

# Synthesis of Copolymers of *N,N*-Dimethyl Acrylamide and Methacrylate Esters and their Surface Tensions

RAYMOND J. WEINERT, *BP America, 4440 Warrensville Center Road, Warrensville, Ohio 44128*, and I. PIIRMA, *Department of Polymer Science, University of Akron, Akron, Ohio 44325*

## Synopsis

A systematic study of the preparation of *N,N*-dimethylacrylamide (NDMA)/methacrylic ester statistical copolymers was conducted. The methacrylic ester comonomers used in the copolymerizations were ethyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-dodecyl, *n*-hexadecyl, and *n*-octadecyl methacrylates. It was found that the NDMA copolymers could be prepared in three molecular weight regions  $1.0 \times 10^4$ ,  $2.0 \times 10^5$ , and greater than  $1.0 \times 10^6$  ( $[\eta]$  in water at 30°C of 0.1, 0.6, and greater than 1.5 dL/g, respectively). The molecular weights of the copolymers were dependent on the solvent employed in the polymerizations and on the presence of chain transfer agent (*t*-dodecyl mercaptan). All copolymer compositional analyses were made by 400 MHz <sup>1</sup>H-NMR spectroscopy. The NDMA/methacrylic ester copolymers decreased the surface tension of water in the order:  $C_4 = C_6 > C_8 > C_{12} > C_{16} > C_2 = C_{18} > P(\text{NDMA})$ , from lowest surface tension (35 dyn/cm) to highest surface tension (59 dyn/cm).

## INTRODUCTION

The size and distribution of functionalized sites on polymeric surfactants in the stabilization of colloidal particles in aqueous systems provide a unique way of incorporating various desired surfactant properties into a single large molecule. Poly(*N,N*-dimethylacrylamide) [P(NDMA)] is a water-soluble polymer which does not form strong hydrogen bridges.<sup>1</sup> The polymer has low chain flexibility with few, if any, molecules in an actual coil: It forms few aggregates while still remaining water soluble.<sup>2</sup> The reactivity of *N,N*-dimethylacrylamide with many comonomers allows one to prepare a wide range of copolymers. Copolymerization of NDMA with hydrophobic monomers can produce copolymers which have intriguing hydrodynamic and surfactant properties. Such copolymers provide a unique way to investigate the effects of copolymer composition, length of the hydrophobic anchor, and stabilizer molecular weight on the surfactant properties of the stabilizer.

## EXPERIMENTAL

### Materials and Procedures

Ethyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-dodecyl, *n*-hexadecyl, and *n*-octadecyl methacrylate (methacrylic ester) monomers were used as received from Poly-sciences.

The *N,N*-dimethyl acrylamide (NDMA) monomer was received from Poly-science. A 10 wt % aqueous solution was made of the NDMA monomer and its pH was determined. In case the NDMA was found to be acidic, because of the residual acrylic acid from the manufacturing process, distillation of the monomer was needed. The acidic NDMA monomer was mixed with anhydrous calcium carbonate (reagent grade from Fisher) and distilled under reduced pressure at a temperature of 115°C. If the pH of the monomer was neutral or basic, the NDMA monomer was used as received.

Distilled water was purified by means of a Barnstead Still until it had an electrical resistivity of 18 M $\Omega$ . This was defined in the experiments as nanopure water.

Benzene (thiophene-free), toluene, *n*-heptane (CMS Omni-Solv), *N,N*-dimethylformamide (DMF), and deuterated chloroform were used as received.

### Preparation of P(NDMA) and P(NDMA–Methacrylic Ester) Copolymers

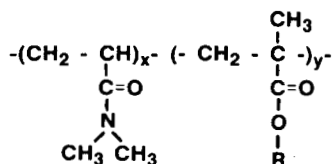
The polymerization experiments were conducted in dry clean 7-oz crown cap glass bottles. The nitrile rubber septa were extracted twice for successive 24-h periods with toluene and followed by ethanol by means of a Soxhlet extractor to remove any inhibitors or retarders to free radical polymerizations which might be contained within the rubber. The septa were dried at 60°C overnight at reduced pressure and stored in a dark cabinet. The bottles were charged with monomer(s), solvents, *t*-dodecyl mercaptan (chain transfer agent), and 2,2'-azobis(2,4-dimethylvaleronitrile) (DuPont: Vazo 52) initiator. The bottles were capped (two hole metal cap) and purged with ultrahigh purity (UHP) argon or nitrogen for 5 min via 6-in. stainless steel needles inserted through the septa. The polymerizations were conducted in a rotating polymerization bath at 60°C. The weight percent of monomer to solvent in all cases was kept below 20% to avoid autocatalytic (Trommsdorff<sup>3</sup>) conditions.

The polymerization of NDMA and NDMA with methacrylic esters was accomplished in benzene, toluene, hexane, and heptane. The use of benzene and toluene permitted the polymerization to be carried out in solution, while the alkane systems caused the copolymers to precipitate as fine powders.

The copolymers produced in benzene or toluene were recovered by pouring the reaction products into large excesses of *n*-alkanes (a nonsolvent for the NDMA copolymers); a fine white polymer was produced. Figure 1 shows the structure of the copolymer.

### Proton Nuclear Magnetic Resonance Spectroscopy (<sup>1</sup>H-NMR) Analysis of NDMA Copolymers<sup>4,5</sup>

The proton nuclear magnetic resonance spectra of the copolymers were recorded on a Varian 4VX 400 instrument using deuterated chloroform as the solvent. The —CH<sub>2</sub>—O— proton resonance of the methacrylate ester of the copolymer exhibits a broad peak at 3.75–4.10 ppm. The N—CH<sub>3</sub> proton resonance exhibits a peak in the 2.74–3.25 ppm region. The —CH— proton resonance region appears at 2.00–2.74 ppm, the —CH<sub>3</sub>— proton resonance of



Where R:

$\text{-CH}_2\text{CH}_3$	(ethyl)	$=\text{C}_2$
$\text{-(CH}_2)_3\text{CH}_3$	(n-butyl)	$=\text{C}_4$
$\text{-(CH}_2)_5\text{CH}_3$	(n-hexyl)	$=\text{C}_6$
$\text{-(CH}_2)_7\text{CH}_3$	(n-octyl)	$=\text{C}_8$
$\text{-(CH}_2)_{11}\text{CH}_3$	(n-dodecyl)	$=\text{C}_{12}$
$\text{-(CH}_2)_{15}\text{CH}_3$	(n-hexadecyl)	$=\text{C}_{16}$
$\text{-(CH}_2)_{17}\text{CH}_3$	(n-octadecyl)	$=\text{C}_{18}$

NOTE: R is defined as the methacrylic ester side chain length.

Fig. 1. Structure of copolymer.

the methacrylate ester side chain appear in the 1.00–2.00 ppm region, and the terminal  $\text{-CH}_3$  proton resonance appears in the 1.10–0.70 ppm region. The deuterated chloroform single hydrogen peak at a proton resonance of 2.75 ppm was used as a reference point. The spectra of many of the copolymers exhibited a sharp peak of residual water at a resonance of about 1.85 ppm, which was confirmed by deuterium oxide exchange experiments.<sup>4</sup> The composition was determined from the areas of the methacrylate ester proton resonance  $\text{-CH}_2\text{-O-}$  versus the  $\text{-N-(CH}_3)_2$  proton resonance in the copolymer (Fig. 2).

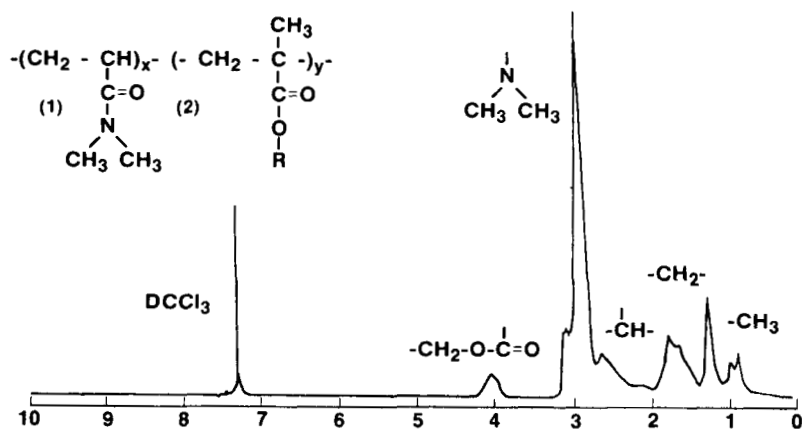


Fig. 2.  $^1\text{H-NMR}$  spectrum of NDMA/HEXYL methacrylate copolymer in  $\text{DCCl}_3$ .

### Surface Tension and Interfacial Tension Determinations

The surface tension measurements were made using nanopure water (18.2 M $\Omega$  resistivity) in chromic acid cleaned glassware. The surface measurements were performed on a Wilhelmy Balance (Wilhelmy plate technique<sup>6-8</sup>) consisting of a Cahn 2000 microbalance (19–100  $\mu$ g range) and an Oriel motorized stage mounted on a vibration isolating table (Newport Corp.). The measurements were made using a roughened platinum plate ( $1 \times 0.0054 \times 0.4197$  cm) and clean 100 mL glass breakers. All measurements were performed at a rate of  $55.4 \pm 0.5$   $\mu$ m/s in duplicate and were recorded on an X-Y recorder. Prior to each measurement the roughened platinum plate was soaked in a 50% Ultrapure HCl/nanopure water solution and then rinsed with nanopure water. The surface tension measurements were made directly with aqueous polymer solutions. All measurements were made in duplicate at zero buoyancy. The force was determined from the following equation:

$$mg - 2(w + a)(\gamma_{LV} \cos \theta) - waz\rho g \quad (1)$$

where  $m$  is the mass reading minus the mass of the plate in air,  $g$  is the gravitational constant 981 cm/s<sup>2</sup>,  $w$  is the plate width,  $a$  is the plate thickness,  $z$  is the depth of immersion of the plate, and  $\rho$  is the density of the plate. The surface tension at the liquid–vapor (water–air) interface was calculated using

$$\gamma_{LV} = mg/[2(w + a)] \quad (2)$$

The accuracy of the surface tension experimental assembly was tested with a series of surface tension standards which were mixtures of ethyl cellosolve and formamide prepared by the method described in ASTM D2578. The experimental values were found to be accurate to within 2 dyn/cm up to 50 dyn/cm, as shown in Table I. Above this threshold, it was necessary to extrapolate the X-Y recording to zero buoyancy for surface tension determinations.

TABLE I  
Data for Ethyl Cellosolve and Formamide Commercial Surface Tension Standards  
Obtained at 25°C<sup>a</sup>

Surface tension predicted from standards (dyn/cm)	Surface tension experimental (dyn/cm)	Surface tension extrapolated (dyn/cm)
32	32	32
36	35	35
40	41	41
44	45	45
50	52	51
54	57	55
66	70	64

<sup>a</sup> Experimental error  $\pm 2$  dyn/cm.

TABLE II  
Data Employed in Determining the Reactivity Ratios in the Copolymerization of Ethyl Methacrylate with NDMA Using the Fineman-Ross Method

Ester in feed (mol)	Ester in polymer (mol)	$F$	$f$
0.252	0.344	0.337	0.525
0.743	0.806	2.895	4.152
0.919	0.941	11.281	15.970
		$r_1$	$r_2$
	Fineman-Ross	1.40	0.61

### Preparation of P(NDMA) and NDMA-Methacrylic Ester Copolymers

A Fineman-Ross<sup>9</sup> experiment was conducted for the ethyl methacrylate-NDMA copolymer system in benzene. The reactions were "short-stopped" at low conversion by the injection of 10 mL of 1000 ppm solution of hydroquinone monomethyl ether (MEHQ) in benzene. The contents of the bottle were emptied into hexane. Water was added to the system and the copolymer was recovered from the water/hexane interface by means of a separatory funnel. The copolymer was dried at 50°C overnight and its composition was determined by <sup>1</sup>H-NMR spectroscopy. The reactivity ratios were graphically determined by the method developed by Fineman and Ross. The reactivity ratios were 1.40 ( $r_1$ ) and 0.61 ( $r_2$ ), respectively, where 1 denotes the methacrylic ester and 2 denotes the NDMA. These reactivity ratios are in good agreement with the reactivity ratios between methyl methacrylate (1) and NDMA (2) of 1.8 ( $r_1$ ) and 0.45 ( $r_2$ ) determined by North and Scallan.<sup>10</sup> The reactivity ratios for ethyl methacrylate with NDMA are tabulated in Table II.

## RESULTS AND DISCUSSION

Polymers in three distinctive molecular weight regions were produced by the addition of *t*-dodecyl mercaptan to the solvents (solution and suspension). Additions of 3 phm *t*-dodecyl mercaptan to benzene (or toluene) or *n*-heptane polymerization systems produced NDMA copolymers with intrinsic viscosities in water, at a temperature of 30°C, of 0.1 and 0.5–0.7 dL/g, respectively. *n*-Heptane systems produced NDMA copolymers with intrinsic viscosities in water, at a temperature of 30°C, of greater than 1 dL/g. These three regions are shown in Figure 3.

The  $K$  and  $a$  values at 25°C for the homopolymers in water were used to calculate the  $M_v$  of the homopolymers (Table III). The  $K$  and  $a$  values for the P(NDMA) dissolved in water at a temperature of 30°C were determined from the plot of  $\ln(M_v)$  vs.  $\ln([\eta])$ . The  $K$  and  $a$  values were graphically determined to be  $53.3 \times 10^{-5}$  dL/mol and 0.575, respectively, as shown in Table III and Figure 4.

Intrinsic viscosities at a temperature of 30°C in water of 0.1, 0.6, and greater than 1.0 dL/g for NDMA copolymers roughly corresponded to molec-

Temperature: 30°C  
 Solvent: Water  
 Composition: 6 wt% Methacrylic Ester

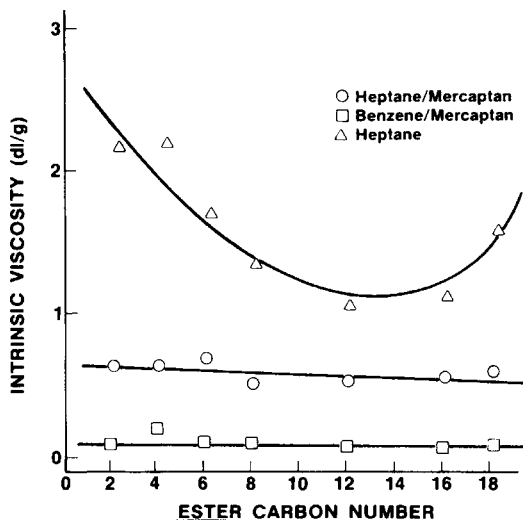


Fig. 3. Effect of polymerization conditions of NDMA copolymer molecular weight (intrinsic viscosity).

ular weights of  $1.0 \times 10^4$ ,  $2.0 \times 10^5$ , and greater than  $1.0 \times 10^6$ . The  $M_v$  values for the NDMA polymers in water were found to be of the same order of magnitude as the  $M_w$ 's calculated from gel permeation chromatography measurements. These values are tabulated in Table IV.

The weight average molecular weights of a series of hexyl methacrylate/NDMA copolymers with 6 wt % hexyl methacrylate at 0.1, 0.6, and 1.4 dL/g were determined by Dr. P. S. Qutubuddin and Mr. A. Batia at Case Western Reserve University utilizing a home-built laser light scattering apparatus. These are tabulated in Table V and show fairly good agreement with viscosity average molecular weight data.

TABLE III  
 Data Employed for the Determination of  $K$  and  $a$  Values of P(NDMA)  
 in Water at 30°C<sup>a</sup>

$[\eta]$ at 25°C in water	$M_v$ ( $\times 10^{-5}$ )	$\ln(M_v)$	$[\eta]$ at 30°C in water	$\ln([\eta])$ 30°C in water
$0.34 \pm 0.05$	1.86	12.13	0.55	-0.60
$1.00 \pm 0.13$	4.94	13.11	1.09	0.09
$1.75 \pm 0.02$	10.59	13.87	1.48	0.39

<sup>a</sup> Calculation: equation:  $\ln[\eta] = \ln K + a \ln(M_v)$ ; intercept:  $\ln K = -7.54$ ,  $K = 53.3 \times 10^{-5}$  dL/g; slope:  $a = 0.575$ .

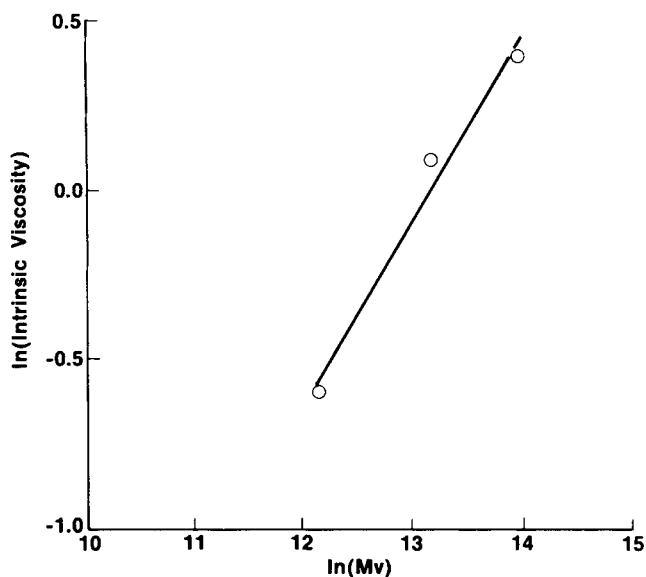

 Fig. 4.  $K$  and  $\alpha$  values for P(NDMA) at 30°C in water.

 TABLE IV  
 Gel Permeation Chromatography Data for P(NDMA)  
 and Its Copolymers<sup>a</sup>

Surfactant type	Methacrylic ester (wt %)	$[\eta]$ , 30°C	$M_v \times 10^{-5}$ (aqueous)	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	$M_w/M_n$
Homopolymer	0	0.1	0.1	$0.5 \pm 0.0$	$0.3 \pm 0.0$	$1.60 \pm 0.0$
Ethyl	15.8	0.1	0.1	$0.5 \pm 0.01$	$0.3 \pm 0.0$	$1.60 \pm 0.0$
Homopolymer	0	0.6	2.0	$3.7 \pm 0.2$	$2.2 \pm 0.01$	$1.65 \pm 0.0$
Homopolymer	0	1.5	10.0	$5.7 \pm 0.2$	$1.9 \pm 0.34$	$3.06 \pm 0.5$

<sup>a</sup>Solvent DMF; temperature 60°C; Comparison to styrene standards.

 TABLE V  
 Light Scattering Data for Surfactants

Hexyl Methacrylate (wt %)	$[\eta]$	$M_v \times 10^{-6}$	$M_w \times 10^{-6}$ light scattering
0.0	0.58	1.9	2.1
11.9	1.67	12.1	36.0

TABLE VI  
Surface Tension of Aqueous Solutions of NDMA Copolymers

Methacrylic ester	Carbon in ester	Surface tension (dyn/cm)
Water		70.0
NDMA homopolymer	0	59.5
Ethyl	2	53.5
Butyl	4	36.5
Hexyl	6	35.5
Hexyl	6	36.5
Octyl	8	42.0
Dodecyl	12	44.0
Hexadecyl	16	50.5
Octadecyl	18	53.0

### Surface Tension Properties of NDMA–Methacrylic Ester Copolymers

Surface tension is related directly to the surface energy of a material in contact with another material, in this case water. As the constituents at the surface and in the liquid phase change, there is a change in the surface energy and the resulting angle of wetting (contact angle  $\theta$ ) between the phases. Surface tension forces (energies) are retractive in their nature, the materials flow into shapes that minimize surface energy, e.g., spheres. The molecules at the interface are stressed by the pull of the molecules below them creating a high energy envelope around the system. The strain on the molecules at the

Composition: 6 Wt% Methacrylic Ester in NDMA Copolymer  
Temperature: 25° C  
Intrinsic Viscosity of Copolymer 30° C Water > 1.0 dL/g  
Concentration: 5g/L

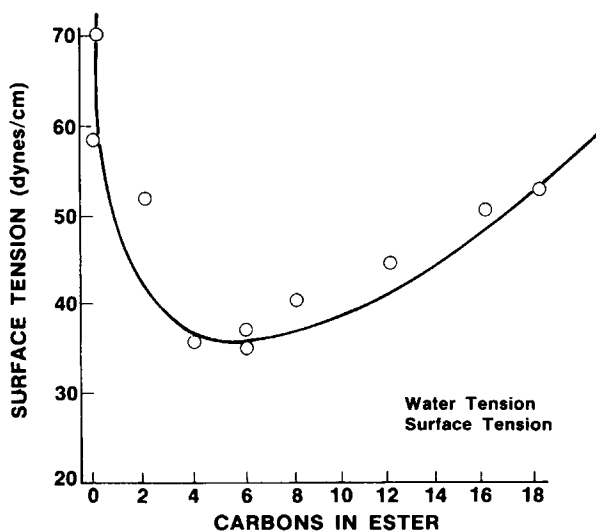


Fig. 5. Effect of methacrylic ester length on the surface tension of water.



liquid-to-vapor interfaces can be measured by physical methods and related to the actual surface energetics of a system.

The surfactant activity of water soluble homopolymers of NDMA [P(NDMA)], and NDMA/methacrylic ester copolymers in aqueous systems were determined through surface tension measurements using the Wilhelmy plate method. The water used in all the experiments was found to have surface tension of 70 dyn/cm. This indicated a slight impurity in the system, since the surface tension of water at room temperature is normally accepted to be 72 dyn/cm.<sup>11</sup> The error will have little effect overall, since all solutions were made in the same water and the temperature was at 25°C (room temperature). All measurements were made in at least duplicate and had a standard deviation of  $\pm 2$  dyn/cm.

The effect of ester carbon length on the surface tension of water was determined for aqueous solutions of NDMA copolymers at constant weight percent composition (6 wt %) and high molecular weights ( $[\eta]_{30} > 1.0$  dL/g) at a concentration of 5 g/L (0.5 g/dL). NDMA homopolymer dissolved in water reduced the surface tension of water to about 50 dyn/cm. The methacrylate ester/NDMA copolymers lowered the surface tension of water even further. Minimum surface tensions were obtained with the aqueous solutions of butyl and hexyl methacrylate/NDMA copolymers which had a surface tension of as low as 3 dyn/cm, as shown in Table VI and Figure 5.

The order of effectiveness for lowering the surface tension of water was found to be:

$$C_4 = C_6 > C_8 > C_{12} > C_{16} > C_2 = C_{18} > \text{P(NDMA)} \quad (3)$$

lower surface tension	higher surface tension	(3)
(higher surface activity)	(lower surface activity)	

The NDMA copolymers were found to be good emulsion stabilizers and are shown to be such in a separate publication.

### References

1. J. E. Brandrup and H. Immergut, *Polymer Handbook*, 2nd ed., 1975, Vol. III, p. 147.
2. L. Trossarelli and M. Meirone, *J. Polym. Sci.*, **57**, 445-452 (1962).
3. E. Trommsdorff, H. Kohle, and P. Legally, *Makromol. Chem.*, **1**, 169 (1948).
4. R. J. Weinert, M. S. Thesis, University of Akron, 1982.
5. Huynh-Ba-Gia and J. E. McGrath, *Polym. Bull.*, **2**, 837-40 (1980).
6. W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1478 (1947).
7. O. J. Murphy and J. E. Wainright, preprint, presentation at the 170th Electrochemical Society, San Diego, Oct. 1986 and *Proceedings of the Symposium on Surfaces, Inhibition and Passivation*, to appear.
8. L. Wilhelmy, *Ann. Phys.*, **119**, 117 (1863).
9. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**(2), 259-265 (1950).
10. A. M. North and A. M. Scallan, *Polymer*, **5**(9), 447-455 (1964).
11. J. Periard and G. Riess, *Kolloid Z. Z. Polym.*, 24801-24820 (1971); **76**, 127905 (1972).

Received October 29, 1988

Accepted November 1, 1988