

SUPPORTING INFORMATION

Dissolution of α -chitin in deep eutectic solvents

Mukesh Sharma, Chandrakant Mukesh, Dibyendu Mondal and Kamalesh Prasad*

Marine Biotechnology and Ecology Discipline, CSIR-Central Salt & Marine Chemicals Research Institute, G. B Marg, Bhavnagar-364002 (Gujarat), India, Phone No : +91-278-2567760. Fax No. +91-278-2567562 Email: kamlesh@csmcri.org / drkamaleshp@gmail.com]

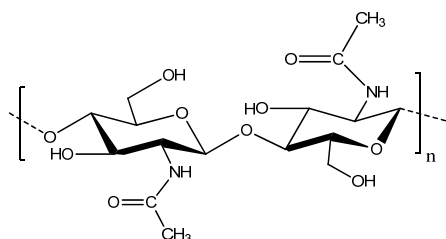


Fig. S1 : Structure of the α -chitin molecule, showing two of the *N*-acetylglucosamine units that repeat to form long chains via β -1,4 linkages.



Fig. S2. Deep eutectic solvents (at 50 °C) used in the paper **A.** choline chloride- Urea 1:2 **B.** choline bromide - urea 1:2 **C.** choline chloride – thiourea 1:2 **D.** chlorocholine chloride-urea 1:2 **E.** betaine hydrochloride-urea 1:4 **F.** choline chloride-ethylene glycol 1: 2 **G.** choline chloride-glycerol 1:2

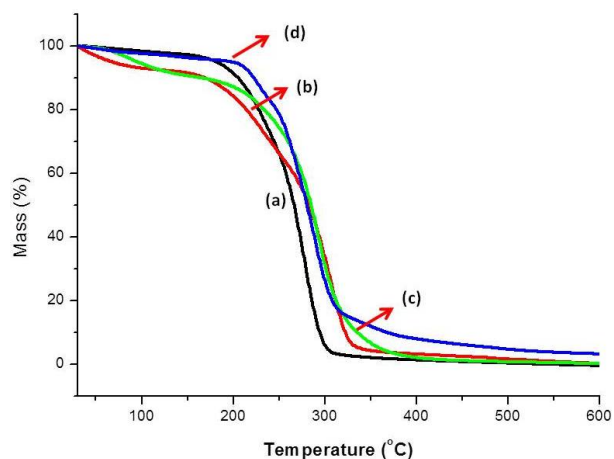


Fig. S3 : TGA- thermo grams for (a) choline chloride - urea 1:2 (b) choline bromide- urea 1:2 (c) betaine hydrochloride - urea 1:2 and (d) choline chloride - thiourea 1:2.



Fig. S4. α -Chitin (6% w/w) solubilized in choline chloride- urea 1: 2 employing different techniques as shown in Table 1



Fig. S5. α -Chitin (6% w/w) solubilized in choline bromide – urea 1:2 by conventional heating.

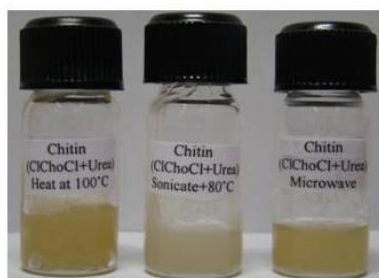


Fig. S6. α -Chitin (6% w/w) solubilized in in chlorocholine chloride – urea 1: 2 employing different techniques as shown in Table 1

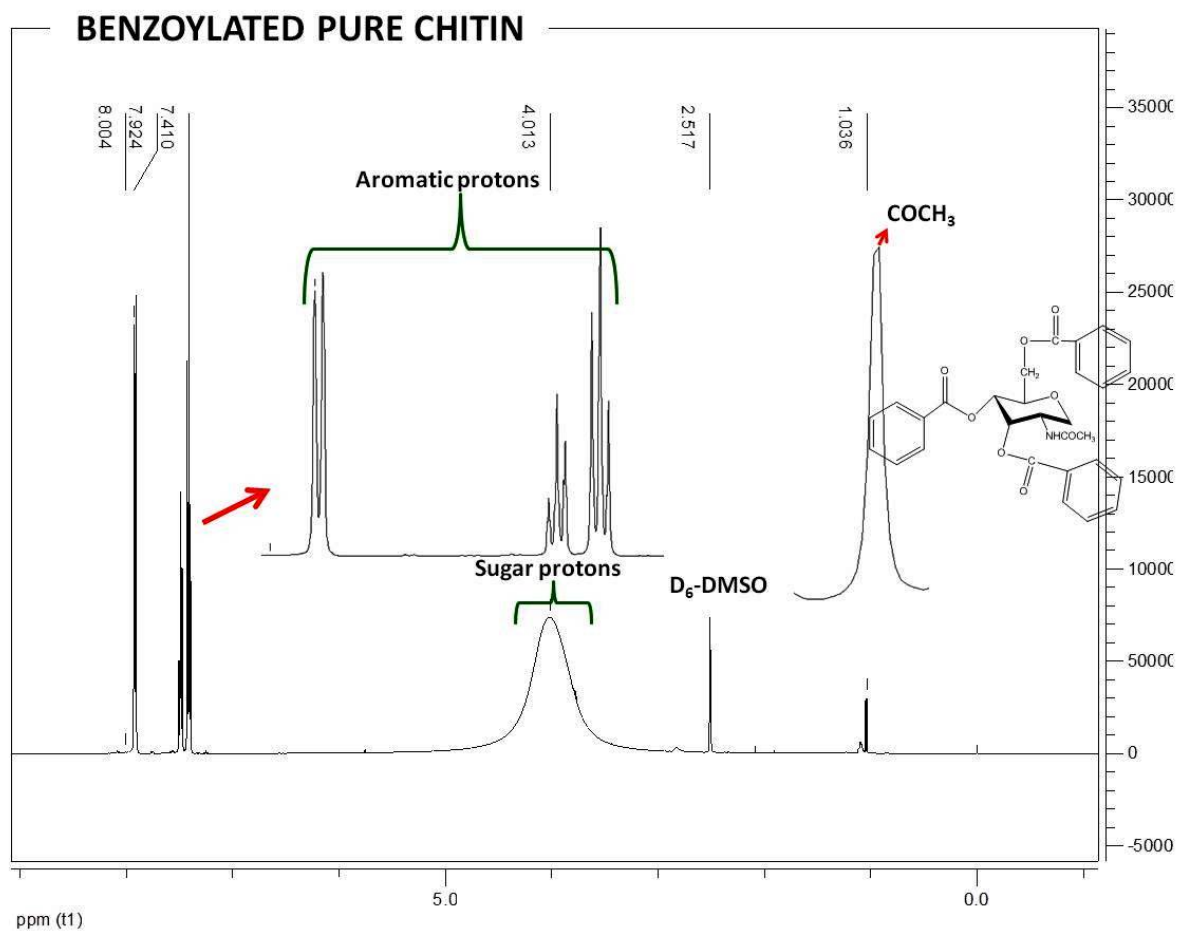


Fig. S7 : ¹H NMR spectra of benzyl derivative of unprocessed α- chitin.

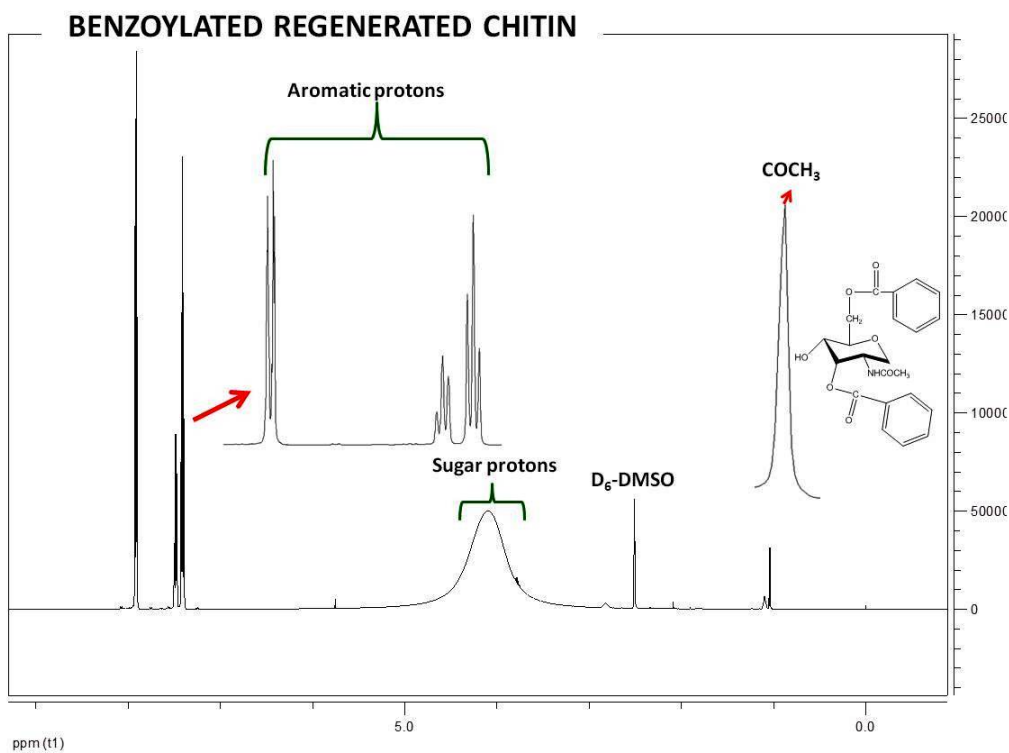


Fig. S8. ¹H NMR spectra of benzoyl derivative of regenerated α-chitin from the solution in choline chloride – thiourea 1:2

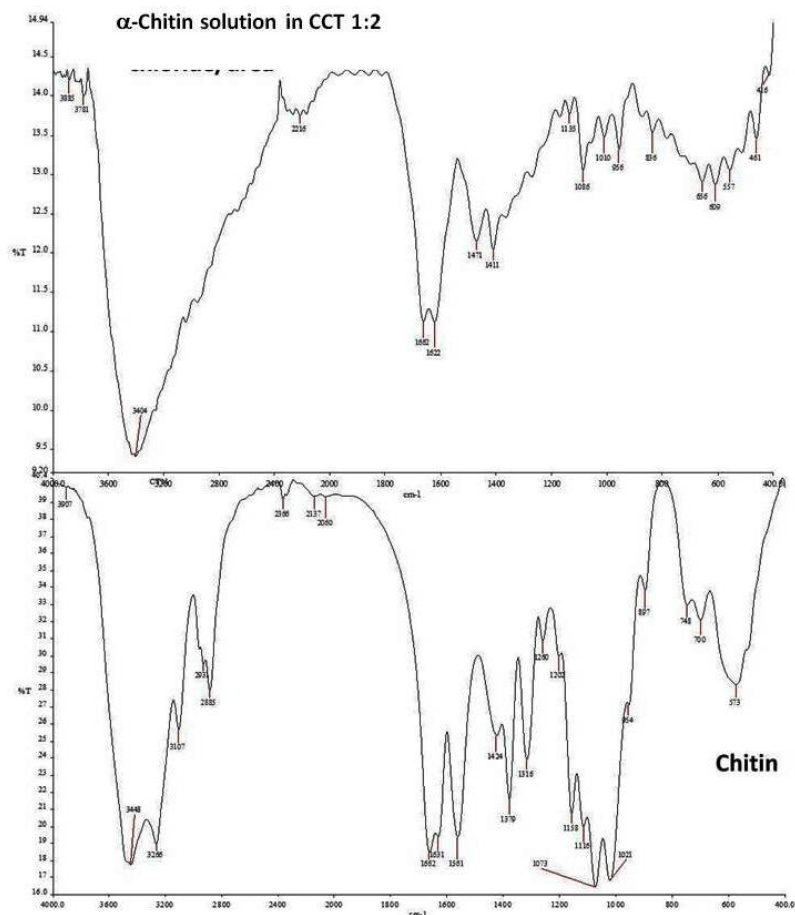


Fig. S9. FT-IR of α -chitin and solution of chitin (2% w/w) in choline chloride- thiourea 1:2

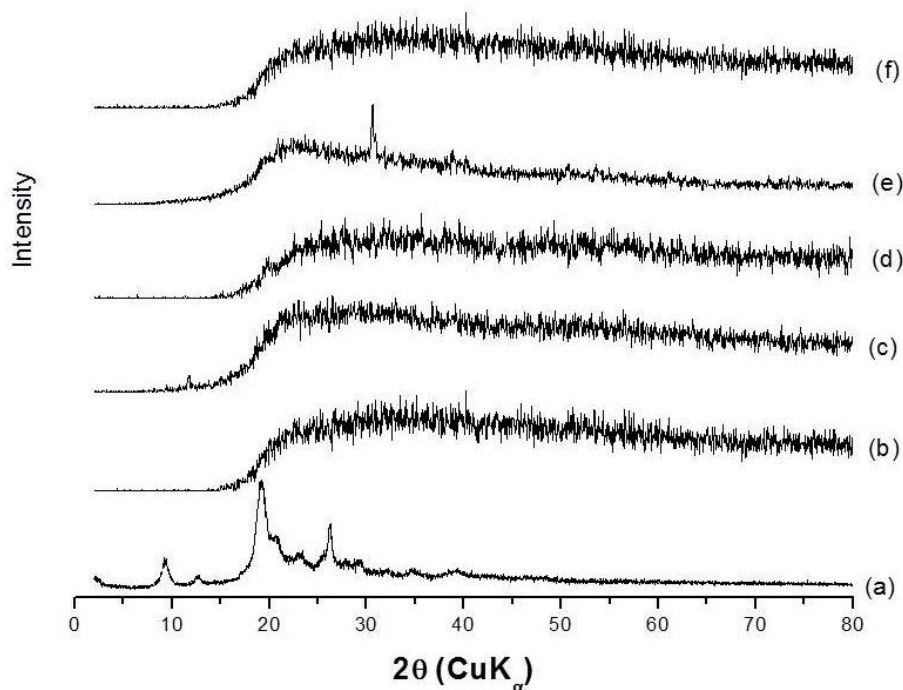


Fig. S10. Powder XRD profile of (a) unprocessed α -chitin and α -chitin samples dissolved in (b) choline chloride - urea 1:2 (c) choline bromide - urea 1:2 (d) chloro choline chloride - urea 1:2 (e) betaine hydrochloride - urea 1:4 and (f) choline chloride - thiourea 1:2

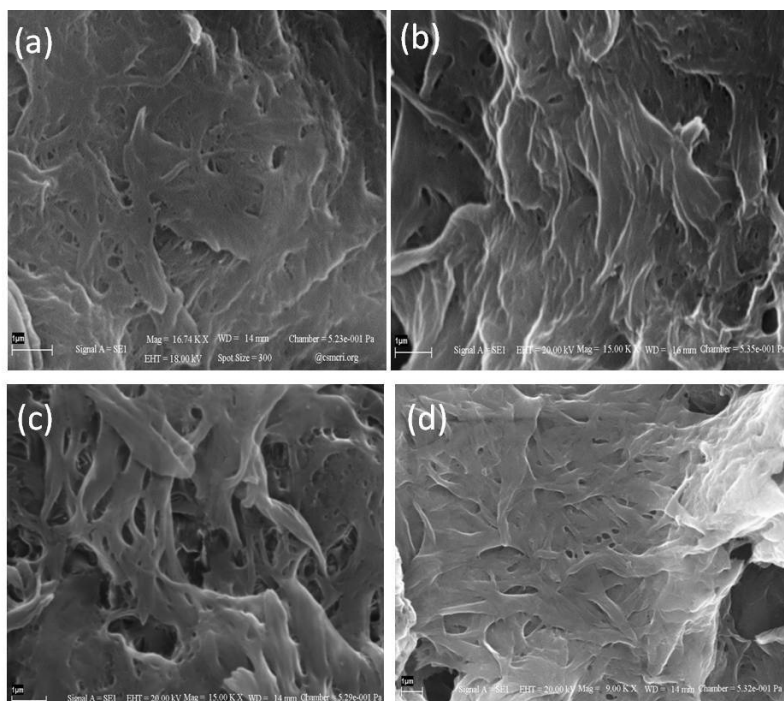


Fig. S11: SEM image of chitin regenerated from solutions prepared in (a) choline bromide – Urea 1:2 (b) chlorocholine chloride - urea 1:2 (c) betaine hydrochloride – urea 1:4 (d) choline chloride – urea 1:2

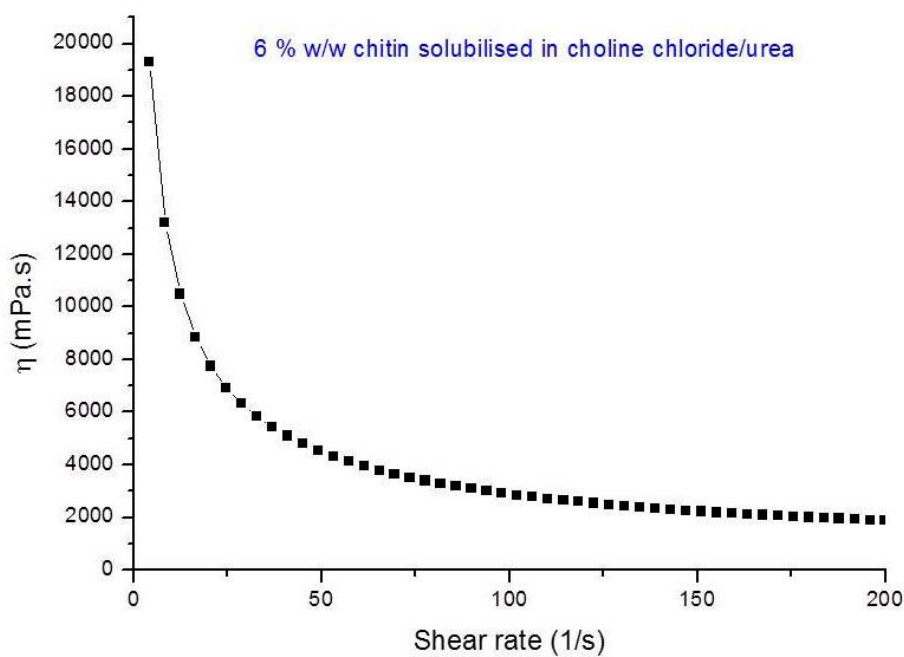


Fig. S12. Shear viscosity of chitin (7% w/w) in choline chloride – thiourea 1:2

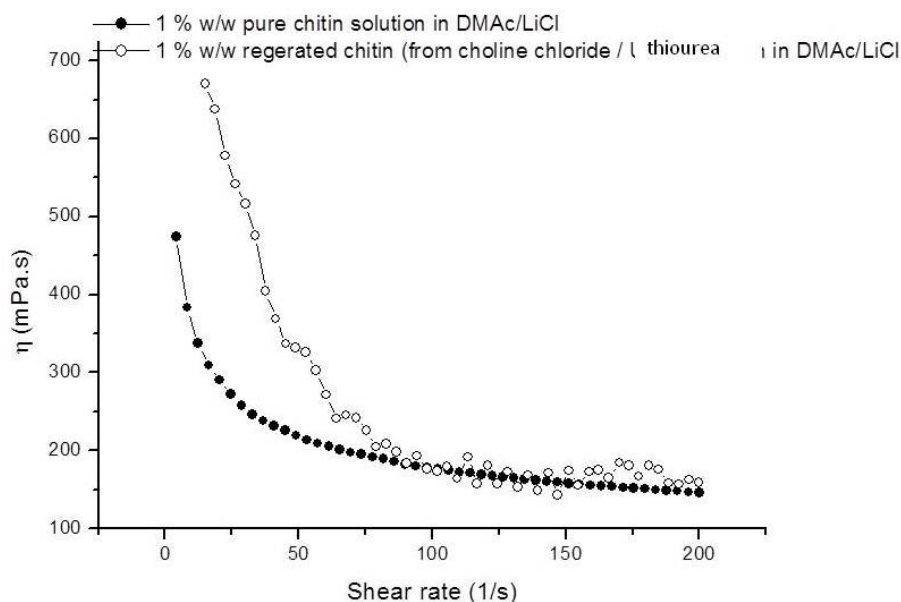
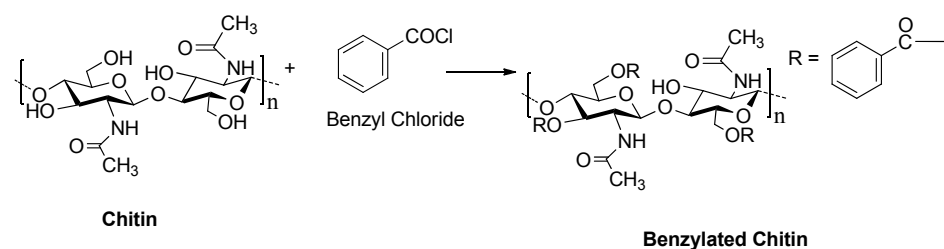


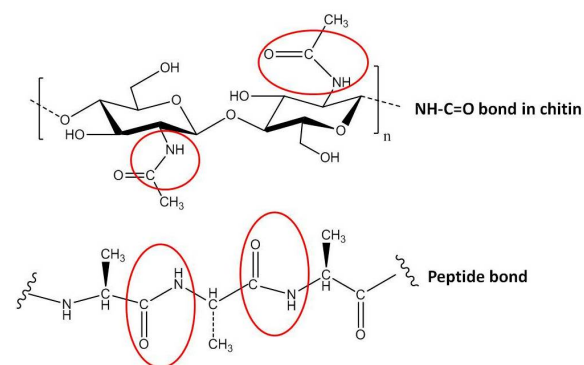
Fig. S13. Shear viscosity of 1% w/w unprocessed α -chitin solution prepared in 5% LiCl/DMAc and 1% w/w regenerated α -chitin (from choline chloride – thiourea 1:2) solution prepared in 5% LiCl/DMAc

Benzoylation of chitin (Following method reported by O. Somorin., N. Nishi., S. Tokura, J. Noguchi. *Polym. J.* 1979, 11, 391-396.)

1.77 ml of 40% KOH (21 mmol) was added to 1.49 g of chitin (7 mmol on the basis of N-acetylglucosamine unit) suspended in 10 ml of DMSO. The mixture was stirred for 3-4 h at 10°C and kept at 4 °C for 10 h. The alkaline chitin was dried and washed with acetone to remove water adhered to the surface. 220 mg of alkaline chitin was suspended in 10 ml DMSO and 8.1 ml (70 mmol) of benzoyl chloride was added and stirred at 5 °C for 20 h. Ice cold water was added to precipitate the derivative. The benzyl derivative was solubilized in d_6 -DMSO and NMR was recorded for the sample.



Scheme S1. Benzylation of chitin in DMSO..



Scheme S2. NH-C=O bond in chitin and peptide bond in polypeptides.

Table S1 : Molecular weight of regenerated chitin regenerated from respective solutions in various deep eutectic solvents dissolved employing different techniques

| Deep Eutectic Solvents | | Dissolution technique ^a | Molecular weight of regenerated α -chitin ($\times 10^5$ Da) ^b | Molecular weight of pure unprocessed α -chitin ($\times 10^5$ Da) ^b |
|-------------------------------|----------------------------|--------------------------------------|---|--|
| Hydrogen Bond acceptors (HBA) | Hydrogen Bond Donors (HBD) | | | |
| Choline Chloride | Urea | Heating at 100 °C | 5.01 | 5.22 |
| | | Ultrasonication and heating at 80 °C | 5.14 | |
| | | Microwave irradiation at 80 °C | 4.95 | |
| Choline Bromide | Urea | Heating at 100 °C | 5.00 | |
| | | Ultrasonication and heating at 80 °C | 5.12 | |
| | | Microwave irradiation at 80 °C | 4.90 | |
| Chlorocholine Chloride | Urea | Heating at 100 °C | 5.10 | |
| | | Ultrasonication and heating at 80 °C | 5.14 | |
| | | Microwave irradiation at 80 °C | 4.50 | |
| Betaine Hydrochloride | Urea | Heating at 100 °C | 4.99 | |
| | | Ultrasonication and heating at 80 °C | 5.00 | |
| Choline Chloride | Thiourea | Heating at 100 °C | 4.25 | |
| | | Ultrasonication and heating at 80 °C | 5.11 | |
| | | Microwave irradiation at 80 °C | 4.99 | |

^a For dissolution freshly prepared DESs were used

^b Using Ostwald viscometer using Mark-Houwink equation.