Electronic Supplementary Information (ESI)

Thermo-switchable surfactant gel**

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1. Experimental Section

Materials. Plamitic acid (Sigma, ≥ 99.0%), *N,N*-dimethyl-1,3-propanediamine (DMPDA, Alfa Aesar, 99.0%, GC) and 1,3-propanesultone (Alfa Aesar, ≥ 99.0%, GC) were used without further purification. Other chemicals were analytical grade, and water was triply distilled by a quartz water purification system. Surfactant PDAS (molecular formula $C_{24}H_{50}N_2O_4S$; molecular weight 462.73) with purity 98.87% (HPLC) was synthesized in the following part ("2. synthesis of PDAS").

The micellar solution was prepared by adding 25 mmol (11.568 g) PDAS, 12.5 mmol (0.731g) NaCl and desired amount of the triply distilled water to a 25 mL measuring cylinder, and then left at room temperature for two or more days to obtain a clearly solution (1.0 M PDAS solution in the presence of 0.5 M NaCl).

Characterization. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz) in CD_3OD at room temperature. ESI HRMS spectra were taken on the Bruker Daltonics Data Analysis 3.2 system. HPLC analysis was performed on Waters HPLC system equipped with Alltech 2000 ELSD detector and using a reverse phase (C18) column.

Rheology. Rheological experiments were taken on a Physica MCR 301 (Anton Paar, Austria) rotational rheometer equipped with concentric cylinder geometry CC17 (ISO3219). Dynamic frequency spectra were conducted in the linear viscoelastic regimes. All the experiments were carried out using stress-controlled mode, and CANNON standard oil was used to calibrate the instrument before the measurements. The temperature was set to ± 0.01 °C in accuracy by Peltier temperature control device, and a solvent trap was used to minimize water evaporation during the measurements.

Cryo-TEM. Cryo-TEM observations of the 1.0 M PDAS solution in the presence of 0.5 M NaCl at 30 °C and 40 °C were prepared in a controlled environment vitrification system. The climate chamber temperature was 25–28 °C, and the relative humidity was kept close to saturation to prevent evaporation from the sample during preparation. Each of 5 μL of the 30 °C and 40 °C specimen was placed on a carbon-coated holey film supported by a copper grid, and gently blotted with filter paper to obtain a thin liquid film (20–400 nm) on the grid. The grid was quenched rapidly into liquid ethane at -180 °C and then transferred into liquid nitrogen (-196 °C) for storage. Then the vitrified specimen stored in liquid nitrogen was transferred into a JEM2010 cryo-microscope using a Gatan 626 cryo-holder and its workstation. The acceleration voltage was 200 kV, and the working temperature was kept below -170 °C. The images were recorded digitally with a charge-coupled device camera (Gatan 832) under low-dose conditions with an under-focus of approximately 3 μm.

2. Synthesis of PDAS

Surfactant PDAS was synthesized via the recently-reported procedure[1] for the surfactant C_{18}AMP3SB. The experimental details are as follows. Plamitic acid (200 mmol, 51.28 g), *N,N*-dimethyl-1,3-propanediamine (DMPDA, 300 mmol, 30.65), and NaF (0.30 g) were introduced into a three-necked flask. The reaction mixture was refluxed at 160 °C under N_2 atmosphere for 8 h, during which the by-product H_2O was absorbed continuously by Al_2O_3 placed in a solvent still head. The excess of DMPDA was removed and the residues were washed with cold acetone [3 × 500 ml containing H_2O (10 ml) to remove NaF], and the purified product was dried to obtain the *N*-plamitamidopropyl-*N,N*-dimethylamine. Then the obtained intermediate, 1,3-propanesultone (300 mmol, 36.64g) and ethyl acetate (500 ml) were introduced to a round flask and refluxed around 80 °C for 8 h. The occurred white precipitate was washed with 3 × 500 ml acetone and

dried to obtain 55.13 g final PDAS with purity 98.87 %, total yield 59.57 %. ^{1}H NMR (300 MHz, CD_3OD): δ0.90 (t, J = 6.62 Hz, 3H), 1.29 (m, 24H), 1.61 (m, 2H), 1.99 (m, 2H), 2.19-2.24 (m, 4H), 2.88 (t, J = 6.71 Hz, 2H), 3.11 (s, 6H), 3.26-3.39 (m, 4H), 3.56 (m, 2H); ^{13}C NMR (75 MHz, CD_3OD): δ14.45, 19.89, 23.70, 23.89, 26.91, 30.40-30.77, 33.04, 37.09, 48.72, 51.47, 63.24, 63.83, 176.58; ESI HRMS: calcd for $C_{24}H_{50}N_2NaO_4S$: 485.3383 $[M+Na]^+$, Found 485.3370. The original spectra are available in pages 4 and 5.

3. Additional Discussion

It is worthy making a brief comparison between the PDAS solution and those previously documented[2] worm solutions with sphere or vesicle to worm transition. The PDAS solution (with 500 mM NaCl) is very different from theose previously reported in the following three ways. Firstly, the enhancement of zero-shear viscosity (η_0) is normally no higher than 2 orders of magnitude, and enhancement of shear viscosity at shear rate of ~ 10 s^{-1} (η_{10}) is usually less than 1 order of magnitude.[2] As for the PDAS solution, η_0 at 30 ºC is no higher than ~ 0.05 Pa·s. However, there is a huge enhancement in rheological properties (Figure 2) when just increase temperature by 10 ºC (i.e. to 40 ºC). One can clearly observe that the enhancement of η_0 is more than 2 orders of magnitude. Though one could not observe a Newtonian plateau for the 40 ºC PDAS solution (Fig. 2a), still one could conclude that its η_0 is at least 5000 Pa·s, which means η_0 increase more than 5 orders of magnitude. The second obvious difference occurs at higher temperature ranges. Upon successive increasing temperature to higher temperatures (30–70 ºC), rheological properties (for instance η_0) of all the worm solutions that reported previously could not further enhance,[2] instead they decrease as normal worm fluids. However, we do not observe a decrease in viscosity in the PDAS solution even when it was heated to 80 ºC (Fig. S1), which is more exciting for high temperature applications. Thirdly, the plateau moduli (G' at higher shear frequency) of all the previously reported are normally no higer than ~ 10 Pa,[2] resulting that they are useless for biomedical applications. Besides, most of the surfactants used in these reports were cationic[2a-c] or anionic[2d], which are well acknowledged as more toxicity and worse biocompatible. Therefore, it is very hard for those previously materials to be developed potential applications in biomedical areas. Differently, the elastic modulus of the PDAS gel-like material can as high as almost 10^3 Pa. Moreover, PDAS is a biocompatible surfactant, and the gelling temperature (from 30 ºC to 40 ºC) can approximately be matched to that of human body, implying that PDAS is more promising to be expected potentail applications in tissue engineering. In a word, the PDAS solution is more interesting and exciting.

4. Figures for Additional Rheological Results and Cryo-TEM.

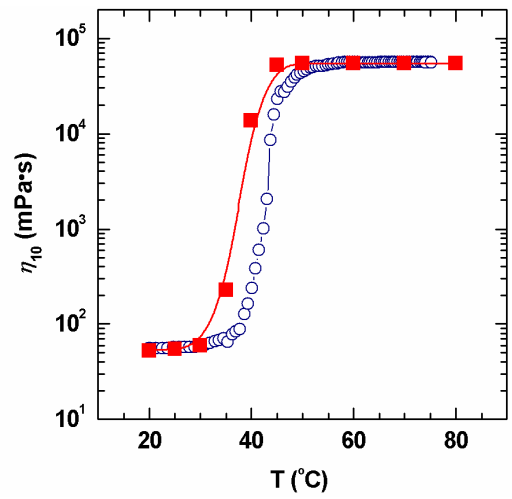


Fig. S1. Shear viscosity at shear rate of 10 s^{-1} as a function of temperature. For circles, measured with a temperature increasing rate of about 1 ºC/min; and for squares, measured at several fixed temperature.

4. Additional Cryo-TEM Images of the Micelles

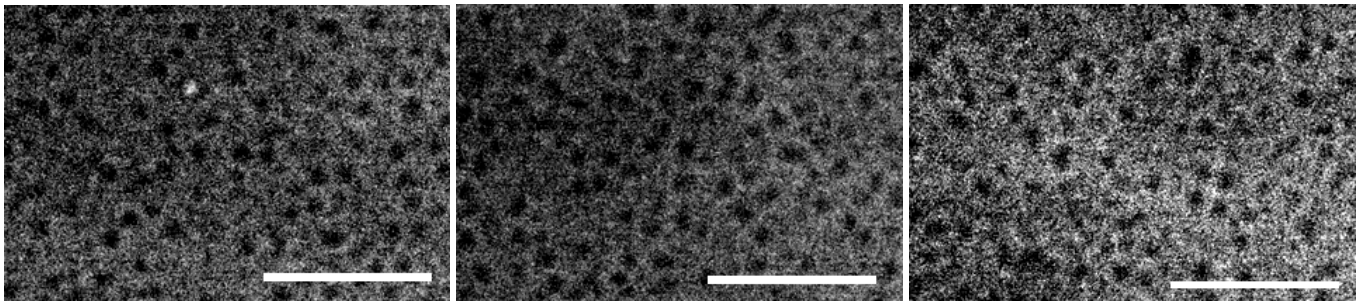


Fig. S2. Cryo-TEM images of the 1.0 M PDAS solution in the presence of 0.5 M NaCl at 30 °C. Bars are 100 nm.

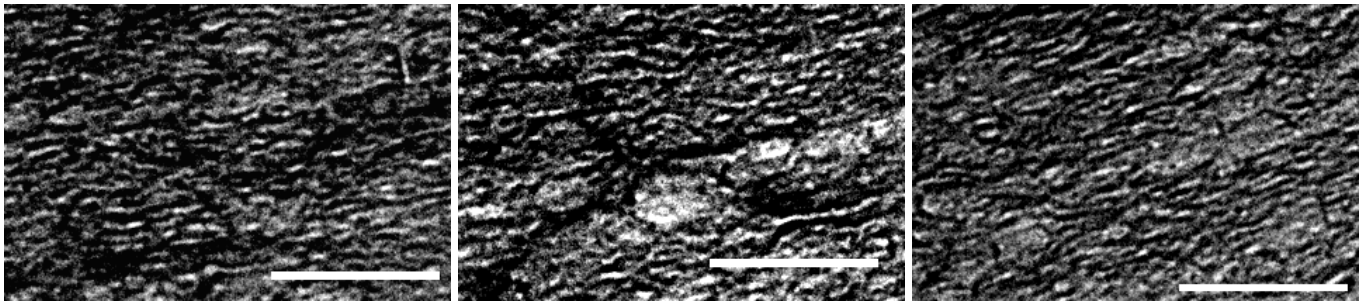


Fig. S3. Cryo-TEM images of the 1.0 M PDAS solution in the presence of 0.5 M NaCl at 40 °C. Bars are 100 nm.

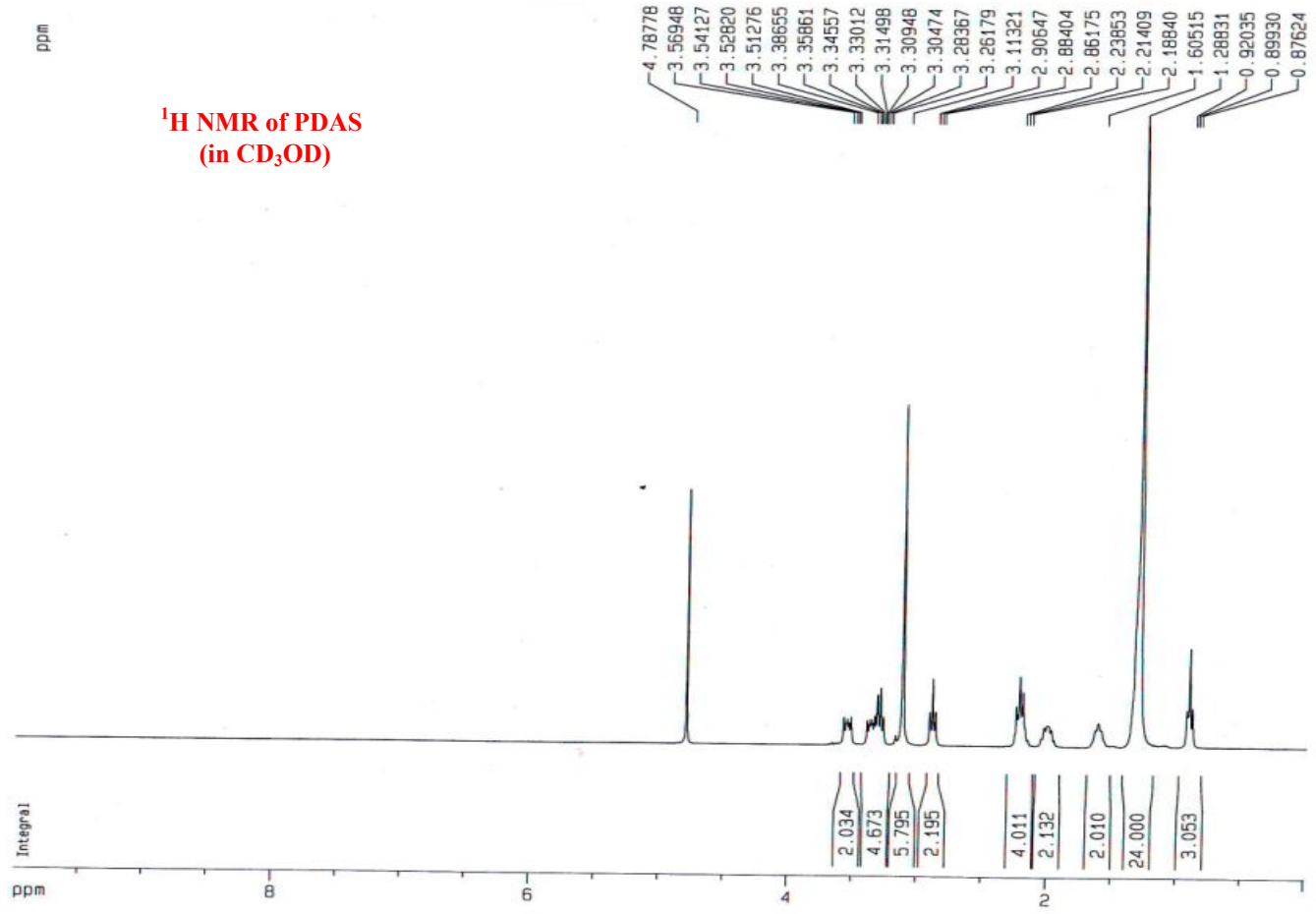
5. References

1 Z. Chu and Y. Feng, *Synlett*, 2009, **(16)**, 2655.

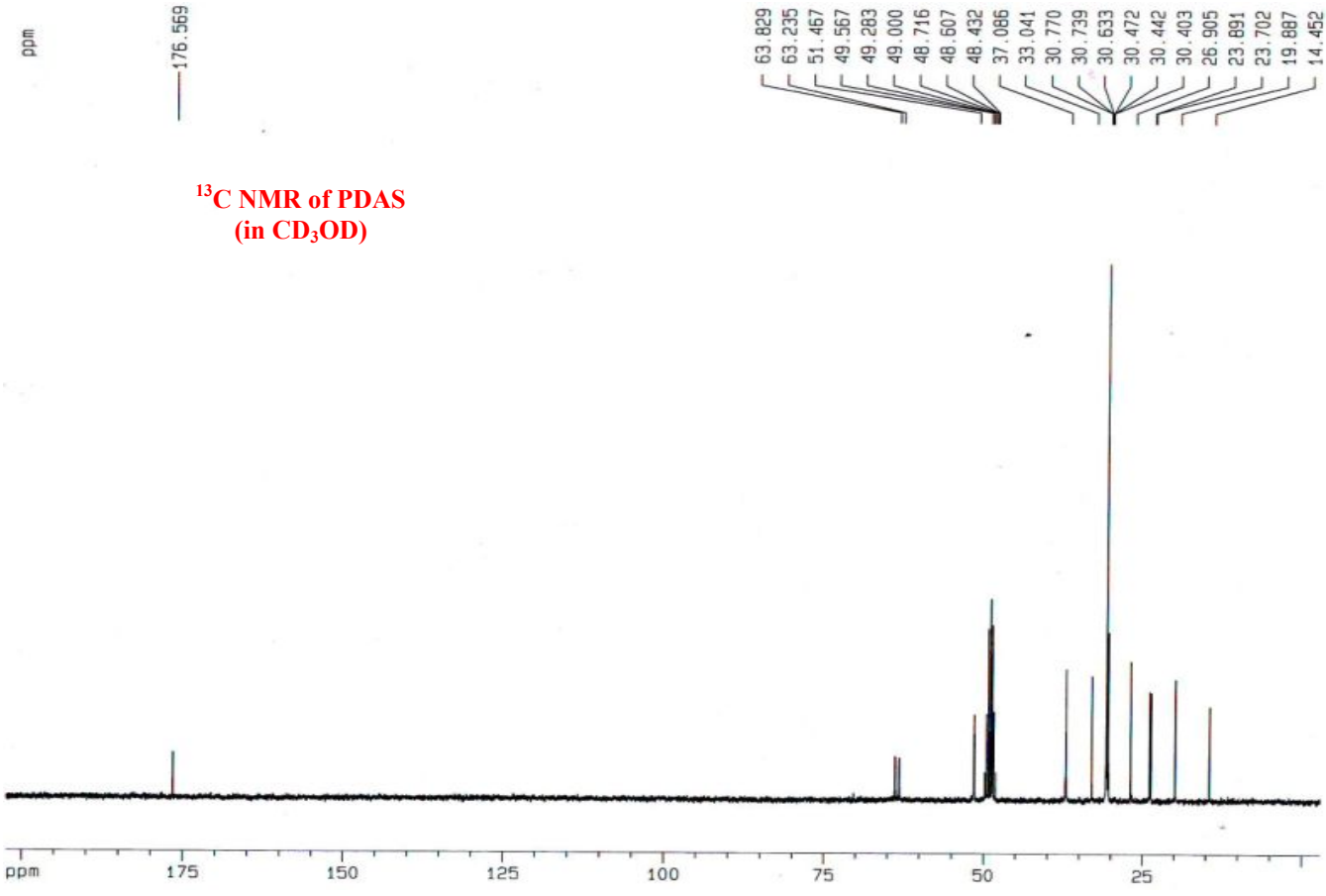
2 (a) T. S. Davies, A. M. Ketner, S. R. Raghavan, *J. Am. Chem. Soc.*, 2006, **128**, 6669; (b) G. C. Kalur, B. D. Frounfelker, B. H. Cipriano, A. I. Norman, S. R. Raghavan, *Langmuir*, 2005, **21**, 10998; (c) R. A. Salkar, P. A. Hassan, S. D. Samant, B. S. Valaulikar, V. V. Kumar, F. Kern, S. J. Candau, C. Manohar, *Chem. Commun.*, 1996, 1223; (d) K. Tobita, H. Sakai, Y. Kondo, N. Yoshino, K. Kamogawa, N.Momozawa, M. Abe, *Langmuir*, 1998, *14*, 4753.

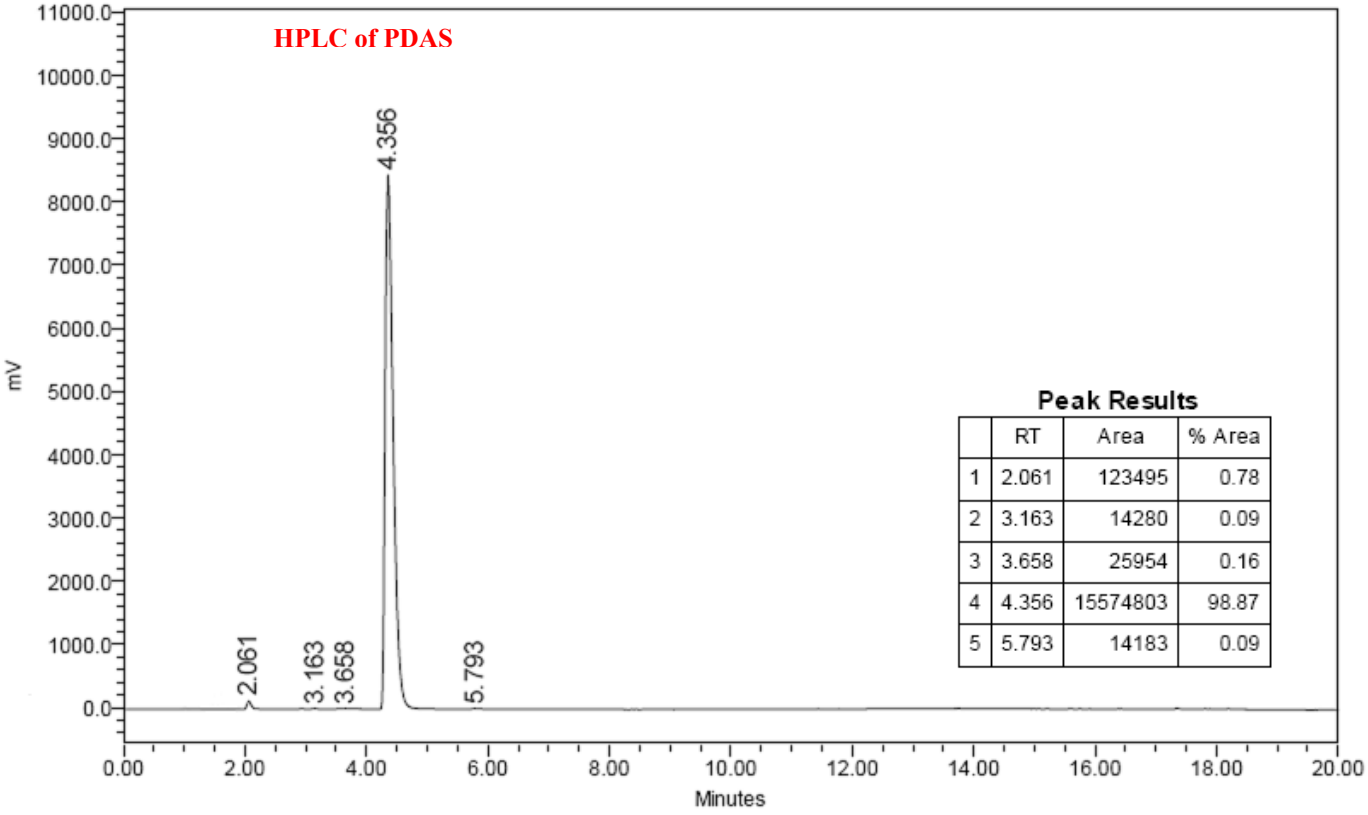
6. ^{1}H NMR , ^{13}C NMR, ESI-HRMS and HPLC Spectra of PDAS

^{1}H NMR of PDAS (in CD_3OD)

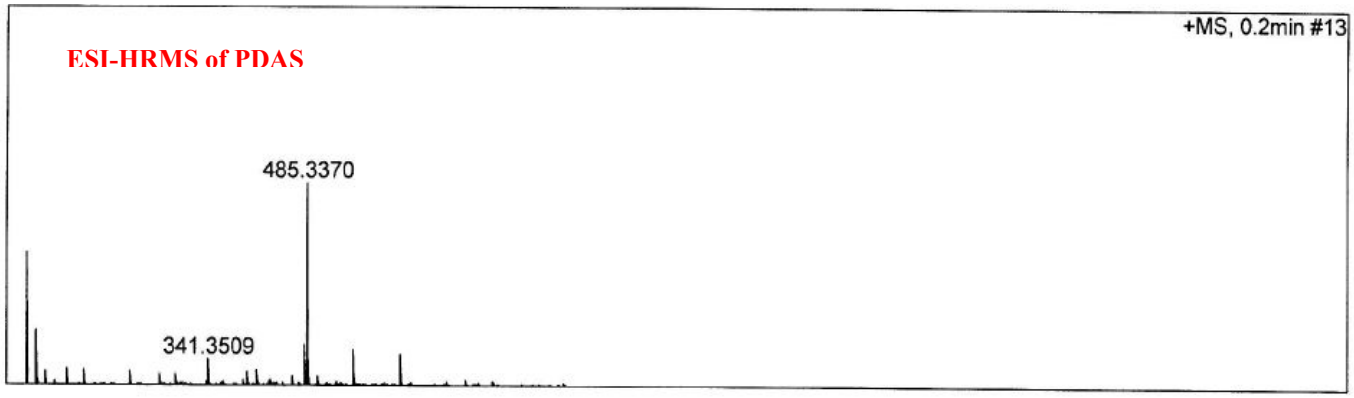


^{13}C NMR of PDAS (in CD_3OD)





	RT	Area	% Area
1	2.061	123495	0.78
2	3.163	14280	0.09
3	3.658	25954	0.16
4	4.356	15574803	98.87
5	5.793	14183	0.09



Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
485.3370	1	C 24 H 50 N 2 Na O 4 S	80.72	485.3383	2.8	1.7	14.7	0.5	even	ok
	2	C 30 H 47 Na 2 O 2	100.00	485.3366	-0.9	-0.8	28.2	6.5	even	ok