Surface-Active Properties of Poly(*N*-alkylsubstituted acrylamide)s and Their Adsorption onto Polystyrene Latex Particles in Water

Keisuke ASADA, Munehiro TATARA, Tadashi TAKAGI, and Katsutoshi NAGAI[†]

*Department of Materials Science and Engineering, Yamagata University,
Jonan, Yonezawa 992, Japan*

(Received August 11, 1995)

ABSTRACT: Surface-active properties of copolymers of *N,N*-dimethylacrylamide (DMA) with *n*-alkylsubstituted acrylamides, namely as *n*-butylacrylamide (NBA), *n*-hexylacrylamide (NHA), *n*-octylacrylamide (NOA), *n*-dodecylacrylamide (NDA), and their adsorption onto polystyrene (PS) latex particles were studied at 25°C in water. Surface tension lowering ($\Delta\gamma$) at a concentration of 0.1 g dL⁻¹, where adsorption at air-water interface is close to saturation, increased with the content of *N*-alkylacrylamide units for respective copolymers containing different *N*-alkylacrylamide units. The dependence was stronger for copolymers with *N*-alkylacrylamides bearing the higher alkyl group. The amount of adsorption (W_s) onto PS particles at saturation also increased with the content of *N*-alkylacrylamide units in the copolymers. W_s linearly increased with $\Delta\gamma$ for copolymers with NBA and those with lower contents of NHA and NOA which do not form intramolecular hydrophobic microdomains, whereas copolymers of NDA and those with higher contents of NHA and NOA, which form the microdomains, exhibited large W_s but a small increase with $\Delta\gamma$. W_s were lower and also slightly increased with $\Delta\gamma$ for polymers of DMA, *N*-acryloylpyrrolidine (APR) and *N*-isopropylacrylamide (IPA). It was deduced that the adsorptions of polymers and copolymers used here at air-water and PS particle-water interfaces are mainly governed by their overall hydrophobicity and that of their alkyl groups of *n*-alkylacrylamide units, respectively.

KEY WORDS *n*-Alkylsubstituted Acrylamides / Polystyrene Latex / Surface Tension / Adsorption / Intramolecular Hydrophobic Microdomains /

Recently, there has been considerable interest in polymeric surfactants in connection with their applications as dispersing agents in water-borne paints, inks and adhesives. Polymeric surfactants are superior to low molecular weight surfactants in stabilization of solid dispersions.¹ This is due to both their strong adsorption onto solid particles and diversity of their conformation adsorbed at the solid surfaces.² Although water-soluble polymers and their hydrophobically modified derivatives are generally utilized as dispersing agents for polymer dispersion systems,^{3–10} relatively few works have been made on the structural requirements of such polymers.

The adsorption of nonionic polymers onto latex particles is mainly governed by a hydrophobic interaction between the polymer and the particle.⁴ We found that copolymers of *N,N*-dimethylacrylamide (DMA) with *n*-alkylacrylamides of different alkyl chain lengths more strongly adsorb onto polystyrene (PS) latex dispersions than PDMA¹¹ and that it is responsible for the enhanced electrolyte stability of the dispersions in the presence of the copolymers.¹² Such copolymers are composed of hydrophilic DMA units and hydrophobic *N*-alkylsubstituted acrylamide units. Homopolymers of *N*-alkylsubstituted acrylamides also have amphiphilic structures because of hydrophilic amide and hydrophobic alkyl groups in their monomeric units. Some of them are water-soluble and exhibit cloud points in water, similarly to nonionic surfactants of low molecular weight.¹³ Thus, polymers and copolymers of *N*-alkylsubstituted acrylamides can be regarded as non-ionic polymeric surfactants.

Although most polymeric surfactants synthesized hitherto are block and graft types of copolymers with

hydrophilic and hydrophobic segments,^{8,9,14–20} water-soluble homopolymers and copolymers other than block and graft copolymers, exhibiting relatively high surface activities, have been also found recently.^{21–23} However, little study has been made systematically on the structures of surface-active polymers, especially nonionic polymers. Polymers and copolymers of *N*-alkylsubstituted acrylamides have some advantages for studying properties of polymeric surfactants: they can be easily synthesized and their hydrophile-lipophile balance can be readily controlled by varying alkyl chain length and copolymer composition.

Lowering in surface tension by amphiphilic polymers in aqueous system is due to the adsorption at nonpolar air-polar water interface, and is also related to their hydrophobicity. Therefore, there may be a relationship between the adsorptions of amphiphilic polymers at air-water and polymer particle-water interfaces. In this work, we studied the surface-active properties of polymers of DMA, *N*-acryloylpyrrolidone (APR) and *N*-isopropylacrylamide (IPA) and copolymers of DMA with *N*-alkylsubstituted acrylamides of *n*-alkyl groups of butyl, hexyl, octyl, dodecyl groups, and their adsorption onto polystyrene (PS) latex particles in aqueous systems, and discuss the relationship between maximum lowering in surface tension and the amount of adsorption onto PS particles at saturation.

EXPERIMENTAL

Materials

DMA, APR, and ST were received from Tokyo Kasei Ind. Co., Ltd., Mitsui Toatsu Chem. Co., Ltd., and Wako Pure Chemicals Ind. Ltd., respectively, and distilled under reduced pressure after dehydration. IPA

[†] To whom all correspondence should be addressed.

was received from Kojin Co., Ltd. and recrystallized from mixed solvents of *n*-hexane and benzene (9:1 by volume). *N*-*n*-butylacrylamide (NBA), *N*-*n*-hexylacrylamide (NHA), *N*-*n*-octylacrylamide (NOA), and *N*-*n*-dodecylacrylamide (NDA) were prepared by the reactions of acryloyl chloride with the corresponding amines. NBA, NHA, and NOA were purified by distillation under reduced pressure. NDA was repeatedly recrystallized from acetone. The structure of the resulting *N*-alkylsubstituted acrylamides was confirmed by ^1H NMR (JOEL JNM-EX270) and no contamination in the monomers was detected by HPLC.

Ion-exchanged water was double-distilled before use. Other solvents were also purified by distillation after dehydration.

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Potassium persulfate (KPS) was used as received.

Polymers and copolymers were synthesized by polymerization and copolymerization with AIBN as initiator in dioxane at 60°C in nitrogen atmosphere and purified by repeated reprecipitation into diethyl ether. Copolymer composition was determined using ^1H NMR spectroscopy. Molecular weights of the polymers and copolymers were in the range of 1.4×10^5 to 3.5×10^5 as determined by GPC measurements using a Toyo Soda HLC-802A in dimethylformamide as solvent.

Anionic polystyrene (PS) latexes were prepared by emulsifier-free emulsion polymerization of ST with KPS as initiator at 70°C. The resulting PS latexes were repeatedly centrifuged to remove some particles of small size. Purified latex particles were 0.86 μm in average diameter with a standard deviation of 0.02 μm , as determined using scanning electron microscopy (Hitachi S-415). Zeta potential of the particles was -14.7 mV in 1.0 mM KCl, as determined from electrophoretic mobility measured by zeta potentiometer (Mitamura 5-17).

Measurements of Properties of Aqueous Polymer Solutions

Surface tension (γ) of aqueous polymer solutions was measured at 25°C on a Wilhelmy-type surface tensiometer (Kyowa Type CBVP A-3) with a platinum measuring plate which was suspended from an electrobalance into the sample solution in a glass container.

Cloud points of aqueous polymer solutions were determined from transmittance at 500 nm as measured using a UV-VIS spectrophotometer (Shimadzu UV-210A).

Fluorescence spectra of pyrene as probe in aqueous polymer solutions were recorded at 25°C on a fluorospectrometer (Hitachi F-4010). Excitation wave length was 340 nm and intensity ratios (I_1/I_3) of pyrene emission peaks at 374 and 385 nm were recorded.

Measurements of Adsorbed Amount of Polymers

The amounts of polymers adsorbed onto PS latex particles in aqueous systems were determined as follow. A PS latex dispersion of a concentration of 0.5 wt% was prepared using aqueous polymer solutions of concentration of 0.2×10^{-2} to 7.6×10^{-2} g dL $^{-1}$ and incubated for 20 h at 25°C. This incubation time was sufficient to reach the equilibrium for adsorption. The dispersions

were filtered using a membrane filter of an average pores of 0.2 μm in diameter. Polymer concentration in the filtrate was determined using a UV-VIS spectrophotometer (Shimadzu MPS-2000). The amount of adsorption was estimated by subtracting the residual amount of polymer in the filtrate from the initial amount in the solution.

RESULTS AND DISCUSSION

Surface Tensions of Aqueous Solutions of Poly(*N*-alkyl-substituted acrylamide)s

Figure 1 shows surface tension against polymer concentration for aqueous solutions of PAPR and P(DMA-*co*-NBA) containing NBA units of 25.7 mol%, as examples. As polymer concentration increases, the surface tension begins to rapidly decrease at a concentration and then gradually approaches a constant value for the polymer and copolymer, respectively. The concentration dependence for PAPR is similar to that for low molecular weight surfactants. In general, the surface tension for the latter remains unchanged at concentrations above their critical micelle concentration.²⁴ On the other hand, no intramolecular or intermolecular association appears to take place in both the polymer and copolymer solutions even at a concentration of 0.1 g dL $^{-1}$, because I_1/I_3 of pyrene fluorescence in their solutions, shown in Table I, are close to that in water. The copolymer exhibits higher surface activity compared with PAPR, though their aqueous solutions have comparable cloud points. Thus, the surface tension at a polymer concentration of 0.1 g dL $^{-1}$ is fairly close to a minimum which corresponds to saturation for the adsorption at air-water interface. Figure 2 shows surface tension at a concentration of 0.1 g dL $^{-1}$ as a function of the product of carbon number (*n*) of the alkyl group in *n*-alkylacrylamide units and mole fraction (*f*) of the units in copolymers, which could be proportional to the hydrophobicity of copolymers. The surface tensions decrease with increase in the product, *nf*, for respective

Figure 1. Dependence of surface tension on polymer concentration for PAPR (○) and P(DMA-*co*-NBA) with NBA content of 25.7 mol% (△) at 25°C in water.

Table I. Characteristics of poly(*N*-alkylsubstituted acrylamide)s

Run No.	Polymer P(M ₁ - <i>co</i> -M ₂)	Content of M ₂	Cloud point ^a	Surface tension ^b	<i>I</i> ₁ / <i>I</i> ₃ ^c	<i>W</i> _s ^d
		mol%	°C	mN m ⁻¹		mg m ⁻²
A-1	PDMA	0	> 100	64.4	1.72	0.93
A-2	PAPR	0	53.0	58.5	1.72	1.03
A-3	PIPA	0	34.0	41.9	1.75	1.56
B-4	P(DMA- <i>co</i> -IPA)	56.0	56.0	50.1	1.73	1.19
C-5	P(DMA- <i>co</i> -NBA)	1.6	> 100	63.9	1.85	1.04
C-6	P(DMA- <i>co</i> -NBA)	12.7	> 100	56.2	1.81	1.65
C-7	P(DMA- <i>co</i> -NBA)	25.7	52.5	48.9	1.81	2.20
C-8	P(DMA- <i>co</i> -NBA)	30.4	40.1	43.9	1.83	2.30
C-9	P(DMA- <i>co</i> -NBA)	36.0	31.4	41.2	1.73	2.54
D-10	P(DMA- <i>co</i> -NHA)	1.5	> 100	60.1	1.70	1.96
D-11	P(DMA- <i>co</i> -NHA)	13.9	42.6	41.1	1.51	2.92
E-12	P(DMA- <i>co</i> -NOA)	1.7	> 100	59.1	1.73	2.30
E-13	P(DMA- <i>co</i> -NOA)	6.9	47.7	45.9	1.37	3.13
F-14	P(DMA- <i>co</i> -NDA)	1.9	> 100	51.9	1.53	2.77
F-15	P(DMA- <i>co</i> -NDA)	2.8	> 100	48.2	1.38	2.87
F-16	P(DMA- <i>co</i> -NDA)	4.4	46.8	45.6	1.35	3.12

^a Determined at a polymer concentration of 0.1 g dL⁻¹. ^b Determined at a polymer concentration of 0.1 g dL⁻¹ at 25°C. ^c Intensity ratio of pyrene fluorescence at 374 and 385 nm in polymer solution of 0.1 g dL⁻¹ at 25°C. ^d Adsorbed amounts of polymers onto PS latex particles at saturation at 25°C.

Figure 2. Dependence of surface tension on *nf* for copolymers of DMA with NBA (○), NHA (△), NOA (□), and NDA (◇).

copolymers containing different *n*-alkylacrylamide units. As expected, the copolymers with highly hydrophobic NDA exhibit great decrease in surface tension even at only small content of NDA units, while the surface tension gradually decreases with increasing comonomer content for copolymers with less hydrophobic NBA.

Surface tension at a concentration of 0.1 g dL⁻¹ for typical polymers and copolymers used in this study is summarized in Table I, together with cloud points and *I*₁/*I*₃ of pyrene fluorescence for polymer solutions of the same concentration. *I*₁/*I*₃ refers to the intensity ratio of the first and third bands in the fluorescence spectrum of pyrene, used to monitor the polarity of the medium surrounding the molecule. The value is high (1.81) in polar water and low (0.61) in nonpolar aliphatic hydrocarbons.²⁵ When pyrene is solubilized into aqueous micelles, it is also relatively lower (1.12).²⁶ The copolymers with higher content of NHA and NOA units and those with NDA exhibit values near 1.5 and lower, and hence these copolymers appear to form intramolecular hydrophobic domains like aqueous micelles, but homopolymers or other copolymers not. A PDMA solution has no cloud point up to about 100°C and hence the polymer is highly hydrophilic. Solutions of PAPR and PIPA exhibit cloud points at 53.0 and 34.0°C,

Figure 3. Adsorption isotherms of copolymers with DMA onto PS latexes at 25°C in water. Copolymer: C-7 (○), D-11 (△), E-13 (□), F-16 (◇), and B-4 (●).

respectively. Thus, PIPA is the most hydrophobic in three polymers and PAPR has an intermediate hydrophilicity between PIPA and PDMA. Surface tension of the polymer solutions decreases in the same order of PDMA, PAPR, and PIPA as that for the cloud points. Similarly, copolymer solutions with lower cloud points also display lower surface tension. However, no definite relationship between cloud point and surface tension, valid for all copolymer solutions, could be found at present.

Adsorption Characteristics of Poly(N-alkylsubstituted acrylamide)s onto PS Latex Particles

Figure 3 shows adsorption isotherms for polymers B-4, C-7, D-11, E-13, and F-16, cloud points of their solutions being in the range of 46.8 to 56.0°C, onto PS latex particles. The amount of adsorption increases and then levels off with increasing polymer concentration. The isotherms are apparently of Langmuir type, and expressed by the following equation:

$$1/W = 1/W_s + (1/aW_s)(1/c) \quad (1)$$

where *W* and *W*_s, in mg m⁻², are the amounts of adsorption at equilibrium concentration *c* in g dL⁻¹ and at

saturation, respectively. The constant, a , expressed in dL g^{-1} , increases with the slope of isotherms in the range of equilibrium concentration where the amount of adsorption is below the plateau levels, which is related to the extent of interaction between polymer and PS latex particle.²⁷ There is a tendency for the constant, a , to decrease with increasing alkyl chain length of *N*-alkylacrylamide units, as discussed elsewhere.¹¹ W_s can be estimated using eq 1 and also presented in Table I. The amount of adsorption at saturation for P(DMA-*co*-NOA) (E-13) is slightly higher than that for P(DMA-*co*-NHA) (D-11), though the former is more hydrophilic than the latter, as judged by cloud points of their solutions. Furthermore, even copolymers with small content of NDA units, F-14 and F-15, with no cloud points below 100°C, give relatively high W_s . Thus, W_s seem not to be directly correlated with the cloud points as a measure of hydrophilic-lipophile balance for the polymers. W_s of polymers with comparable content of *N*-alkylacrylamide units, C-5, D-10, E-12, and F-14, increase with alkyl chain length of their units, which is similar to surface tension lowering for the copolymers. This suggests that W_s may be correlated to maximum lowering of surface tension.

W_s are plotted against surface tension lowering ($\Delta\gamma$) at a concentration of 0.1 g dL^{-1} in Figure 4. Curve A in Figure 4 represents the relationship between W_s and $\Delta\gamma$ for three polymers and P(DMA-*co*-IPA). These exhibit low W_s , which are slightly dependent on $\Delta\gamma$. For P(DMA-*co*-NBA)s, there is a fairly good correlation between the W_s and $\Delta\gamma$, as shown by curve B, in which W_s linearly increases with $\Delta\gamma$. The relationship for copolymers with NHA, NOA, and NDA is represented by curve C. W_s greatly increases and then gradually with $\Delta\gamma$. The gradual increase is observed for copolymers forming hydrophobic domains in their aqueous solutions, as mentioned before.

The three curves suggest interesting points in regard to the adsorption of poly(*N*-alkylsubstituted acrylamide)s at air-water and PS particle-water interfaces. For homopolymers and P(DMA-*co*-IPA) having small alkyl or alkylene groups, adsorption onto PS particles is almost insensitive to structural variation of polymers, indicating that the hydrophobicity of chain backbones could be a main factor governing adsorption.¹¹ Copolymers with NBA leave their hydrophobic the butyl groups bare in water, as shown by I_1/I_3 close to that in water, and hence the butyl groups in addition to the chain backbones contribute the adsorption onto PS particles. Thus, W_s should increase with the content of NBA units. The increase in the content of NBA units also makes copolymers more hydrophobic, resulting in increased $\Delta\gamma$. Copolymers with low content of NHA and NOA units, which do not form hydrophobic domains in their solutions, display a relationship similar to that for copolymers with NBA. Their longer alkyl chains make larger contribution to adsorption onto PS particles. For copolymers forming hydrophobic domains, some of alkyl groups are concealed in the domains, making their hydrophobic effect lower. This seems to be responsible for the gradual increase in W_s shown by curve C in Figure 4. The domains are left open, with the alkyl groups directed toward the air, at the air-water interface and

Figure 4. Amount of adsorption at saturation (W_s) versus surface tension lowering ($\Delta\gamma$). Copolymers of DMA: NBA (○), NHA (△), NOA (□), NDA (◇), and IPA (●), polymers of DMA (▲), APR (■), and IPA (◆).

the alkyl groups greatly contribute to surface tension lowering. Thus, the hydrophobicity of the alkyl groups in the polymers and copolymers of *N*-alkylsubstituted acrylamides used here could be a large factor governing adsorption at the PS particle-water interface, whereas adsorption at air-water interface may be related to overall hydrophobicity.

We are now investigating the dependence of $\Delta\gamma$ on copolymer composition for copolymers of DMA with *n*-alkylacrylamides in detail, which will be reported in near future.

CONCLUSIONS

The adsorption of copolymers of DMA with *N*-alkylacrylamides of *n*-butyl to *n*-dodecyl groups and homopolymers of DMA, APR, and IPA at air-water and PS particle-water interfaces was examined in aqueous systems and the relationship between both adsorptions was studied. The surface tension of aqueous solutions began to suddenly decrease at a certain concentration and then came close to a constant value. Surface tension lowering ($\Delta\gamma$) at a polymer concentration of 0.1 g dL^{-1} near the surface saturation at air-water interface increased with the content of *n*-alkylacrylamide units for respective copolymers with different *n*-alkylacrylamide units. The dependence was stronger for copolymers with *N*-alkylacrylamide of the higher alkyl group. The amount of adsorption (W_s) onto PS latex particles at saturation linearly increased with $\Delta\gamma$ for copolymers with NBA and those containing small amounts of NHA and NOA units which do not form intramolecular hydrophobic domains in their aqueous solutions. Copolymers with higher content of NHA and NOA units and those with NDA forming the domains exhibited a gradual increase in W_s with increasing $\Delta\gamma$. W_s of homopolymers were lower and slightly depended on $\Delta\gamma$. Based on the results obtained here, it was deduced that the adsorptions of copolymers at the air-water and PS-water interfaces are dependent on the overall hydrophobicity of copolymers and that of their alkyl groups as well as their chain backbones, respectively.

REFERENCES

1. M. J. Rosen, "Surfactants and Interfacial Phenomena," 2nd ed, Wiley, New York, N.Y., 1989, Chapter 9.
2. A. Takahashi, *J. Jpn. Soc. Colour Mater. (SHIKIZAI)*, **67**, 496 (1994).
3. "Polymer Adsorption and Dispersion Stability," E. D. Goddard and B. Vincent, Ed., American Chemical Society, Washington, D.C., 1984.
4. K. Furusawa and T. Tagawa, *Colloid Polym. Sci.*, **263**, 353 (1985).
5. T. Cosgrove, T. L. Crowley, K. Ryan, and J. R. P. Webster, *Colloids Surface*, **51**, 255 (1990).
6. J. Meadows, P. A. Williams, M. J. Garvey, and R. Harrop, *J. Colloid Interface Sci.*, **139**, 260 (1990).
7. P.-L. Kuo and T.-C. Chang, *J. Appl. Polym. Sci.*, **44**, 869 (1992).
8. Th. F. Tadros and B. Vincent, *J. Phys. Chem.*, **84**, 1575 (1980).
9. M. B. Einarson and J. C. Berg, *J. Colloid Interface Sci.*, **155**, 165 (1993).
10. B. Vincent, *Adv. Colloid Interface Sci.*, **4**, 193 (1974).
11. K. Asada, J. Kido, N. Kuramoto, and K. Nagai, *Kobunshi Ronbunshu*, **52**, 504 (1995).
12. K. Asada, J. Kido, N. Kuramoto, and K. Nagai, *Kobunshi Ronbunshu*, **52**, 559 (1995).
13. S. Ito, *Kobunshi Ronbunshu*, **46**, 437 (1989).
14. H.-Q. Xie, X.-D. Wu, and J.-S. Guo, *J. Appl. Polym. Sci.*, **54**, 1079 (1994).
15. S. Kobayashi, H. Uyama, E. Ihara, and T. Saegusa, *Macromolecules*, **23**, 1586 (1990).
16. M. Miyamoto, K. Aoi, H. Yamanaka, and T. Saegusa, *Polym. J.*, **24**, 405 (1992).
17. S. Shoda, E. Masuda, M. Furusawa, and S. Kobayashi, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 1489 (1992).
18. I. Piirma, *Makromol. Chem., Macromol. Symp.*, **35/36**, 467 (1990).
19. S. Kanaoka, M. Minoda, M. Sawamoto, and T. Higashimura, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 1127 (1990).
20. C. Maltesh, Q. Xu, P. Somasundaran, W. J. Benton, and H. Nguyen, *Langmuir*, **8**, 1511 (1992).
21. T. Okubo, *J. Colloid Interface Sci.*, **125**, 386 (1988).
22. R. J. Weinert, *J. Appl. Polym. Sci.*, **38**, 1295 (1989).
23. H. E. Rios, J. S. Rojas, I. C. Gamboa, and R. G. Barraza, *J. Colloid Interface Sci.*, **156**, 388 (1993).
24. D. Attwood and A. T. Florence, "Surfactant Systems," Chapman and Hall, London, 1983, p 8.
25. K. Kalyanasundaram and J. K. Thomas, *J. Am. Chem. Soc.*, **99**, 2039 (1977).
26. F. M. Winnik, A. R. Davidson, G. K. Hamer, and H. Kitano, *Macromolecules*, **25**, 1876 (1992).
27. H. Inoue, K. Konno, T. Kawai, and M. Katsumoto, *Nippon Kagaku Kaishi*, 358 (1995).