-containing shapes, low viscosity, and good solubility and compatibility. Therefore, dendrimers have exhibited potential applications in many areas.^{1–3} Hydroxyl-terminated dendrimers have been applied in nanoreactors,⁴ surfactants,⁵ macroinitiators,⁶ enhancement of water solubility,⁷ and further functionalization.⁸ However, dendrimers are usually prepared step by step, using either a divergent or convergent method. These complex synthetic procedures that involve isolating and purifying the products at every step limit large-scale preparation and application.⁹ Recently, Yaowu et al.¹⁰ synthesized a hydroxyl-terminated poly(ester-amine) dendrimer [PEA(OH)] through the Michael addition of diethanolamine (DEA) to an acrylate-terminated dendrimer via a divergent strategy. In each step, only a small excess of reagent was required. One of the raw materials

(acrylate-terminated dendrimer) must be purified by column chromatography and the yields of dendrimers were not over 85%.

In this work, PEA(OH) with high yield and purity is synthesized by a method similar to Yaowu et al.¹⁰ However, the reaction conditions are very mild and the synthetic procedure involves no complicated purification steps, such as column chromatography, which facilitates large-scale production and application. Furthermore, the surfactivity as well as solubility of PEA(OH) in water is studied.

EXPERIMENTAL

Materials

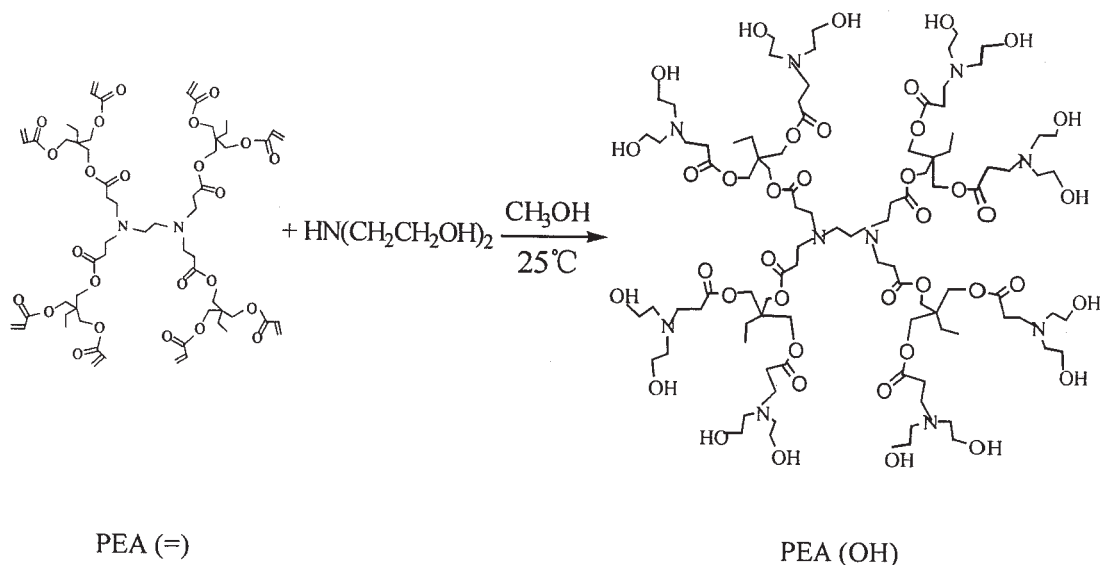
Dendritic PEA(OH) terminated with acrylic double bonds [PEA(=)] was prepared following the method of Xu et al.¹¹; DEA and methanol were purchased from the Third Reagent Company of Shanghai. DEA was dried in a vacuum (150 Pa) at 30°C for 5 h before use.

Measurements

The IR spectra were carried out with a Magna-550 Fourier-transform IR spectrometer. Proton NMR (¹H-NMR) spectra were recorded on an INOVA (400 MHz) using CDCl₃ as a solvent. Elemental analysis was carried out with a Shimadzu EA-1110 CHNSO. High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-8A using a C₁₈ column (4.6 × 250 mm) and a mixture of CH₃CN and H₂O(40:60

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Scheme 1 Synthesis of PEA(OH).

v/v) as an eluent (total flux = 0.7 mL/min, detection wavelength = 216 nm). Surface tension was measured with a JZHY-180 interfacial tensiometer.

The PEA(=) (6.55 g, 0.00526 mol), DEA (4.43 g, 0.0422 mol), and methanol (12 mL) were added in turn to a three-necked flask equipped with a mechanical stirrer, a thermometer, and a condenser. The mixture was maintained at 25°C for 22 h with stirring. Then it was connected to a vacuum line for complete removal of methanol to yield a colorless, transparent, viscous liquid product [PEA(OH)].

A series of PEA(OH) water solutions with different concentrations were prepared. Their surface tensions were measured at 20°C and their cloud points were observed by gradually raising the temperature from 20°C.

RESULTS AND DISCUSSION

Synthesis of PEA(OH)

Dendrimers with peripheral hydroxyls were first prepared by Newkome.⁷ It was pointed out that purification of the products proved extremely difficult. This was because of similar solubility properties of the products and the raw material with multihydroxyls, so that an exact needed amount of raw material was used and a modification of reaction conditions was deemed appropriate to attain satisfactory products. Thus, an exact 1:8 molar ratio of PEA(=) to DEA was adopted in our work and several variations of reaction conditions were investigated. The results are shown in Table I.

It was found that when the reaction time was varied from 6 to 22 h, the purity of PEA(OH) rapidly increased, but it decreased slightly when the reaction

time increased from 22 to 46 h. Thus, 22 h is the suitable reaction time. Methanol is often used as a solvent in similar Michael addition reactions.^{12,13} The data in Table I show that the purity of PEA(OH) first increased when the mass percent of methanol in the reaction system rose from 13 to 46% and then slightly decreased when the amount of methanol continued increasing. Therefore, 46% is considered as the appropriate methanol content. Comparing entries 3, 10, 11, 12, and 13 in Table I shows that the purity of PEA(OH) slightly increased when the reaction temperature rose from 20 to 25°C, but decreased when the reaction temperature rose from 25 to 40°C. Thus, 25°C is the appropriate reaction temperature. PEA(OH) with 94.6% purity and almost quantitative yield was obtained by removal of methanol under reduced pressure after PEA(=) was reacted with DEA(1:8 mol/

TABLE I
Effects of Reaction Conditions on Purities of PEA(OH)

Entry	w (CH ₃ OH) ^a (%)	Temperature (°C)	Time (h)	Purity (%)
1	46	25	6	58.4
2	46	25	11	79.6
3	46	25	22	94.6
4	46	25	32	91.6
5	46	25	46	92.3
6	13	25	22	55.3
7	26	25	22	73.6
8	37	25	22	88.6
9	54	25	22	93.9
10	46	20	22	90.9
11	46	30	22	91.6
12	46	35	22	90.8
13	46	40	22	89.2

^a The mass percent of methanol in the reaction system.

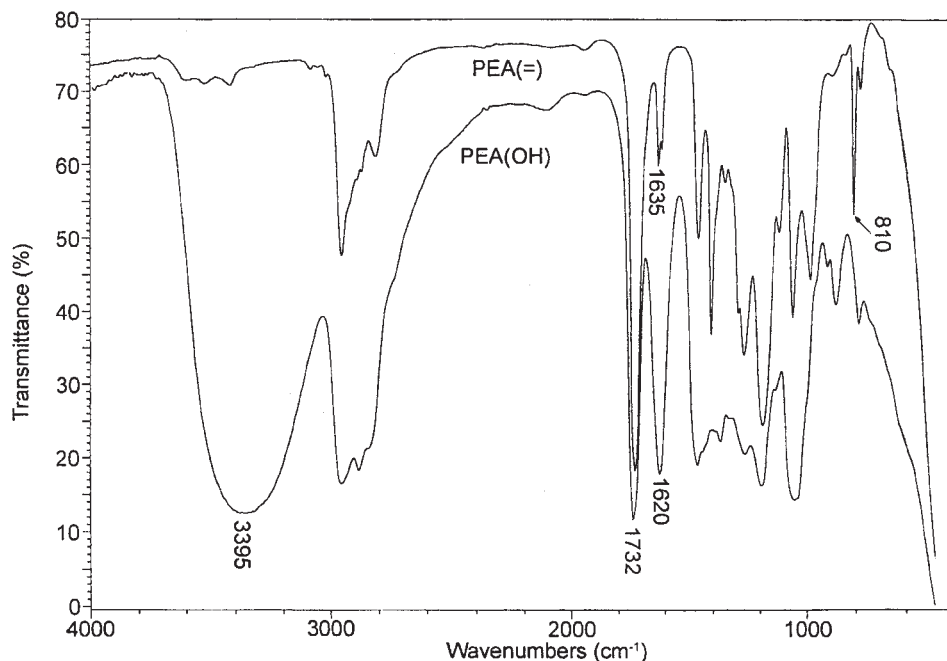


Figure 1 The IR spectra of PEA(OH) and PEA(=).

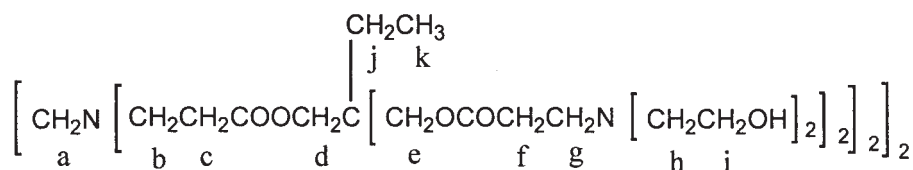
mol) in methanol at 25°C for 22 h, which showed that PEA(OH) can be synthesized under mild conditions and the synthetic procedure involved no complicated purification steps. In addition, methanol can be cycled.

Characterization of PEA(OH)

The IR spectrum of PEA(OH) (Fig. 1) indicated that

hydroxyl (3395 cm^{-1}) and ester carbonyl (1732 cm^{-1}) coexist in the product. A large number of hydroxyls and ester carbonyls in the structure of PEA(OH) form hydrogen bonds,¹⁴ which produce the characteristic absorption peak at 1620 cm^{-1} , but the acrylic double bond (1635, 810 cm^{-1}) has disappeared.

The structure of PEA(OH) is shown in the following form:



In the $^1\text{H-NMR}$ spectrum of PEA(OH) (Fig. 2), peaks related to acrylic double bond protons (δ 5.89–6.38) have disappeared, but the signals corresponding to protons in the structure of PEA (OH) could be found: δ 0.82–0.92 (12H, k), 1.32–1.50 (8H, j), 2.50–2.53 (28H, a, c, f), 2.57–2.76 (32H, h), 2.77–2.78 (16H, g), 2.82–2.87 (8H, b), 3.62–3.70 (32H, i), 3.99–4.10 (24H, d, e). The experimental integration of peak i was a little more than the theoretical one, which indicated that a small amount DEA starting material was included in PEA(OH).

The purity of PEA(OH) calculated according to the integration of peaks i and k was 95.7%, which conformed to 94.6% evaluated by HPLC (Fig. 3).

The elemental analysis data of PEA(OH) in Table II show that the experimental data of C, H, and N were

basically consistent with the theoretical ones. The purity of PEA(OH) estimated by elemental analysis data was 95.2%, which conformed to 94.6% evaluated by HPLC and 95.7% by $^1\text{H-NMR}$.

An analysis of IR, $^1\text{H-NMR}$, and elemental analysis verifies that PEA(OH) is successfully synthesized.

Surfactivity of PEA(OH)

Figure 4 provides the surface tensions of aqueous PEA(OH) and aqueous poly(ethylene glycol) (PEG 2000) at 20°C. The surface tensions of aqueous PEA(OH) are obviously lower than those of linear, similar molecule weight aqueous PEG 2000 at the same concentration, especially at low concentration. The 0.02 mass % PEA(OH) water solution showed

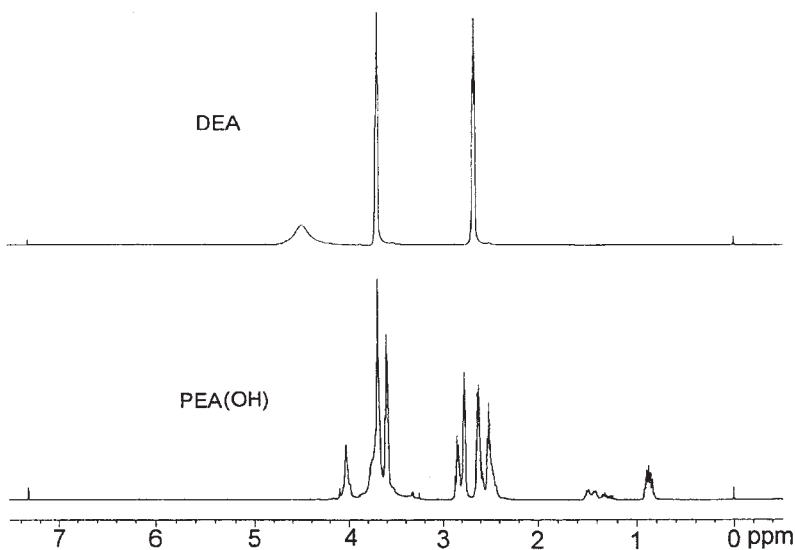


Figure 2 The ^1H -NMR spectrum of PEA(OH).

very low surface tension. The reason is that the surfactant's ability to reduce surface tension is based on the molecule-array compactibility on its solution surface.¹⁵ The structures of the dendritic PEA(OH) molecules are well defined and not wound to each other, so that the PEA(OH) molecules can array compactly on its aqueous surface. However, the structures of linear PEG 2000 molecules are very large and wound

to each other, leading to PEG 2000 molecules loosely arranged on its aqueous surface. Thus, PEA(OH) has better surfactivity than PEG 2000.

Further study showed that aqueous PEA(OH) with 0.1–50 mass % exhibits cloud points, as shown in Figure 5. This phenomenon can be explained by the fact that, similar to the PEG nonionic surfactant, the solubility of PEA(OH) in water relies on hydrogen bonds between PEA(OH) and water molecules. A low temperature is beneficial to the stable existence of hydrogen bonds. Therefore, PEA(OH) can be well mixed with water at any ratio below 20°C. When the PEA(OH) aqueous concentration is very low, dendritic PEA(OH) molecules can fully extend in water and hydroxyls, carbonyl oxygen atoms, and nitrogen atoms in the PEA(OH) structure can form hydrogen bonds with hydrogen and oxygen atoms in water molecules. Thus, the PEA(OH) shows good solubility in water below 0.1 mass %. When the PEA(OH) content is relatively high, multiple hydroxyl groups on the periphery of the PEA(OH) structure make a primary contribution to the solubility, leading to PEA(OH) that mixes well with water above 50 mass %. Moreover, the solubility of PEA(OH) in water is dependent on the temperature between 0.1 and 50 mass %, and 0.1–50 mass % aqueous PEA(OH) exhibits its cloud points.

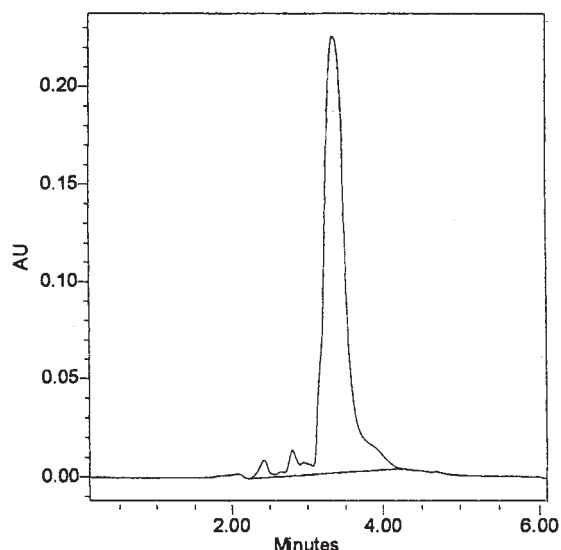


Figure 3 The HPLC spectrum of PEA(OH).

TABLE II
Elemental Analysis Data of PEA(OH)

Name	Formula	Elemental Anal. Calcd (Theor.)		
		C (%)	H (%)	N (%)
PEA(OH)	$\text{C}_{94}\text{H}_{176}\text{O}_{40}\text{N}_{10}$	54.13 (52.34)	8.45 (8.87)	6.72 (7.13)

Using this property, remnant DEA mixed in the PEA(OH) can be removed by centrifugation of the PEA(OH) water mixture and removal of the upper layer of water at the temperature above its cloud point. However, separation of defect and perfect structure dendrimers is difficult. An attempt to achieve a uniform PEA(OH) dendrimer by column chromatography is in progress.

CONCLUSIONS

PEA(OH) dendrimer was synthesized from PEA(=) and DEA (1:8 mol/mol) in methanol at 25°C for 22 h. The reaction conditions were mild, the synthetic procedure involved no complicated purification steps, and the yield and purity were high. PEA(OH) is a surfactant with surfactivity that is better than that of PEG 2000. Aqueous PEA(OH) exhibits cloud points between the mass concentrations of 0.1 and 50%.

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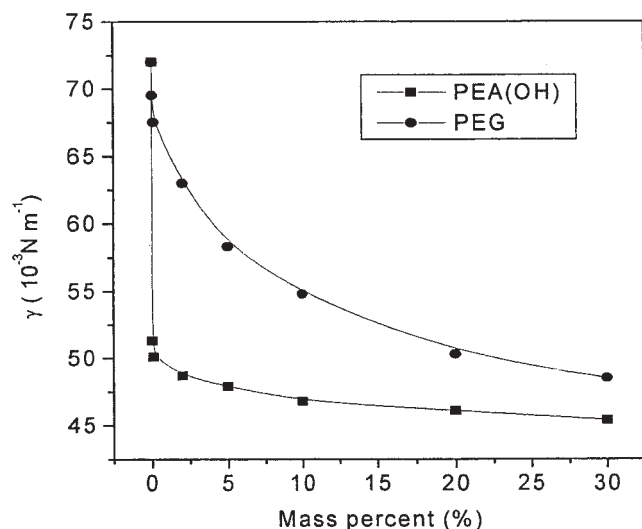


Figure 4 The surface tension of PEA(OH) and aqueous PEG 2000 (20°C).

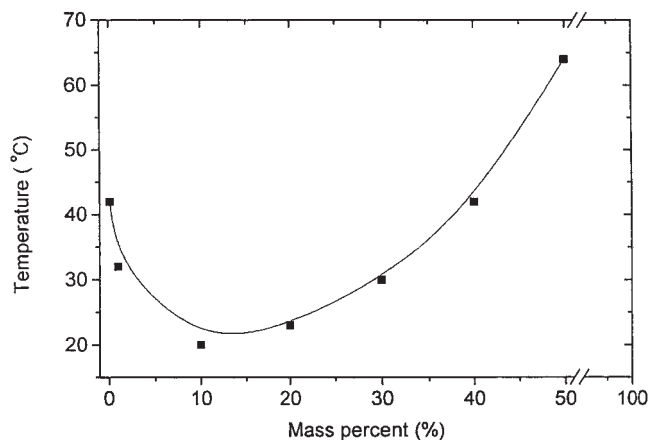


Figure 5 Cloud points of aqueous PEA(OH) (101,325 Pa).

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