Synthesis and Characterization of Novel Hydrophobically End-Capped Poly(ethylene oxide)s [PEOs]

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Summary: We report on the synthesis and characterization of a novel hydrophobically modified end-capped poly(ethylene oxide)s. The end-capping agent of this polymer was designed and synthesised from a renewable resource material namely, gallic acid (i.e. 3,4,5-trihydroxybenzoic acid), the byproduct of tannin industry. The hydroxyl groups at 3, 4 and 5 positions of gallic acid provide an opportunity for varying the hydrophobicity of the compound. The hydrophobic end-capping compound, 3,4,5-tridodecyloxy bezoylazide was prepared from gallic acid and PEGs with different chain lengths (of number average molecular weights, 10000 and 35000 g/mol) were end-capped using 3,4,5-tridodecyloxybenzoyl azide. The quantitative analysis of end-capping in the polymers was demonstrated by ^{1}H-NMR spectroscopy and the rheological studies were carried out in the surfactant solutions.

Keywords: end-capped PEOs; hydrophobically modified polymers; water-soluble polymers

Introduction

Conventional water-soluble polymers have certain drawbacks in which their solution properties are adversely affected by external working conditions such as, temperature, pH, shear and the presence of salts[1–2]. In order to overcome these drawbacks, hydrophobically modified polymers [HMPs] have emerged as most promising materials[3–5] and particularly, the major focus is given on the hydrophobically end-capped poly(ethylene oxide)s [PEOs]. These materials are industrially important since they can be tailored to exhibit specific rheological properties to suit applications in coatings, paper, cosmetics, pharmaceuticals, thickeners for food, health care products and oil production. Hydrophobically modified Ethoxylated URethanes (HEUR) fall in this class of polymers[6–9].

Here, we report on the synthesis and characterization of a novel hydrophobically modified end-capped poly(ethylene oxide). The end-capping hydrophobic part of this polymer was designed and developed from a renewable resource material namely, gallic acid (i.e. 3, 4, 5-trihydroxybenzoic acid), one of the byproducts of tannin industry. The hydroxyl groups at 3, 4 and 5 positions were reacted with 1-bromododecane, which gave 3 arms of $C_{12}H_{25}$ alkyl chains at these positions. The hydrophobic chains play an important role in the associating mechanism.

Experimental

Materials

Poly(ethylene oxide)s (PEO) of number average molecular weights 10000 and 35000 kg/mol were obtained from Fluka. Gallic acid, 1-bromohexane, 1-bromododecane, dibutyltin dilaurate (DBTDL), sodium azide, sodium dodecyl sulfate (SDS) were procured from Aldrich and MERCK and were used as received. All solvents and

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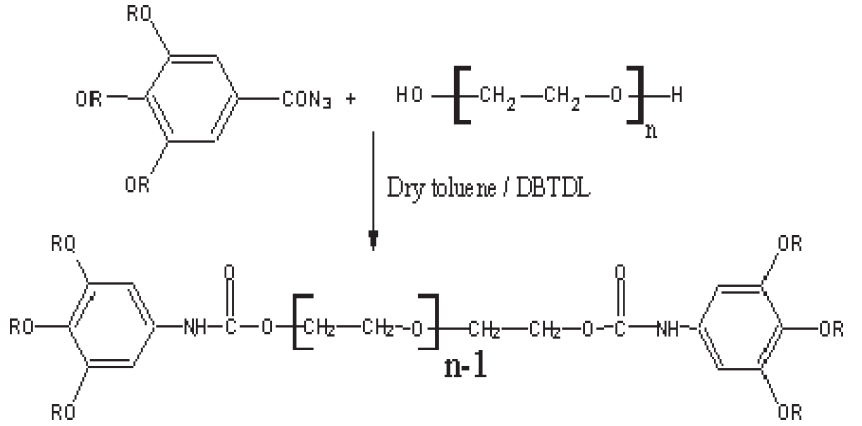

Scheme 1.

reagents required for the reactions were purified as per standard procedures. Deionized water (Q-Millipore, 18 MΩ) was used for the preparation of polymer solutions.

Synthesis of 3, 4, 5-Tridodecyloxybenzoyl Azide

The synthesis of hydrophobic compound involves the following steps, I. Preparation of methyl ester of gallic acid, II. O-alkylation of methyl gallate with 1-bromododecane, III. Hydrolysis of methyl-3,4,5-tridodecyloxybenzoate to 3,4,5 tridodecyloxybenzoic acid, IV. Preparation of 3, 4, 5-tridodecyloxybenzoyl azide.

Synthesis of End-Capped Poly(Ethylene Oxide)

Hydrophobically end-capped PEOs (Ga_2-PEO10K-C_{12} and Ga_2-PEO35K- C_{12}) were synthesized by reacting 10 equivalent excess of 3, 4, 5-tridodecyloxybenzoyl azide with poly(ethylene oxide) in dry toluene at 100 °C for 72h. DBTDL was used as a catalyst to enhance the reaction. The reaction is shown in Scheme 1, where $R = C_{12}H_{25}$.

Purification and Characterization of an End-Capped Polymer

The product was precipitated out in excess of petroleum ether. White powder like precipitate was filtered and dried. It was then redissolved in warm acetone and then filtered through 1 μm syringe filter and precipitated into petroleum ether. The structure and end-capping efficiency was determined from ^{1}H NMR spectroscopy. ^{1}H NMR spectral results indicate that each polymer chain contained two hydrophobic moities. The results are summarized in Table 1.

Results and Discussion

The hydrophobic compound 3, 4, 5-tridodecyloxybenzoyl azide was prepared which can undergo in-situ isocyanate formation and reaction with PEOs to form an end-capped PEOs. The advantage of using PEO

Table 1.
Extent of end-capping determined from ^{1}H NMR Spectroscopy.

PEOs	R	Designation	$(CH_2)/(OCH_2CH_2)$		Hydrophobe per chain	End capping efficiency
			Theor	Expt		
PEO(10K)	$C_{12}H_{25}$	Ga_2-PEO10K-C_{12}	0.1319	0.1347	2.04	100
PEO(35K)	$C_{12}H_{25}$	Ga_2-PEO35K-C_{12}	0.0377	0.0376	1.99	100

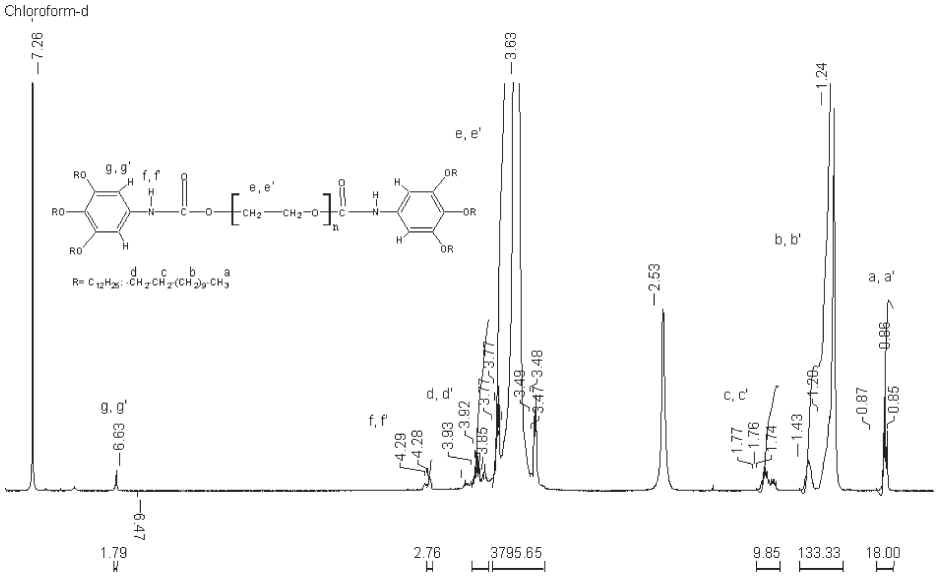

Figure 1.
^{1}H NMR spectrum of end-capped PEO (Ga_2-PEO35K-C_{12}) in CDC.

for end-capping is that, the hydrophilicity of the system can be changed by varying the molecular weight of the PEO. Accordingly, in our work we have used two PEOs of MW 10K and 35K. The hydrophobically end-capped PEOs were obtained in the form of white powders. The structural characterization and the end-capping efficiency were carried out using ^{1}H NMR spectroscopy.

We show in Figure 1, the ^{1}H NMR spectrum of Ga_2-PEO35K-C_{12}. The assignments for all peaks are shown in the spectrum. Table 1, shows the end-capping efficiency on both PEO 10K and 35K and

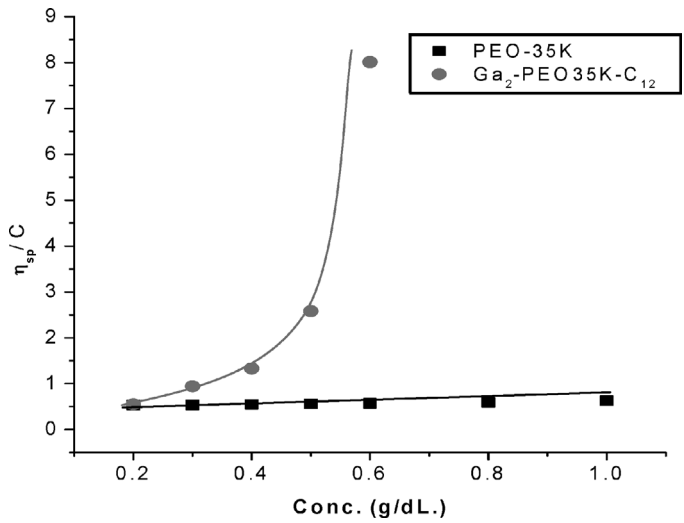

Figure 2.
Zero shear viscosity behavior of end-capped PEO (Ga_2-PEO35K-C_{12}) in 0.0081 M SDS solution.

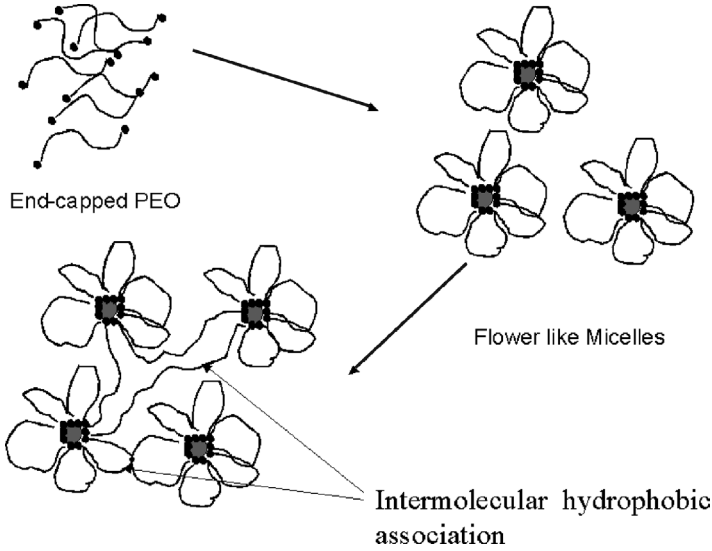

Figure 3.
Formation of Flower like micelles in end-capped PEO.

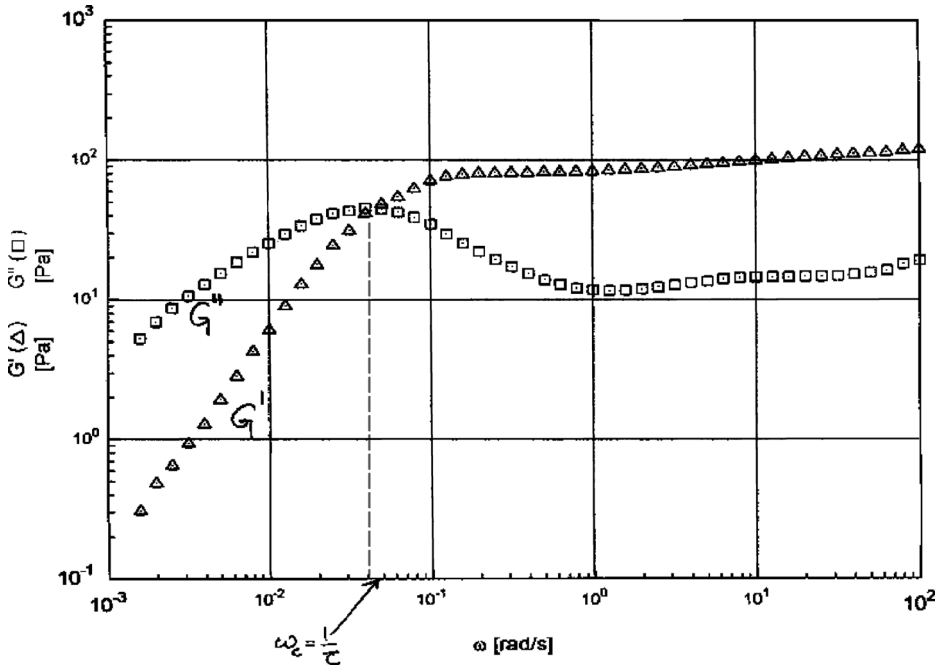

Figure 4.
Viscoelastic behavior of end-capped PEO (Ga_2-PEO35K-C_{12}) 3 wt% in 0.05 M SDS solution at 25 °C.

indicate the complete end-capping of the PEOs. These hydrophobically end-capped PEOs were found to be insoluble in water, which could be due to the presence of six alkyl chains at the PEO chain ends. However, addition of small amount of co-solvent such as methanol, ethanol and n-propanol or surfactant (e. g. sodium dodecyl sulfate) makes them soluble, homogenous, transparent and highly elastic fluids.

Rheology

The rheological experiments were conducted on a strain controlled RFS II, Rheometrics Fluid Spectrometer using cone-and-plate geometry. We shown in Figure 2, the reduced viscosity of Ga_2-PEO35K-C_{12} as a function of polymer concentration and the results are compared with the unmodified PEO. It can be readily seen that the viscosity of the end-capped PEO increases exponentially. This could be attributed to the fact that, above a certain polymer concentration, the hydrophobically end-capped PEOs form flower like micelles and these micelles aggregate to form the transient networks (as shown in Figure 3).

The formation of transient network results into dramatic increase in viscosity leading to a gel like behavior. These gels exhibit the visco-elastic behavior.

The viscoelastic response of Ga_2-PEO35K-C_{12} (3.0 wt% in 0.05 M SDS) to a small amplitude oscillatory deformation at 25 °C is shown in Figure 4. At low frequencies, the storage modulus (G') is lower than the loss modulus (G''), which indicates the presence of viscous nature in the fluid. However, upon increase in frequency, G' becomes larger than G''. The existence of a plateau modulus with the cross over of G' and G'' at $\omega = 1/\tau$, where ω = frequency and τ = relaxation time, can also be observed. These observations indicate the viscoelastic response of the hydrophobically end-capped PEOs. Further work is underway on the detailed structural elucidation and rheological properties of these interesting materials and will be published later.

Conclusions

Synthesis and characterization of novel hydrophobically end-capped PEOs have been reported. The hydrophobic end-capping group was designed and synthesized from a renewable resource material namely, gallic acid, the byproduct of tannin industry. The end-capping efficiency was determined by ^{1}H NMR spectroscopy and was 100%. The rheological studies were carried out in surfactant solutions. These hydrophobically end-capped PEOs form highly viscoelastic fluids/gels in surfactants and alcohol-water mixtures (at moderate concentrations) as a result of the formation of transient networks due to associations. Because of their enhanced rheological properties, they show promising application in cosmetics, food and pharmaceuticals.

[1] US 4, 228, 277 (1980), M. L. Landoll.
[2] US 4, 243, 802 (1981), M. L. Landoll.
[3] J. E. Glass, ''Polymers in Aqueous Media: Performance Through Associations'', ACS 223, **1989**.
[4] S. W. Shalaby, C. L. Macormick, G. B. Buttler, ''Water-Soluble Polymers: Synthesis, Solution Properties and Applications'', ACS Symposium Series 467, Washington, **1991**.
[5] J. Bock, P. L. Valint Jr, S. J. Pace, D. B. Siano, D. N. Schultz, S. R. Turner, in ''Water-Soluble Polymers for Petroleum Recovery'', Eds G. A. Stahl, D. N. Schultz, plenum Press, New York, **1988**, p 9, 147.
[6] E. J. Schaller, ''Rheology Modifiers for water Borne Paints'', Surface Coatings Australia. **1985**, 22 (10), p6.
[7] J. P. Kaczmarski; Glass, J. E. Proc. ACS, Div. *Polym. Mater. Sci. Eng.*, **1991**, 65, 175.
[8] J. E. Glass, *J. Coatings Technol.*, **2001**, 73, 913.
[9] R. D. Jenkins, The Fundamental Thickening mechanism of associative polymer in latex system: A rheological studies. Ph.D. Thesis, Lehigh University, Bethlehem, PA, **1990**.

