

High-Internal Phase Emulsions Under Shear.

II.

Co-surfactancy and Shear Stability

Peter N. Yaron^{ac}, Andrew J. Scott^a, Philip A. Reynolds^a, Jitendra P. Mata^{ab} and John

*W. White^{*a}*

^aResearch School of Chemistry, Australian National University, Canberra, ACT 0200,
Australia. Fax: 02 6125 0750; Tel: 02 6125 3575.

^b Bragg Institute, ANSTO, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

^c Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA
15213, USA

* jww@rsc.anu.edu.au

Supplementary Information.

PAM Syntheses. A system of nomenclature is introduced which has its base in the nature of the RAFT agent and monomers used. The block co-polymer was assigned the letter P (from 2-{[(dodecylsulfanyl)carbonothioyl]sulfanyl}propanoic acid or DoPATTC). Beyond that a number was used to denote the number of hydrophobic monomer units (in this case zero) and hydrophilic monomer units used in the polymerisation. Thus the synthesised polymer was denoted as P0-AM7, “AM” indicating the number of acrylamide units [11]. The product, bright yellow flakes, T_g 43 °C (by differential scanning calorimetry), was characterized by ^1H and ^{13}C spectra on a Varian 300 FT-NMR. Progress of the RAFT polymerisation was monitored by ^1H NMR, using $\text{CDCl}_3/\text{d}_6\text{-DMSO}$ as solvent. Gel Permeation Chromatography (GPC) was conducted using a Waters Breeze System operating a Waters 1515 Isocratic pump, column oven (35 °C) and Waters 2414 Refractive Index Detector.

Emulsion constituents

Table 1. Component amounts used for the SANS emulsion experiments performed on LOQ. Errors associated with the balance are $\pm 1 \times 10^{-4}$ g, but we have rounded the weights up to the point where, generally, differences between emulsions we wish to compare are 0.5 of the last significant digit quoted. That is, a weight of 0.30 g. has a variability between emulsions of 0.005 g.

Emulsion	Contrast	Emulsion	E25/66T (g)	PAM (g)	Hexadecane (g)	d-hexadecane (g)	AN/D2O (g)
1% PIBSA [8]	CM	c3	0.30	-	0.125	0.900	17.75
1% PIBSA [8]	UM	c5	0.30	-	0.910	-	17.55
1% PIBSA 0.5% C ₁₂ PAM	CM	d5	0.30	0.075	0.125	0.900	17.66
1% PIBSA 0.5% C ₁₂ PAM	UM	d7	0.30	0.075	0.910	-	17.66
1% PIBSA 0.05% C ₁₂ PAM	CM	d1	0.30	0.0075	0.125	0.900	17.75
1% PIBSA 0.05% C ₁₂ PAM	UM	d3	0.30	0.0075	0.910	-	17.75
1% PIBSA 0.5% C ₁₄ PAM	CM	a9a	0.30	0.078	0.126	0.922	17.75
1% PIBSA 0.5% C ₁₄ PAM	UM	a8a	0.30	0.078	0.910	-	17.75
1% PIBSA 0.25% C ₁₄ PAM	CM	a9d	0.30	0.039	0.126	0.922	17.75
1% PIBSA 0.25% C ₁₄ PAM	UM	a8d	0.30	0.039	0.910	-	17.75
1% PIBSA 0.05% C ₁₄ PAM	CM	a9c	0.30	0.0078	0.126	0.922	17.75
1% PIBSA 0.05% C ₁₄ PAM	UM	a8c	0.30	0.0078	0.910	-	17.75
1% PIBSA 0.005% C ₁₄ PAM	CM	a9b	0.30	0.00078	0.126	0.922	17.75
1% PIBSA 0.005% C ₁₄ PAM	UM	a8b	0.30	0.00078	0.910	-	17.75
1% PIBSA 0.5% C ₁₆ PAM	CM	a10a	0.30	0.080	0.126	0.922	17.66
1% PIBSA 0.5% C ₁₆ PAM	UM	a7a	0.30	0.080	0.926	-	17.66
1% PIBSA 0.25% C ₁₆ PAM	CM	a10d	0.30	0.040	0.126	0.922	17.75
1% PIBSA 0.25% C ₁₆ PAM	UM	a7d	0.30	0.040	0.926	-	17.75
1% PIBSA 0.05% C ₁₆ PAM	CM	a10c	0.30	0.0080	0.126	0.922	17.75
1% PIBSA 0.05% C ₁₆ PAM	UM	a7c	0.30	0.0080	0.926	-	17.75
1% PIBSA 0.005% C ₁₆ PAM	CM	a10b	0.30	0.0008	0.126	0.922	17.75
1% PIBSA 0.005% C ₁₆ PAM	UM	a7b	0.30	0.0008	0.926	-	17.75
0.3% PIBSA [8]	CM	c8	0.090	-	0.290	0.909	17.75
0.3% PIBSA [8]	UM	c9	0.090	-	1.080	-	17.75
0.3% PIBSA 0.5% C ₁₂ PAM	CM	d6	0.090	0.075	0.290	0.909	17.66
0.3% PIBSA 0.5% C ₁₂ PAM	UM	d8	0.090	0.075	1.080	-	17.66
0.3% PIBSA 0.25% C ₁₂ PAM	CM	b11a	0.090	0.038	0.290	0.909	17.75
0.3% PIBSA 0.25% C ₁₂ PAM	UM	a11a	0.090	0.038	1.090	-	17.75
0.3% PIBSA 0.05% C ₁₂ PAM	CM	d2	0.090	0.0075	0.290	0.909	17.75
0.3% PIBSA 0.05% C ₁₂ PAM	UM	d4	0.090	0.0075	1.090	-	17.75
0.3% PIBSA 0.025% C ₁₂ PAM	CM	f3	0.090	0.0038	0.290	0.909	17.75
0.3% PIBSA 0.025% C ₁₂ PAM	UM	f4	0.090	0.0038	1.090	-	17.75
0.3% PIBSA 0.005% C ₁₂ PAM	CM	f1	0.090	0.0008	0.290	0.909	17.75
0.3% PIBSA 0.005% C ₁₂ PAM	UM	f2	0.090	0.0008	1.09	-	17.75
0.3% PIBSA 0.5% C ₁₆ PAM	CM	b1a	0.090	0.080	0.290	0.909	17.75
0.3% PIBSA 0.5% C ₁₆ PAM	UM	a1a	0.090	0.080	1.090	-	17.75
0.3% PIBSA 0.25% C ₁₆ PAM	CM	b1d	0.090	0.040	0.290	0.909	17.75
0.3% PIBSA 0.25% C ₁₆ PAM	UM	a1d	0.090	0.040	1.090	-	17.75
0.3% PIBSA 0.05% C ₁₆ PAM	CM	b1c	0.090	0.0080	0.290	0.909	17.75
0.3% PIBSA 0.05% C ₁₆ PAM	UM	a1c	0.090	0.0080	1.090	-	17.75
0.3% PIBSA 0.005% C ₁₆ PAM	CM	b1b	0.090	0.0008	0.290	0.909	17.75
0.3% PIBSA 0.005% C ₁₆ PAM	UM	a1b	0.090	0.0008	1.090	-	17.75
0.3% PIBSA microemulsion	CM	-	0.90		2.86	9.26	0.6
5% C ₁₂ PAM microemulsion	UM	-	-	0.89	-	-	17.75

Emulsion rheology

Table 2. Shear stress as a function of applied shear for all emulsions. ‘*’ indicates shear rates with a detectable change in the incoherent scattering background along with anomalously low viscosities which we have attributed to the loss of sample in the beam path. ‘N/A’ indicates emulsions’ that failed to form.

Shear stress, τ , in units of Pa Emulsion			Shear Rate					
	Contrast	Name	0.1 Hz	1 Hz	100 Hz	500 Hz	1000 Hz	2000 Hz
1% PIBSA [8]	CM	c3	-	29.8	132	325	350	600
1% PIBSA [8]	UM	c5	-	23.5	172	325	430	640
1% PIBSA 0.5% C ₁₂ PAM	CM	d5	-	15.1	-	223.5	-	420
1% PIBSA 0.5% C ₁₂ PAM	UM	d7	-	216	-	228.5	-	544
1% PIBSA 0.05% C ₁₂ PAM	CM	d1	-	26.1	-	271	-	550
1% PIBSA 0.05% C ₁₂ PAM	UM	d3	-	20.2	-	283	-	784
1% PIBSA 0.5% C ₁₄ PAM	CM	a9a	10.2	21.7	-	345	-	720
1% PIBSA 0.5% C ₁₄ PAM	UM	a8a	1.72	3.81	-	170	-	540
1% PIBSA 0.25% C ₁₄ PAM	CM	a9d	17.4	47.5	-	385	-	*
1% PIBSA 0.25% C ₁₄ PAM	UM	a8d	5.48	19.3	-	275	-	*
1% PIBSA 0.05% C ₁₄ PAM	CM	a9c	9.6	37.6	-	385	-	*
1% PIBSA 0.05% C ₁₄ PAM	UM	a8c	5.32	23.6	-	260	-	*
1% PIBSA 0.005% C ₁₄ PAM	CM	a9b	18.5	63.3	-	330	-	*
1% PIBSA 0.005% C ₁₄ PAM	UM	a8b	6.27	23.6	-	305	-	*
1% PIBSA 0.5% C ₁₆ PAM	CM	a10a	7.38	15	-	270	-	640
1% PIBSA 0.5% C ₁₆ PAM	UM	a7a	6.46	23	-	315	-	*
1% PIBSA 0.25% C ₁₆ PAM	CM	a10d	8.25	24.5	-	280	-	340
1% PIBSA 0.25% C ₁₆ PAM	UM	a7d	2.3	5.18	-	190	-	720
1% PIBSA 0.05% C ₁₆ PAM	CM	a10c	11.2	29.9	-	350	-	*
1% PIBSA 0.05% C ₁₆ PAM	UM	a7c	10.9	36.7	-	365	-	*
1% PIBSA 0.005% C ₁₆ PAM	CM	a10b	7.64	32.8	-	360	-	*
1% PIBSA 0.005% C ₁₆ PAM	UM	a7b	16.7	44.9	-	450	-	*
0.3% PIBSA [8]	CM	c8	-	10.1	86	195	320	520
0.3% PIBSA [8]	UM	c9	-	9.8	90	195	320	520
0.3% PIBSA 0.5% C ₁₂ PAM	CM	d6	-	9.36	-	131.5	-	312
0.3% PIBSA 0.5% C ₁₂ PAM	UM	d8	-	6.62	-	105	-	282
0.3% PIBSA 0.25% C ₁₂ PAM	CM	b11a	4.2	13.2	-	170	-	420
0.3% PIBSA 0.25% C ₁₂ PAM	UM	a11a	0.342	0.96	-	85	-	340
0.3% PIBSA 0.05% C ₁₂ PAM	CM	d2	-	8.76	-	137.5	-	348
0.3% PIBSA 0.05% C ₁₂ PAM	UM	d4	-	25	-	101.5	-	306
0.3% PIBSA 0.025% C ₁₂ PAM	CM	f3	-	7.85	-	170	-	376
0.3% PIBSA 0.025% C ₁₂ PAM	UM	f4	-	9.4	-	181	-	384
0.3% PIBSA 0.005% C ₁₂ PAM	CM	f1	-	9.2	-	175	-	460
0.3% PIBSA 0.005% C ₁₂ PAM	UM	f2	-	7.8	-	170	-	420
0.3% PIBSA 0.5% C ₁₆ PAM	CM	b1a	0.342	0.96	-	85	-	340
0.3% PIBSA 0.5% C ₁₆ PAM	UM	a1a	-	4.73	-	265	-	480
0.3% PIBSA 0.25% C ₁₆ PAM	CM	b1d	N/A	N/A	N/A	N/A	N/A	N/A
0.3% PIBSA 0.25% C ₁₆ PAM	UM	a1d	N/A	N/A	N/A	N/A	N/A	N/A
0.3% PIBSA 0.05% C ₁₆ PAM	CM	b1c	N/A	N/A	N/A	N/A	N/A	N/A
0.3% PIBSA 0.05% C ₁₆ PAM	UM	a1c	N/A	N/A	N/A	N/A	N/A	N/A
0.3% PIBSA 0.005% C ₁₆ PAM	CM	b1b	3.81	10	-	60	-	*
0.3% PIBSA 0.005% C ₁₆ PAM	UM	a1b	2.53	8.37	-	70	-	280

Table 3 Yield stress values, in units of Pa, obtained from y-intercept values extrapolated from shear stress versus shear rate plots. ‘N/A’ indicates negative extrapolated values. These values were due to the anomalously low viscosity values obtained at 2000 Hz for these emulsions that affected the fits.

Yield stress, τ_c , in units of Pa of emulsions from shear stress vs. shear rate plots

Emulsion	τ_c (Pa)
1% PIBSA [1]	143
1% PIBSA 0.5% C12 PAM	12.8
1% PIBSA 0.05% C12 PAM	16.9
1% PIBSA 0.5% C14 PAM	2.9
1% PIBSA 0.25% C14 PAM	N/A
1% PIBSA 0.05% C14 PAM	N/A
1% PIBSA 0.005% C14 PAM	N/A
1% PIBSA 0.5% C16 PAM	2.5
1% PIBSA 0.25% C16 PAM	N/A
1% PIBSA 0.05% C16 PAM	N/A
1% PIBSA 0.005% C16 PAM	N/A
0.3% PIBSA [1]	43
0.3% PIBSA 0.5% C12 PAM	7.1
0.3% PIBSA 0.25% C12 PAM	10.5
0.3% PIBSA 0.05% C12 PAM	6
0.3% PIBSA 0.025% C12 PAM	6.9
0.3% PIBSA 0.5% C16 PAM	3.4
0.3% PIBSA 0.25% C16 PAM	N/A
0.3% PIBSA 0.05% C16 PAM	N/A
0.3% PIBSA 0.005% C16 PAM	2

Table 4 Yield stress (in Pa) values obtained from Princen (equation 2) [17].

UM 0.3% PIBSA 0.5% C16 PAM	UM 0.3% PIBSA 0.005% C16 PAM	UM 1% PIBSA 0.5% C16 PAM	UM 1% PIBSA 0.25% C16 PAM	UM 1% PIBSA 0.05% C16 PAM	UM 1% PIBSA 0.005% C16 PAM
0.032	0.004	0.038	0.011	0.013	0.014
UM 1% PIBSA 0.5% C14 PAM	UM 1% PIBSA 0.25% C14 PAM	UM 1% PIBSA 0.05% C14 PAM	UM 1% PIBSA 0.005% C14 PAM		
0.027	0.020	0.009	0.008		
UM 0.3% PIBSA 0.5% C12 PAM	UM 0.3% PIBSA 0.025% C12 PAM	UM 0.3% PIBSA 0.05% C12 PAM	UM 0.3% PIBSA 0.005% C12 PAM	UM 1% PIBSA 0.5% C12 PAM	UM 1% PIBSA 0.05% C12 PAM
0.019	0.004	0.005	0.004	0.028	0.008

Model fitting of isotropically averaged SANS data. Model fit parameters of the SANS data from all contrast matched (CM) and contrast unmatched (UM) emulsions as a function of the shear profile applied in Figure 2. Typical errors for all emulsion

fits in the free parameters are: $\phi_{\text{micelle}}: \pm 0.0009$; shell SLD: $\pm 5 \times 10^{-8} \text{ \AA}^{-2}$; background: ± 0.003 ; $(\rho_{\text{water}} - \rho_{\text{layer}}) \times A_V: \pm 0.06$; fraction of bilayer (frac): ± 0.009 .

Table 5. Values of the free parameters obtained from model fitting for 0.3% PIBSA 0.025% C₁₂ PAM contrast-matched (CM) and contrast unmatched (UM) emulsions.

CM 0.3% PIBSA 0.025% C₁₂ PAM	1 Hz	500 Hz	1 Hz-2	2000 Hz	1 Hz-3 Hz
Radius (Å)	26.9	28.7	26.5	26.7	21.5
Φ_{micelle} (Vol. Frac.)	0.028	0.022	0.029	0.020	0.024
background (cm⁻¹)	0.33	0.33	0.32	0.32	0.31
$(\rho_{\text{water}} - \rho_{\text{layer}}) \times \sigma$	17.1	16.0	19.3	20.9	34.8

UM 0.3% PIBSA 0.025% C₁₂ PAM	1 Hz	500 Hz	1 Hz-2	2000 Hz	1 Hz-3 Hz
shell SLD (Å⁻²)	1.31E-07	1.11E-06	3.24E-07	1.78E-06	4.06E-07
background (cm⁻¹)	0.36	0.35	0.35	0.33	0.35
$(\rho_{\text{water}} - \rho_{\text{layer}}) \times \sigma$	9.71	8.89	10.15	11.95	15.34
frac	0.28	0.12	0.26	0.07	0.27

Table 6 Micelle radii ($\text{\AA}$) in emulsions, averaged over all shear rates. Notation C_{12} , C_{14} , C_{16} denotes length of PAM tail.

1.0% PIBSA emulsions		0.3% PIBSA emulsions	
CM	PAM%	CM	PAM%
31(1)	0	31(1)	0
31(1)	C_{12} 0.05	27(3)	C_{12} 0.005
30(1)	C_{12} 0.50	26(2)	C_{12} 0.025
20(1)	C_{14} 0.005	28(2)	C_{12} 0.05
24(1)	C_{14} 0.05	30(1)	C_{12} 0.50
31(1)	C_{14} 0.25	-	-
36(2)	C_{14} 0.50	-	-
20(1)	C_{16} 0.005	20(2)	C_{16} 0.005
25(1)	C_{16} 0.05	-	-
25(2)	C_{16} 0.25	-	-
28(2)	C_{16} 0.50	30(2)	C_{16} 0.5

Anisotropic SANS data

Table 7 SANS anisotropy (%) at 500 Hz shear interval. Notation C_{12} , C_{14} , C_{16} denotes length of PAM tail.

1% PIBSA emulsions			0.3% PIBSA emulsions		
CM	UM	PAM%	CM	UM	PAM%
0	9	0	0	7	0
7	22	C_{12} 0.05	3	28	C_{12} 0.005
10	40	C_{12} 0.50	6	30	C_{12} 0.025
7	15	C_{14} 0.005	7	25	C_{12} 0.05
8	20	C_{14} 0.05	12	40	C_{12} 0.50
6	26	C_{14} 0.25	-	-	-
12	25	C_{14} 0.50	-	-	-
2	9	C_{16} 0.005	4	12	C_{16} 0.005
3	10	C_{16} 0.05	-	-	-
15	40	C_{16} 0.25	-	-	-
20	45	C_{16} 0.50	7	35	C_{16} 0.50