Polymer Bulletin 44, 385–391 (2000)

Polymer Bulletin

Preparation and characterization of dodecylamine-modified poly(aspartic acid) as a biodegradable water-soluble polymeric material

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Received: 18 February 2000/Accepted: 28 March 2000

Summary

The reaction of poly(succinimide) (PSI) with dodecylamine (DDA) in DMF produced a partially dodecylamine-modified poly(succinimide) (DDA-PSI). When the mole ratio of the DDA units and the succinimide units in PSI (M_w = 22,000) varied from 0.1 to 0.5 in the feed, the mole fraction of the N-dodecyl aspartamide units in PSI increased from 4 to 46 mol-%, and the M_w of DDA-PSI was almost constant at M_w = *ca* 20,000. Sodium DDA-modified poly(aspartate) (DDA-PASP-Na) was obtained in high yield by hydrolysis using NaOH solution. DDA-PASP-Na exhibited biodegradability (14 ~ 21 %) and a high MnO_2-dispersion property (10.3 g-MnO_2 / g-polymer).

Introduction

It is well known that water-soluble amphiphilic polymers having hydrophilic and hydrophobic units are self-organized by hydrophobic association in an aqueous solution and possess surfactantlike properties, and are widely used as surfactants, emulsifiers, flocculating agents and dispersants [1-3]. Although amphiphilic block copolymers, *e.g.*, block copolymers of acrylic acid and styrene, and alternative copolymers of maleic acid and alkyl vinyl ether have been investigated [4-6], amphiphilic random copolymers have lately attracted attention because they can be easily designed and synthesized [7-9]. However, most amphiphilic polymers are only slightly biodegradable, which might possibly produce significant damage to the environment. Therefore, they should be designed to be completely biodegradable and thus removed from the environment.

Poly(aspartic acid) (PASP) is of potential interest for use as a biodegradable water-soluble poly(carboxylic acid). Recently, we reported that a high molecular weight PSI with a linear structure was synthesized by the acid-catalyzed polycondensation of ASP and then easily hydrolyzed to PASP with a high biodegradability [10, 11]. However, the MnO_2-dispersion property, which is one important property for a dispersant or detergent builder, was not enough to use PASP in place of poly(acrylic acid). It is expected that the dispersion property of PASP might be improved if PASP could be converted into an amphiphilic polymer. Poly(succinimide) (PSI) was easily reacted with a primary amine to produce poly(asparatamide) with functional groups in the side-chain. For example, Neri et al. reported that PSI was prepared by the polycondensation of L-aspartic acid

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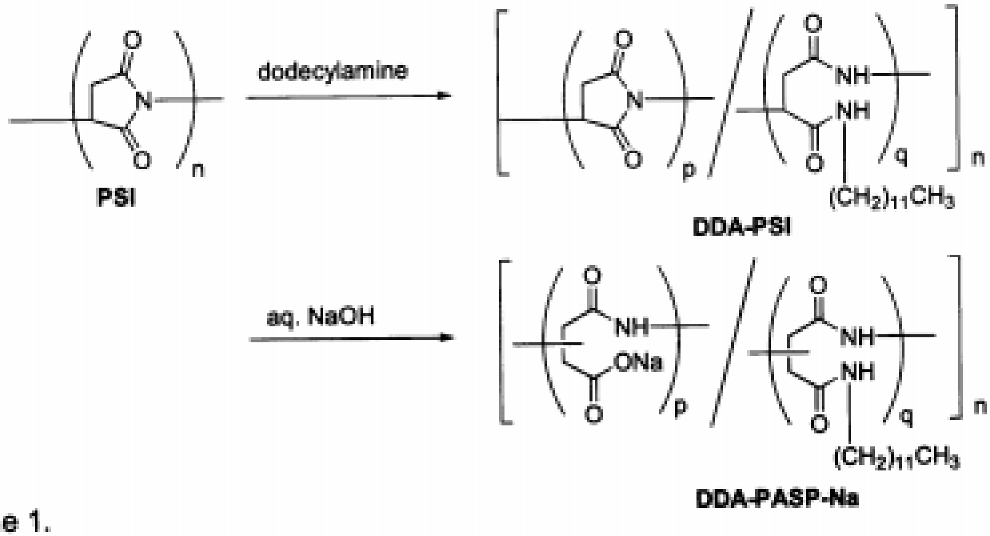
(ASP) in a large amount of *o*-phosphoric acid and then reacted with ethanolamine to produce poly[(2-hydroxyethyl)-aspartamide] as a plasma expander [12]. Thus PSI that reacted with suitable amounts of alkylamine might be converted into an amphiphilic PASP with hydrophobic units in the side-chain.



Scheme 1.

In this article, we report the preparation and dispersing capacity of dodecylamine modified PASP-Nas by the reaction of PSIs with dodecylamine followed by alkali hydrolysis. In addition, their solution property and biodegradability in terms of biodegradable surfactants and dispersants were determined. (*Scheme1*)

Experimental

Materials and measurements. L-Aspartic acid (ASP) was obtained from the Mitsubishi Chemical Corporation (Japan). *N,N*-Dimethylformamide (DMF), 85 % *o*-phosphoric acid, dodecylamine and sodium hydroxide were commercially available and used without further purification. Molecular weights of the polymers were estimated in DMF containing LiBr (20 mmol • L^{-1}) by gel permeation chromatography (G.P.C.) (column, PLgel 5μm MIXED-C x 2; detector, refractive index; standard, polystyrene). ^{1}H NMR spectra were measured using a JEOL JNM-GSX 400 MHz spectrometer. Absorption spectra were recorded using a Shimadzu UV-2500pc u.v.-vis recording spectrophotometer. Fluorescence spectra were recorded using a Hitachi F-4500 fluorescence spectrophotometer with excitation at 343 nm. The reduced viscosity was measured by using a Ubbelohde type viscometer. The quantitative analysis of manganese was carried out using an Inductive Coupled Plasma-Atomic Emission Spectrometer (Nippon Jarrell-Ash ICAP-55). Poly(succinimide) (PSI) was prepared by the acid-catalyzed bulk polycondensation of ASP in accordance with the description in a previous paper [11].

Preparation of amine-modified poly(succinimide). A typical procedure for the preparation of the dodecylamine-modified poly(succinimide) is as follows: To a solution of poly(succinimide) (10.0 g, 103 mmol) in dry DMF (90 mL) was added dodecylamine (2.0 g, 10.3 mmol) under N_2. After stirring for 7 h at 100 °C, the reaction mixture was poured into MeOH (500 mL). After filtration, the precipitate was washed with MeOH (500 mL x 2), and dried at 100 °C for 24 h under reduced pressure to yield the dodecylamine-modified poly(succinimide) (10.1 g, 84 %).

Preparation of amine-modified poly(aspartic acid). A typical procedure for the preparation of the dodecylamine-modified poly(aspartic acid) is as follows: To a solution of NaOH (1.0 g, 25.0 mmol) in deionized water (37.5 mL) was added the dodecylamine-modified poly(succinimide) (2.5 g, 21.6 mmol) with ice cooling. After stirring for 24 h, the reaction mixture was poured into MeOH (300 mL), and then the precipitate was filtered and dried at 50 °C under reduced pressure to yield the dodecylamine-modified poly(aspartic acid) sodium salt (3.1 g).

Dispersion capacity of modified poly(aspartic acid). The dispersion capacity was evaluated by the dispersion of manganese (IV) oxide powder in accordance with the description in a previous paper [13]. The sample (25 mg), MnO_2 (1.0g) and H_2O (50 mL) were placed in a 50 mL test tube equipped with a cap and then measured. After the solution was shaken one hundred times, it was allowed to stand for 4 h at 25 °C and then the suspension (15 mL) was collected. The concentration of manganese was determined using ICP luminescence.

Biodegradability of modified poly(aspartic acid). The biodegradability of PASP was estimated using OECD 301C (Modified MITI Test). A sample was treated with the standard activated sludge, which was obtained from the Chemicals Inspection & Testing Institute, Japan, at 25 ± 1 °C for 28 days. Aniline was used as the standard to check the activity of the standard activated sludge. The biological oxygen demand (BOD) and total organic carbon amount (TOC) indicate the consumption of the oxygen and total organic carbon amount during the evaluation, respectively. Both are generally used for evaluating the biodegradability. The BOD and TOC were measured using an OM3001 coulometer (Ohkura Electric Co., Ltd.) and a Total Carbon Analyzer TOC-5000A (Shimadzu Corporation), respectively. The removed TOC was calculated from the difference between the amount of the total organic carbon before and after the evaluation of the biodegradability.

Results and discussion

The reaction of poly(succinimide) (PSI) with a dodecylamine (DDA) was carried out for the purpose of introducing a hydrophobic group into PSI. *Table 1* summarizes the results of the reactions of PSI with DDA. When the molar ratio of DDA and succinimide units in PSI (M_w = 22,000) varied from 0.1 to 0.5, the polymers were obtained in adequate yields and the molecular weights (M_w) of the dodecylamine-modified poly(succinimide)s (DDA-PSI) were almost constant. *Figure 1a* shows the ^{1}H NMR spectrum of the polymer obtained from the reaction with the molar ratio of DDA and succinimide units in PSI at 0.1 in the feed. The signals at 5.1 - 5.5 ppm and at 2.4 - 2.9 and 3.0 - 3.3 ppm were assigned to the methine and methylene proton of the succinimide repeating unit, respectively, and the signals that originated from the dodecylamine units were observed at 0.85, 1.2, 1.35 and 3.0 ppm. In addition, the signal

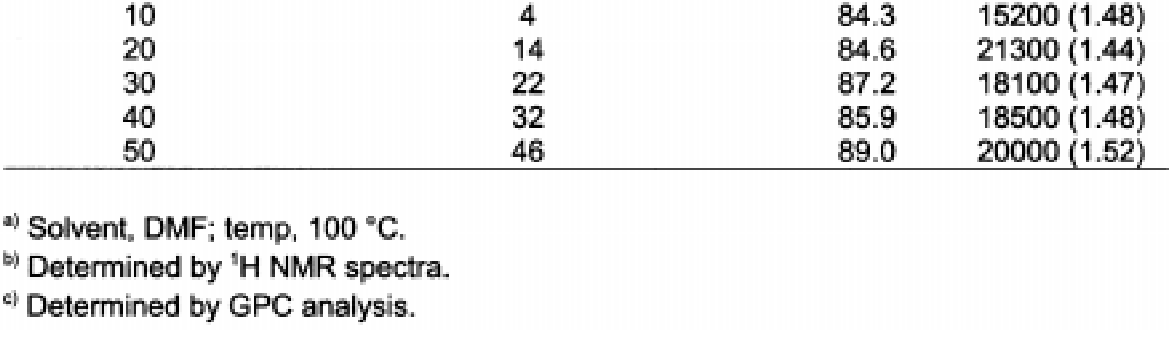


Table 1. Reaction of poly(succinimide) (PSI) with dodecylamine (DDA) [a]

Mole ratio of DDA and PSI (mol-%)	Mole fraction of *N*-dodecyl aspartamide unit in PSI (mol-%) [b]	yield (%)	M_w (M_w/M_n) [c]
10	4	84.3	15200 (1.48)
20	14	84.6	21300 (1.44)
30	22	87.2	18100 (1.47)
40	32	85.9	18500 (1.48)
50	46	89.0	20000 (1.52)

[a] Solvent, DMF; temp, 100 °C.

[b] Determined by ^{1}H NMR spectra.

[c] Determined by GPC analysis.

at 4.3 - 4.8 ppm was assigned to the methine proton of the aspartic acid unit, which was caused by the ring opening of the succinimide units. These results indicated that the aminolysis of PSI smoothly proceeded to yield the DDA-PSI. On the basis of the ^{1}H NMR spectrum, the mole fraction of the dodecyl aspatamide units and aspartic acid units were determined to be 4 and 11%, respectively. The mole fraction of the dodecyl aspartamide units in PSI increased from 4 to 46 % with increasing molar ratio of the DDA and succinimide units in PSI in the feed.

DDA-PSI was easily hydrolyzed in quantitative yield in alkali medium for conversion into sodium dodecylamine-modified poly(aspartate) (DDA-PASP-Na). *Figure 1b* shows the ^{1}H NMR spectra of DDA$_4$-PASP-Na in D_2O. The signals observed at 3.4 ppm are assigned to the methylene proton adjacent to the amino compounds and the signals at 4.9 and 4.7 ppm and at 2.8 - 3.1 ppm are assigned to the methine and methylene protons of the aspartic acid unit, respectively. The ratio of the α-opening/β-opening was estimated to be *ca.* 3/7 as compared with the integral value of the methine proton at 4.9 and 4.7 ppm, which was similar to poly(aspartic acid) [11]. This result indicated that the *N*-dodecyl aspartamide unit scarcely affected the hydrolysis reaction of the succinimide units. In addition, the signal at 1.1 ppm is assigned to the methyl proton, and that at 1.5 or 1.7 ppm is assigned to the methylene proton of the DDA units.

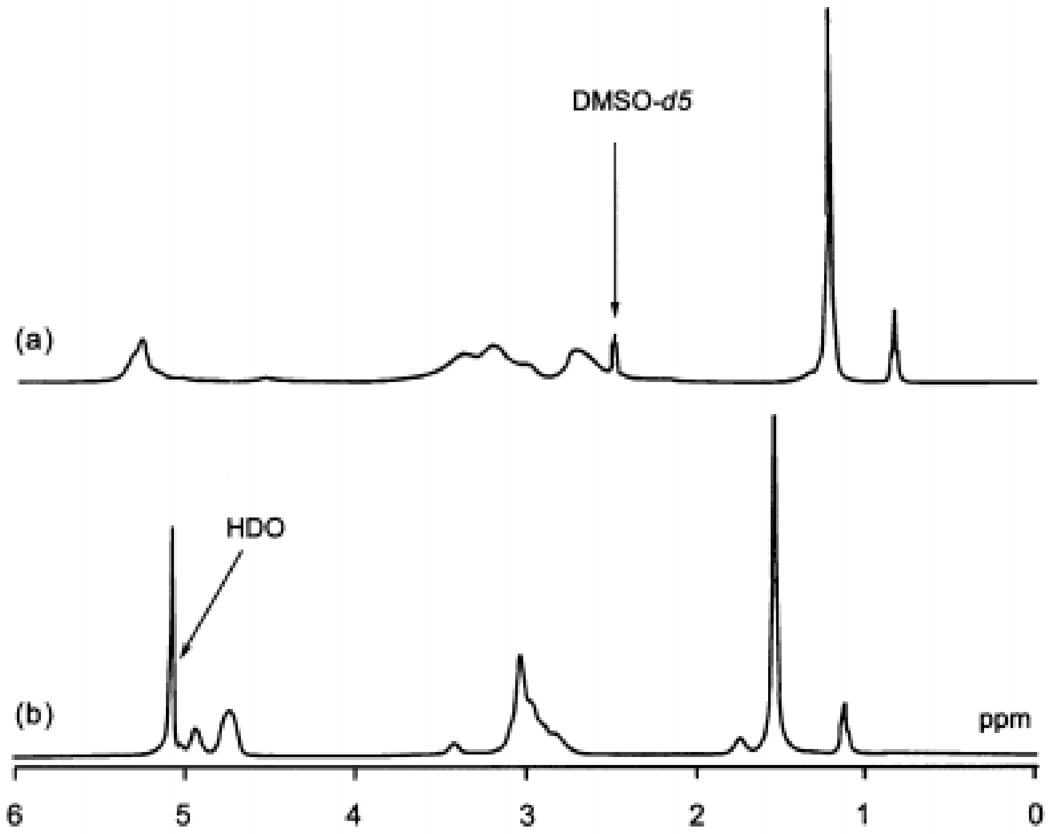
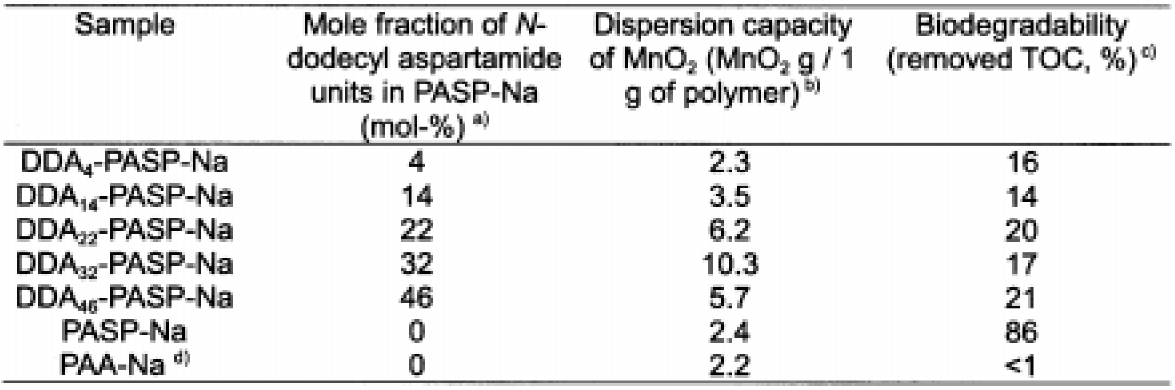


Figure 1. ^{1}H NMR spectra (400 MHz, 24°C) of dodecylamine-modified PSI in DMSO-d_6 (a) and sodium dodecylamine-modified poly(aspartate) in D_2O

Table 2. MnO_2-Dispersion and biodegradable properties of sodium dodecylamine-modified poly(aspartic acid)s (DDA-PASP-Na)



Sample	Mole fraction of *N*-dodecyl aspartamide units in PASP-Na (mol-%) [a]	Dispersion capacity of MnO_2 (MnO_2 g / 1 g of polymer) [b]	Biodegradability (removed TOC, %) [c]
DDA_4-PASP-Na	4	2.3	16
DDA_{14}-PASP-Na	14	3.5	14
DDA_{22}-PASP-Na	22	6.2	20
DDA_{32}-PASP-Na	32	10.3	17
DDA_{46}-PASP-Na	46	5.7	21
PASP-Na	0	2.4	86
PAA-Na [d]	0	2.2	<1

[a] Determined by ^1H NMR spectra.

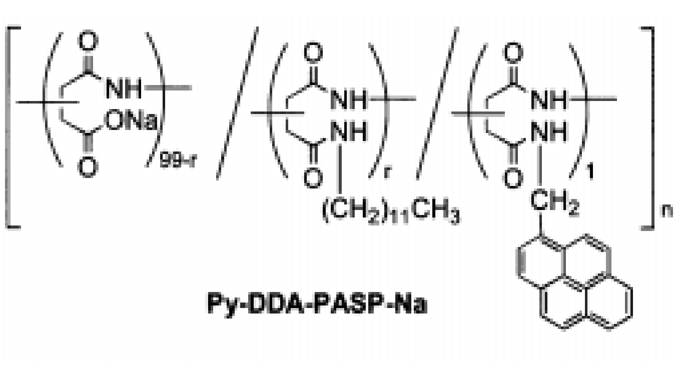
[b] Using 0.05 % polymer aqueous solution; temp., 25 °C; time, 4h.

[c] Using activated sludge; temp., 25 ± 1 °C; time, 28 days.

[d] Sodium poly(acrylate), M_w = 8000

In order to estimate the dispersant property, the MnO_2 dispersion capacity of sodium poly(aspartate) (PASP-Na), DDA-PASP-Na and sodium poly(acrylate) (PAA-Na) was carried out in aqueous solution. These results are listed in Table 2. The dispersion capacity of DDA-PASP-Na increased with increasing mole fraction of the DDA unit except for DDA_4-PASP-Na and was higher than that of PAA-Na. In the case of DDA_{32}-PASP-Na, the highest value of 10.3 g of MnO_2/1 g of DDA-PASP-Na was obtained.

In order to investigate the solution property of DDA-PASP-Na in aqueous solution, the pyrene-labeled DDA-PSIs were synthesized by the reaction of PSI and DDA (similar molecular ratio in Table I) along with 1-mol-% 1-aminomethylpyrene (Py) and converted into sodium pyrene/dodecylamine-modified poly(aspartate) (Py-DDA-PASP-Na) (Scheme 2). It is known that the ratio of band III to band I (I_3/I_1) in the pyrene fluorescence spectra depends on the polarity in the microenvironments where pyrene exists and is greater in less polar media [14]. As shown in *Figure 2a*, the I_3/I_1 value at pH 7 significantly increased in the range from 0 to 20 mol-% of the DDA content, and slightly increased in the range from 20 to 50 mol-%. This result indicated that the hydrophobic microdomains formed even in a low DDA content and the hydrophobic association proceeded by increasing the DDA content. The self-organization due to the hydrophilic association was significantly affected by the pH value, and a detailed study will be reported in the continued article.



Scheme 2.

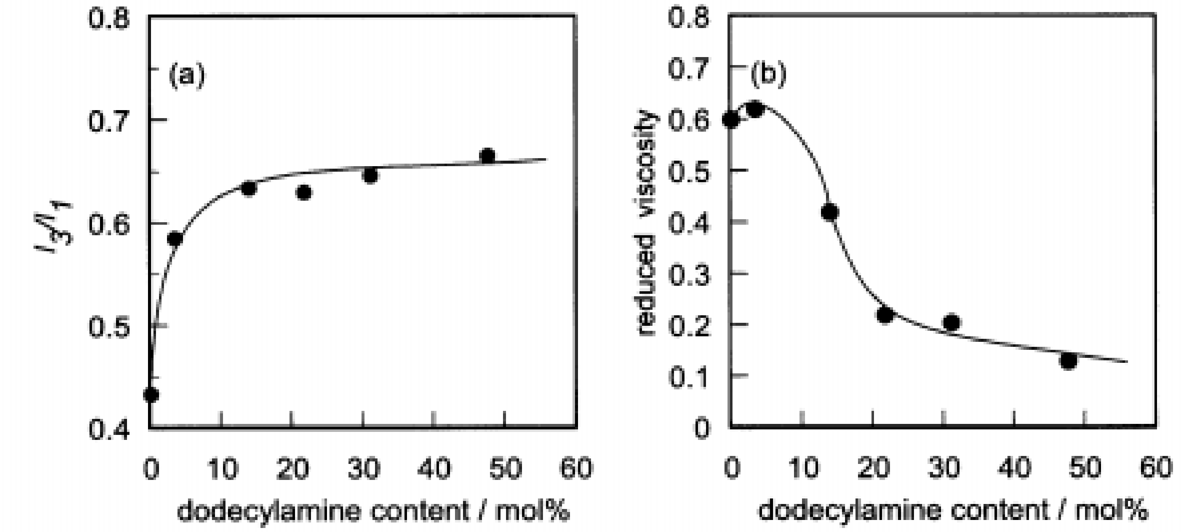


Figure 2. Plot of the I_3/I_1 ratio in pyrene florescence spectra of the Py-labeled DDA-PASP-Na at pH 7 (a) and the reduced viscosity at pH 7 and 0.1 g•dL^{-1} (b) as a function of the DDA content.

On the other hand, the reduced viscosity of DDA-PASP-Na decreased from 10 mol-% DDA content and with the increasing mole fraction of DDA units in the polymer, as shown *Figure 2b*, suggesting that the polymer extent in aqueous solution decreased with increasing DDA unit. These results indicated that the intramolecular hydrophobic association occurred by inducing the *N*-dodecyl aspatamide units in PASP-Na. This tendency was similar to the measurement of the MnO_2 dispersion capacity. This result suggested that DDA-PASP-Nas possessed a surface activity and the intramolecular hydrophobic association might affect the MnO2 dispersion capacity.

The biodegradability was estimated by the OECD 301C method (Modified MITI Test) and evaluated by the removed TOC value because the BOD values of the same sample were more scattered than the TOC value. Values for the amine-modified PASP were 14 - 21 %, which was significantly lower than that of PASP. However, these PASP derivatives apparently exhibited biodegradability compared with PAA-Na, *i.e.*, the biodegradation degree, which was measured based on the data of DDA_4-PASP-Na and DDA_{46}-PASP-Na, showed 16 % and 21 %, respectively. The decrease in the biodegradability was similar to the result that PASP obtained from the thermal bulk polycondensation which contained the branched and/or opened amide groups shows a low biodegradability [11]. This result indicated that the biodegradability was significantly affected by the branched structure.

Conclusion

The reaction of poly(succinimide) (PSI) with dodecylamine (DDA) proceeded to form the partially DDA-modified PSI. DDA was effectively introduced into PSI without decreasing the molecular weight throughout the reaction. Sodium DDA-modified poly(aspartate) (DDA-PASP-Na) was easily obtained by the alkali hydrolysis of the corresponding PSI derivative. The MnO_2-dispersing property of DDA-PASP-Na was higher than that of PASP-Na. The results of the viscosity measurement and the fluorescence study using DDA-PASP-Na and its pyrene-labeled one indicated that the introduction of the DDA unit into PASP-Na caused the intramolecular hydrophobic association. Although the biodegradability of DDA-modified PASP was lower than that of PASP, the PASP derivatives apparently exhibited biodegradability compared with PAA-Na. These results suggested that the DDA-modified PASP had the possibility of being used as a biodegradable dispersant.

References

1. Zhang YX, Da AH, Hogen-Esch TE, Butler GB (1991) In Water Soluble Polymers: Synthesis, Solution Properties and Application; Shalaby SW, MaCormick CL, Butler GB. (Eds.); ACS Symposium Series 467. ACS, Washington, DC. (pp 159)
2. MaCormick CL, Bock J, Schultz DN (1989) Encyclopedia of Polymer Science and Engineering; John Wiley, 17:730.
3. Bock J, Varadaraj R, Schultz DN, Maurer JJ (1994) In Macromolecular Complexes in Chemistry and Biology. Solution Properties of Hydrophobically Associating Water-Soluble Polymers; Dubin P, Bock J, Davis R, Schultz DN, Thies C. (Eds.); Springer-Verlag, Berlin, (pp 33)
4. Astafieva I, Zhong ZF, Eisenberg A (1993) Macromolecules 26: 7339.
5. Zhong L, Barlow RJ, Eisenberg A (1995) Macromolecules 28: 6055.
6. Dubin PL, Strauss UP (1970) J Phys Chem 74: 2842.
7. Yamamoto H, Mizusaki M, Yoda K, Morishima Y (1998) Macromolecules 31: 3588.
8. Chang Y, McCormick CL (1993) Macromolecules 26: 6121.
9. Morishima Y, Nomura S, Ikeda T, Seki M, Kamachi K (1995) Macromolecules 28: 2874.
10. Tomida M, Nakato T, Kuramochi M, Shibata M, Matsunami S, Kakuchi T (1996) Polymer 37: 4435.
11. Nakato T, Kusuno A, Kakuchi T (2000) J Polym Sci, Part A: Polym Chem 38: 127
12. Neri P, Antoni G, Benvenuti F, Cocola F, Gazzei G (1973) J Med Chem 16: 893.
13. Abe Y, Matsumura S (1980) Yukagaku 29: 748.
14. Kalyanasundaram K, Thomas JK (1977) J Am Chem Soc 99: 2039.