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Novel approach for the synthesis of hydrophobe modified polyacrylamide. Direct *N*-alkylation of polyacrylamide in dimethyl sulfoxide

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Abstract

We found that dimethyl sulfoxide (DMSO) dissolves PAAm. Direct *N*-alkylation of the amide groups of polyacrylamide was performed under homogeneous condition in DMSO. By using *tert*-butoxide, the amide groups of PAAm were turned into amide cations, followed by a coupling reaction with alkyl bromide to give *N*-alkylated PAAm. ^{1}H NMR suggests that the incorporation of alkyl bromide proceeded quantitatively. Intrinsic viscosity measurements and ^{13}C NMR spectra in DMSO suggest that undesirable side reactions such as cross linking or hydrolysis of the amide groups did not take place during the reaction.

Keywords: Polyacrylamide; Dimethyl sulfoxide; Hydrophobe modified polyacrylamide

1. Introduction

Polyacrylamide (PAAm) and its partially hydrolyzed derivatives are among the most important water soluble polymers in industrial use such as water treatment and paper production. In addition, there has been a growing interest in another type of derivative called hydrophobe modified PAAm (HM-PAAm) [1–3]. HM-PAAm is a copolymer of AAm and a small amount of HM-AAm such as *N*-alkylated AAm. Aqueous solutions of HM-PAAm show enhanced viscosity due to association of hydrophobes. Thus, HM-PAAm is widely used as a rheology modifier in various applications such as paints, cosmetics and pharmaceuticals.

HM-PAAm is prepared by radical copolymerization of AAm and HM-AAm in water [4]. As HM-AAm is insoluble in water, a surfactant is used to solubilize HM-AAm [4]. However, such a (micro)heterogeneous process often leads to a polymer having a blocky sequence of HM-AAm [5–7]. The microstructure has a strong influence on the rheological properties of the polymer solution [6]. HM-PAAm may also be prepared by post-polymerization modification. In this approach, one starts with PAAm, and the modification is carried directly to PAAm. When the reaction is performed under homogeneous conditions, a random distribution of the hydrophobes along the polymer chain is expected [8]. In addition, one can control the parameter of interest such as hydrophobe content or the structure of a hydrophobe, while keeping the molecular weight and distribution of the backbone polymer constant. However, PAAm is soluble only in water and a very limited number of polar organic solvents such as ethylene glycol or formamide [9–11], and none of them seems suitable for the chemical modification of PAAm, which typically involves reaction between the amide group and an electrophile. We discovered, however, that dimethyl sulfoxide (DMSO) dissolves PAAm. In this article, we will present a novel post-polymerization approach for the synthesis of HM-PAAm in DMSO.

2. Experimental section

2.1. Materials

PAAm was purchased from Polysciences (Warrington, PA, USA) as a 10% solution in water. The solution was dialyzed against water, and lyophilized to recover PAAm as a white solid. The molecular weight as calculated from the intrinsic viscosity in 0.1 M NaCl using the empirical equation, $[\eta] = 9.33 \times 10^{-3} M^{0.75}$ (cm^3/g) [12], was 4.8×10^5 g/mol. Anhydrous DMSO (Aldrich), potassium *tert*-butoxide (Aldrich, 95%), dodecyl bromide (Janssen Chimica, 98%), and hexadecyl bromide (Aldrich, 97%) were commercially available and used as received.

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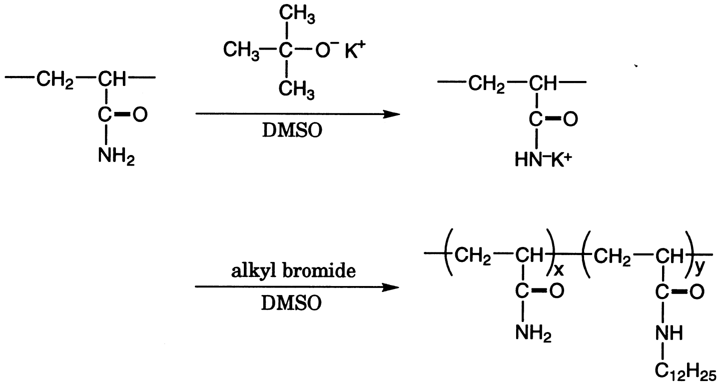

Fig. 1. Synthetic route of HM-PAAm.

2.2. Preparation of HM-PAAm

The synthetic scheme for the modification of PAAm (Fig. 1) is based on the reaction developed to alkylate poly(styrene-*co*-acrylamide) (containing 4–14 mol% acrylamide) in 2-ethoxyethyl ether [13]. A three-neck round-bottom flask (250 ml) equipped with a condenser, a nitrogen gas inlet/outlet, a rubber septum, and a magnetic stirrer bar was charged with PAAm (2 g, 28 mmol AAm) and anhydrous DMSO (90 ml), and PAAm was allowed to dissolve by stirring at 80°C for 1 day under nitrogen atmosphere. After cooling down to ambient temperature, 10 ml of an anhydrous DMSO solution of potassium *tert*-butoxide (166 mg, 1.4 mmol), which was prepared under anhydrous condition, was added dropwise with vigorous stirring, and the mixture was stirred for 1 h. Dodecyl bromide (142 mg, 0.56 mmol) was then added dropwise. The coupling reaction was allowed to proceed at 65°C for 24 h. Nitrogen atmosphere was maintained throughout the reaction. The reaction mixture was homogeneous throughout the reaction. After terminating the reaction by adding 250 ml of water, the reaction mixture was dialyzed against water. The polymer was isolated by lyophilization as white solid. The yield was nearly 100% based on PAAm.

2.3. Polymer characterization

Intrinsic viscosity was measured on a Schott Geräte AVS 440 Viscosity Measuring Unit using a Ubbelohde capillary viscometer at 25.0°C. NMR spectra were measured on a Varian ARX-500 spectrophotometer operating at 500.1 MHz for ^{1}H and 125.8 MHz for ^{13}C. Polymer samples were dissolved in DMSO-d_6 (Aldrich, 99.9 at.% D) at 2% (w/v). All the spectra were recorded at 50°C. Chemical shifts are reported as ppm downfield from tetramethyl silane (TMS).

Table 1
Characteristics of the parent and modified PAAms

	DS		$[\eta]$ (cm^3/g)[a]
	Calculated[b]	^{1}H-NMR	
PAAm	–	–	102
C12-1.0-PAAm	1	1.0	101
C12-2.1-PAAm	2	2.1	100
C16-2.0-PAAm	2	2.0	97

[a] Measured in DMSO at 25°C.

[b] Calculated assuming the complete incorporation of the alkyl bromide used.

3. Results and discussion

3.1. Dissolution of PAAm in DMSO

Due to the polar nature (dielectric constant, $\kappa = 46.0$ at 35°C [14]), DMSO is one of the most common organic solvents for water soluble polymers [11]. However, it has not been reported as a solvent for PAAm [9–11,15]. In fact, at ambient temperature, mixtures of PAAm and DMSO in the concentrations up to 5% only gave a turbid suspension with precipitate even after stirring for a prolonged period of time (several months); however, heating the mixture accelerated the dissolution remarkably. For example, at 80°C, a 2% homogeneous solution was obtained after stirring for 1 day. The solution remained homogeneous when it was brought back to ambient temperature. In order to investigate any possible chemical degradation of PAAm by heating in DMSO, PAAm was once dissolved in DMSO at 80°C, and recovered by dialysis against water followed by lyophilization. The molecular weight of the DMSO treated sample, as calculated by the intrinsic viscosity in 0.1 M NaCl, was the same as that of the untreated PAAm. This result suggests that PAAm dissolves in DMSO without any chemical degradation.

The significantly smaller intrinsic viscosity of PAAm in DMSO (102 cm^3/g, Table 1) than the value in 0.1 M NaCl (169 cm^3/g) indicates the poor solvent quality of DMSO to PAAm. The extremely slow dissolution of PAAm in DMSO at ambient temperature can be ascribed to the relatively high glass transition temperature of PAAm ($T_g = 165$ or 188°C [16]), in addition to the poor solvent quality of DMSO. Thus, DMSO molecules cannot penetrate and swell solid

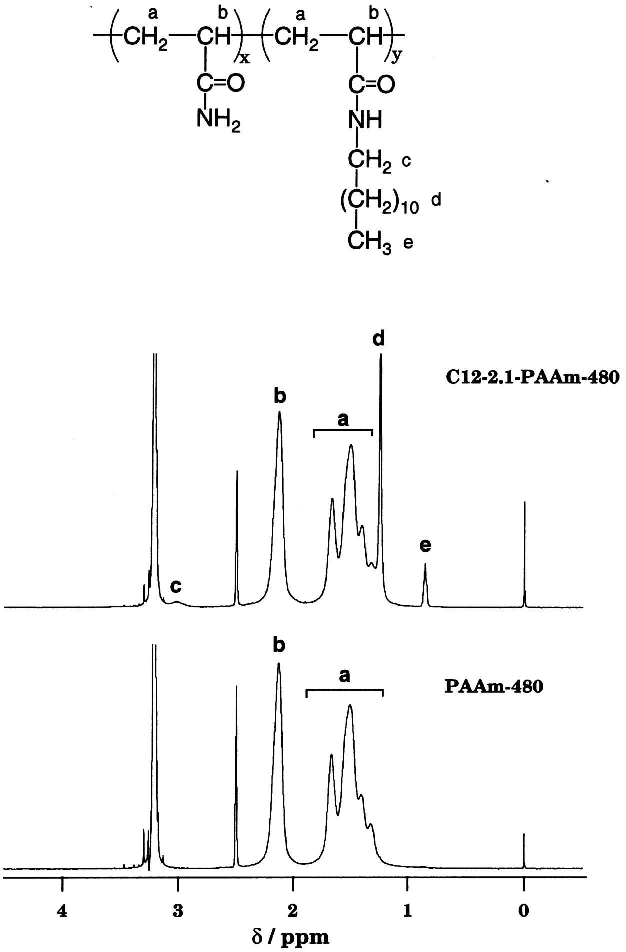

Fig. 2. ^{1}H NMR spectra of C12-2.1-PAAm-480 (top) and the unmodified PAAm-480 (bottom) in DMSO-d_6 at 323 K.

PAAm easily at ambient temperature where PAAm is in a glassy state. However, PAAm chains become more mobile at elevated temperatures and DMSO can penetrate solid PAAm more easily, which accelerates the dissolution. Actually, if solid PAAm was swollen with a minimum amount of water, successive addition of DMSO leads to a homogeneous solution without heating.

3.2. Synthesis and characterization of HM-PAAm

^{1}H NMR spectra of the unmodified and modified PAAms are shown in Fig. 2. The spectrum of the modified PAAm shows three additional peaks due to the hydrophobe protons (peaks c, d, and e). Formation of a carbon–nitrogen bond was evidenced by the peak c [17]. The absence of the triplet at 3.6 ppm (α-methylene protons of an alkyl bromide) indicates that the product is free of the unreacted alkyl bromide. The hydrophobe content was calculated by integrating the peak of the terminal methyl protons of the alkyl chain (peak e) and the methyne protons of the PAAm chain (peak b). The good agreement that was found between the DS measured by ^{1}H NMR and that calculated by assuming a complete incorporation of the alkyl bromide in the initial reaction mixture suggests that the coupling reaction proceeded quantitatively. Characteristics of the parent PAAm and HM-PAAms are listed in Table 1.

The amide cation may attack another amide group of PAAm, leading to cross linking through imide bond. The cross linking (intermolecular and/or intramolecular) would affect strongly the hydrodynamic volume of the polymer coil. Table 1 also lists the intrinsic viscosity for the unmodified and modified PAAms in DMSO. The intrinsic viscosities for all the samples agree within experimental error, which strongly suggests that the cross linking did not take place during the reaction. No evidence of imide bond formation or hydrolysis was found in the ^{13}C NMR spectra.

The rheological characterization of the modified polymers in water and the hydrophobe distribution along the PAAm chain are in progress.

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References

[1] Glass JE, editor. Polymers in aqueous media: performance through association. Washington, DC: American Chemical Society, 1989.
[2] Shalaby SW, McCormick CL, Butler GB, editors. Water-soluble polymers: synthesis, solution properties, and applications. Washington, DC: American Chemical Society, 1991.
[3] Dubin P, Bock J, Davis R, Schulz DN, Thies C, editors. Macromolecular complexes in chemistry and biology. Berlin: Springer, 1994.
[4] Evani S. US Patent 4432881, 1984.
[5] Dowling KC, Thomas JK. Macromolecules 1990;23:1059–1064.
[6] Hill A, Candau F, Selb J. Macromolecules 1993;26:4521–4532.
[7] Ezzell SA, Hoyle CE, Creed D, McCormick CL. Macromolecules 1992;25:1887–1895.
[8] Magny B, Lafuma F, Iliopoulos I. Polymer 1992;33:3151–3154.
[9] Thomas WM. In: Mark HF, editor. Encyclopedia of polymer science and technology, 1. New York: Interscience, 1964. p. 177.
[10] Kulicke WM, Kniewske R, Klein J. Prog Polym Sci 1982;8:373–468.
[11] Brandrup J, Immergut H, editors. Polymer handbook. New York: Wiley, 1989.
[12] François J, Sarazin D, Schwartz T, Weill G. Polymer 1979;20:969–975.
[13] Jannasch P, Wesslén B. J Polym Sci A, Polym Chem 1995;33:1465–1474.
[14] Harris RK. Nuclear magnetic resonance spectroscopy: a physicochemical view. Harlow, London: Longman, 1986.
[15] Molyneux P. Water-soluble synthetic polymers: properties and behavior, Boca Raton, FL: CRC Press, 1984.
[16] Klein J, Heitzmann R. Makromol Chem 1978;179:1895.
[17] Volpert E, Selb J, Candau F. Macromolecules 1996;29:1452–1463.