

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

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Synopsis

A systematic study was made on the preparation of *N,N*-dimethylacrylamide (NDMA)/methacrylic ester statistical copolymers. 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: 1.0×10^4 , 2.0×10^5 , and greater than 1.0×10^6 ($[\eta]$ 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 a chain transfer agent (*t*-dodecyl mercaptan). All copolymer compositional analyses were made by 400 MHz $^1\text{H-NMR}$ spectroscopy. The NDMA/methacrylic ester copolymers decreased the surface tension of water in the order: $C_4 = C_6 > C_8 > C_{12} > C_{16} > C_2 = C_{18} > \text{P(NDMA)}$, lowest surface tension (35 dyn/cm) to highest surface tension (59 dyn/cm).

INTRODUCTION

The size and distribution of functionalized sites on polymeric surfactants used 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.¹ The polymer has low chain flexibility with few, if any, molecules in an actual coil. It forms few aggregates² while still remaining water-soluble. 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-science.

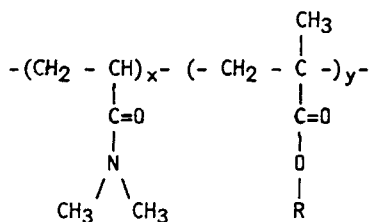
The *N,N*-dimethylacrylamide (NDMA) monomer was received from Poly-science. A 10 wt % aqueous solution was made of the NDMA monomer and the pH determined. If the NDMA was found to be acidic, there was residual acrylic acid from the manufacturing process present and distillation of the monomer was needed. 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 MΩ. 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 for successive 24-h periods with toluene and followed by ethanol with 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 ultra high purity (UHP) argon or nitrogen for 5 min via 6-in. stainless steel needles inserted through



Where R :

| | | |
|---|------------------------|-------------------|
| -CH ₂ CH ₃ | (ethyl) | = C ₂ |
| -(CH ₂) ₃ CH ₃ | (<i>n</i> -butyl) | = C ₄ |
| -(CH ₂) ₅ CH ₃ | (<i>n</i> -hexyl) | = C ₆ |
| -(CH ₂) ₇ CH ₃ | (<i>n</i> -octyl) | = C ₈ |
| -(CH ₂) ₁₁ CH ₃ | (<i>n</i> -dodecyl) | = C ₁₂ |
| -(CH ₂) ₁₅ CH ₃ | (<i>n</i> -hexadecyl) | = C ₁₆ |
| -(CH ₂) ₁₇ CH ₃ | (<i>n</i> -octadecyl) | = C ₁₈ |

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

Fig. 1. Structure of copolymer.

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 (Trommsdorff³) 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 (co)polymers to precipitate as fine powders.

The (co)polymers produced in benzene or toluene were recovered by pouring the reaction products into large excesses of *n*-alkanes [a nonsolvent for the NDMA (co)polymers]; a fine white polymer was produced (Fig. 1).

Proton Nuclear Magnetic Resonance Spectroscopy (¹H-NMR) Analysis of NDMA Copolymers^{4,5}

The proton nuclear magnetic resonance spectra of the copolymers were recorded on a Varian 4VX 400 instrument using deuterated chloroform as the solvent. The —CH₂—O— proton resonance of the methacrylate ester of the copolymer exhibits a broad peak at 3.75–4.10 ppm. The N—CH₃ 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 —CH₂— proton resonances of the methacrylate ester side chain appear in the 1.00–2.00 ppm region, and the terminal —CH₃ proton resonance appears in the 1.10–0.70 ppm region. The deuterated chloroform single hydrogen peak at 2.75 ppm was used as a reference point. The spectra of many of the (co)polymers exhibited a sharp peak of residual water at a resonance of about 1.85 ppm, which was confirmed by deuterium oxide exchange experiments.⁴ The composition was determined from the areas of the methacrylate ester proton resonance —CH₂—O— vs. the —N—(CH₃)₂ proton resonance in the copolymer (Fig. 2).

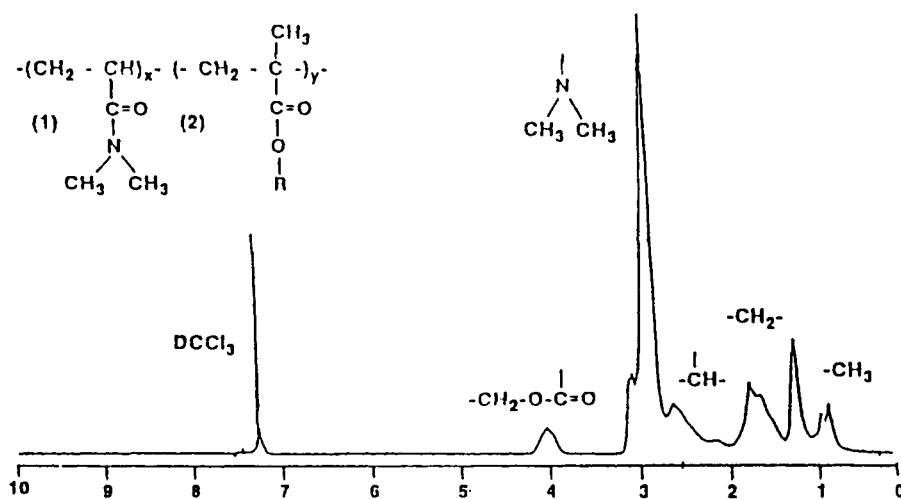


Fig. 2. ¹H-NMR spectrum of NDMA/hexyl methacrylate copolymer in DCCl₃.

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)⁶⁻⁸ consisting of a Cahn 2000 microbalance (10–100 μg 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) using clean 100 mL glass beakers. All measurements were performed at a rate of 55.4 ± 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 9M 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^2 , w is the plate width, a is the plate thickness, z is the depth of immersion of the plate, and ρ 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^a

| 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 |

^a Experimental error ± 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-Ross⁹ 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 a 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 the composition determined by ¹H-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 0.62 (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.¹⁰ 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 (parts per hundred monomer) *t*-dodecyl mercaptan to benzene (or toluene) or *n*-heptane polymerization systems produced NDMA (co)polymers with intrinsic viscosities of 0.1 and 0.5–0.7 dL/g, respectively, in water at a temperature of 30°C. *n*-Heptane systems produced NDMA (co)polymers with intrinsic viscosities of greater than 1 dL/g in water at a temperature of 30°C. 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 53.3×10^{-5} dL/mol and 0.575, respectively, as shown in Table III and Figure 4.

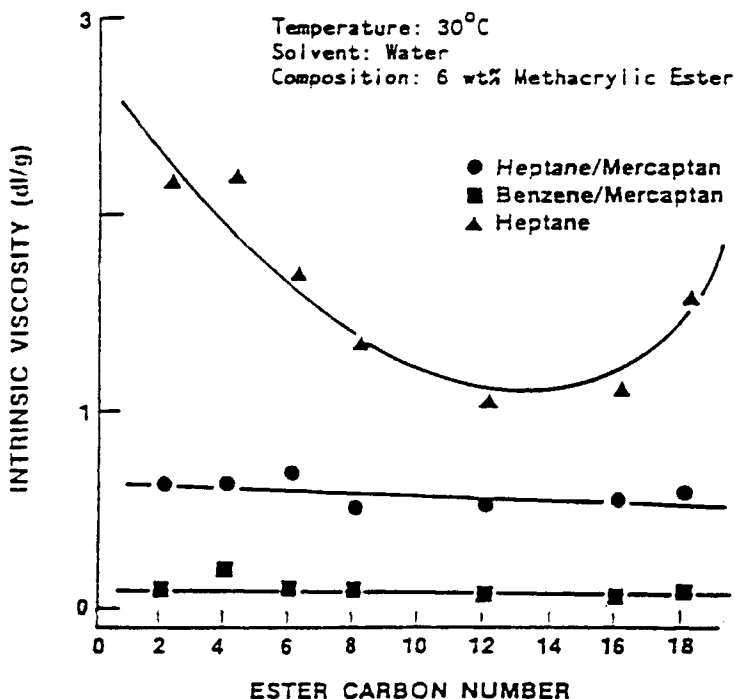


Fig. 3. Effect of polymerization conditions on NDMA copolymer molecular weight (intrinsic viscosity).

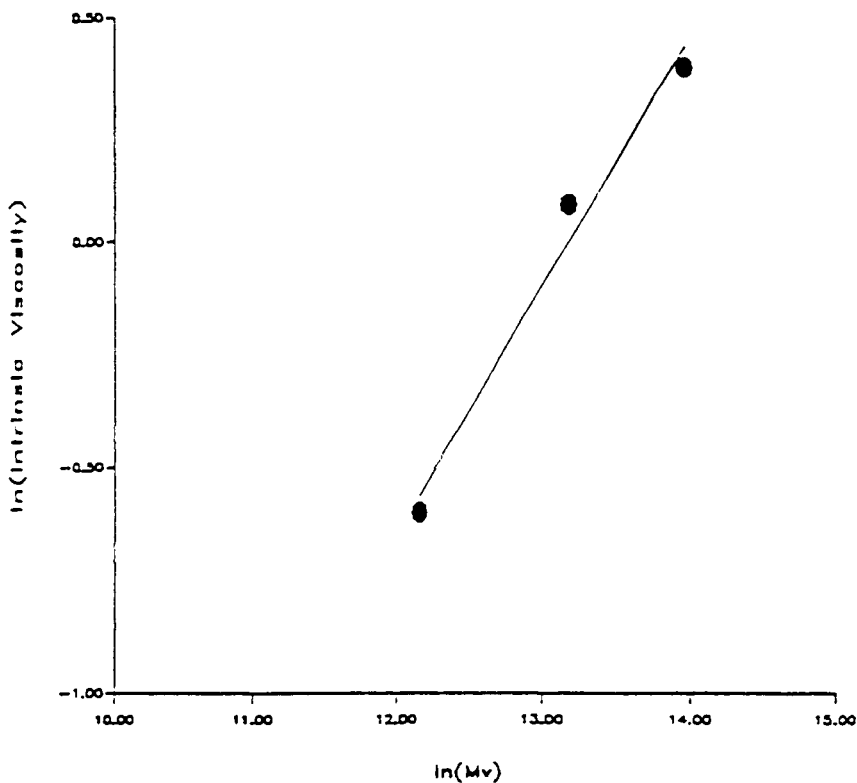
Intrinsic viscosities of 0.1, 0.6, and greater than 1.0 dL/g for NDMA (co)polymers at a temperature of 30°C in water roughly corresponded to molecular weights of 1.0×10^4 , 2.0×10^5 , and greater than 1.0×10^6 . The M_v values for the NDMA polymers in water were found to be of the same order of magnitude 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% 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 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^a

| $[\eta]$ 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 ± 0.05 | 1.86 | 12.13 | 0.55 | -0.60 |
| 1.00 ± 0.13 | 4.94 | 13.11 | 1.09 | 0.09 |
| 1.75 ± 0.02 | 10.59 | 13.87 | 1.48 | 0.39 |

^a 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. Calculated K and a values for P(NDMA) at 30°C in water.TABLE IV
Gel Permeation Chromatography Data For P(NDMA) and Its Copolymers^a

| Surfactant type | Methacrylic ester (wt %) | $[\eta]$ at 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 ± 0.0 | 0.3 ± 0.0 | 1.60 ± 0.0 |
| Ethyl | 15.8 | 0.1 | 0.1 | 0.5 ± 0.01 | 0.3 ± 0.0 | 1.60 ± 0.0 |
| Homopolymer | 0 | 0.6 | 2.0 | 3.7 ± 0.2 | 2.2 ± 0.01 | 1.65 ± 0.0 |
| Homopolymer | 0 | 1.5 | 10.0 | 5.7 ± 0.2 | 1.9 ± 0.34 | 3.06 ± 0.5 |

^aSolvent DMF; temperature 60°C; comparison to styrene standards.TABLE V
Light Scattering Data for Surfactants

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

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 (e.g., 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 θ) between the phases. Surface tension forces (energies) are retractive in their nature, and 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 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 a 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.¹¹ 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 ± 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 30 dyn/cm, as shown in Table VI and Figure 5.

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 |

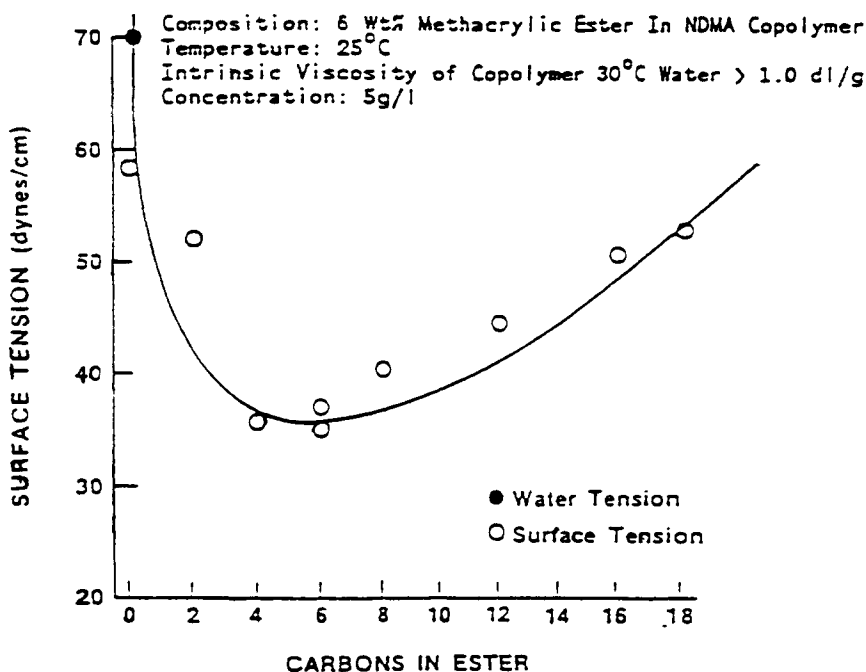
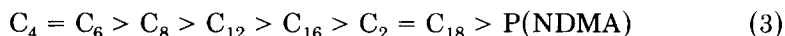


Fig. 5. Effect of methacrylic ester length on the surface tension of water.

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



lower surface
tension

higher surface
tension

(higher surface activity)

(lower surface activity)

The NDMA (co)polymers were found to be good emulsion stabilizers and are shown to be such in a separate publication.¹²

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