

Rheological Properties of Aqueous Dispersions of Conductive Poly(Benzimidazobenzophenanthroline)

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ABSTRACT

Poly(benzimidazobenzophenanthroline), BBL, is a semiconductive polymer that is practically insoluble in any solvents. For many its applications, e.g. as thin films for photovoltaics applications, it would be desirable to be able to process the polymer from its solution. In the present work it was found that the BBL can be dispersed in water by precipitation in alkaline water, dialysis and sonication right after the synthesis. Dispersions with higher solids content and colloidal stability can be prepared by modifying the polymer synthesis - by adding poly(ethylene oxide), PEO, to BBL chain ends (BBL-PEO) the polymer becomes amphiphilic. The rheological properties of the dispersions were monitored by oscillatory and flow measurements.

INTRODUCTION

Poly(benzimidazobenzophenanthroline) (BBL), Figure 1, is a fully conjugated ladder-type polymer that can be used both as a p- and n-type semiconductor.¹⁻⁴ Its electrochemical properties, especially n-type conduction, have raised interest for its use in organoelectronic devices. To date organic transistors, photovoltaics and photodetectors have been demonstrated using this polymer. Despite BBLs desirable conductive properties, it has had only

limited use due to its poor solubility. Several authors have therefore paid attention to methods to solubilise or disperse BBL by sonication^{5,6} or with the aid of surfactants⁶. We have reported a method to prepare aqueous BBL dispersions by attaching poly(ethylene oxide) (PEO) to the chain ends of BBL, Figure 1.⁷ These materials have been found to have electrochemical properties similar to BBL. This preparation scheme involves a one pot polymer synthesis followed by a straightforward purification. The resulting BBL-PEO paste can be processed further into a dilute dispersion. This method can also be used to prepare dispersions of unmodified BBL. In this work, we report on the viscoelastic properties of these dispersions.

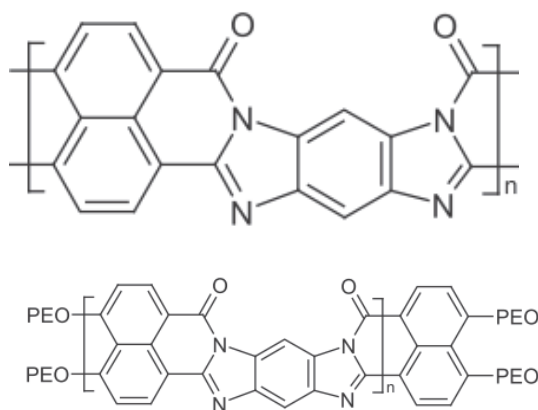


Figure 1. Chemical structures of BBL and BBL-PEO.

MATERIALS AND METHODS

Synthesis of BBL and BBL-PEOs was done as reported earlier.⁸ The samples (e.g. BBL10-PEO17) are coded by denoting the number of repeating units in BBL and PEO blocks, respectively.

TA instruments AR2000 stress controlled rheometer equipped with a double concentric cylinder geometry was used for rheological characterisation. Aqueous BBL-PEO dispersions were prepared from stock suspensions by dilution to the desired concentration followed by sonication. The precipitated pristine BBL was diluted to desired concentration and pipetted after vigorous shaking and sonication.

Prior all the rheological measurements the samples were sheared at 100 1/s for ten minutes to remove any possible mechanical history. The aggregation was followed by oscillatory time sweep. The measurements were made within the linear viscoelastic regime, LVE, (10% strain) at 6.28 rad/s frequency. After this an oscillatory frequency sweep was performed from 300 to 0.100 rad/s followed by measurement of flow curve at shear rates increasing from 0.100 to 1000 1/s.

RESULTS AND DISCUSSION

The dispersions of the studied polymers show a tendency to aggregate after sonication which could be observed visually. When the samples were allowed to rest it was observed that with time they formed gels. These aggregation processes were studied by rheology comparing samples with different PEO content and polymer concentration. In Figure 2 is shown how BBL10-PEO17 sample shows gel-like response directly after the pre-shearing step ($G' > G''$). Allowing the sample to rest for 5 days leads to significant increase in the dynamic moduli due to aggregation.

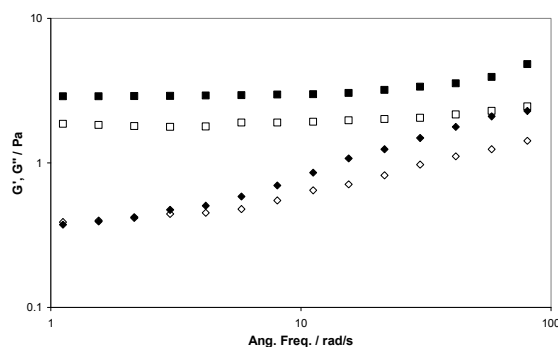


Figure 2. Frequency sweep of BBL10-PEO43 (5 mg/mL) directly after pre-shear (G' \square , G'' \diamond) and after 20 hours (G' \blacksquare , G'' \blacklozenge).

In order to probe the dynamics of the aggregation process, the moduli were followed with time. In Fig. 3 and 4 the time sweeps of different BBL and BBL-PEO samples are shown. It can be seen that the moduli of the samples start to increase instantaneously after cessation of the shear and show two regimes, initial rapid increase in both moduli followed by a slower increase before reaching a plateau. After 20h the sample moduli had reached a plateau value.

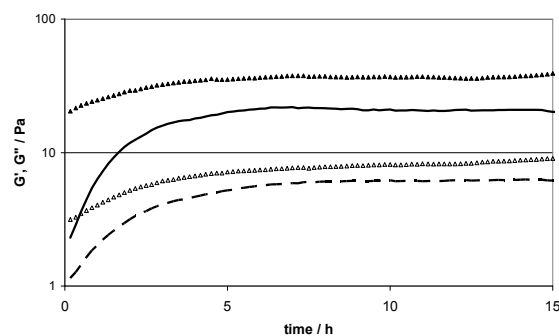


Figure 3. Oscillatory time sweep of BBL10 (G' full line, G'' dotted line) and BBL20 (G' \blacktriangle , G'' \triangle). Both polymer concentrations 5 mg/mL.

When the samples are compared at similar BBL contents it is observed that the BBLs that have been modified with relatively short PEO chains (DP 17) show the highest G' values, see Fig. 4, while the

BBL and BBL with longer PEO chains have lower values of G' .

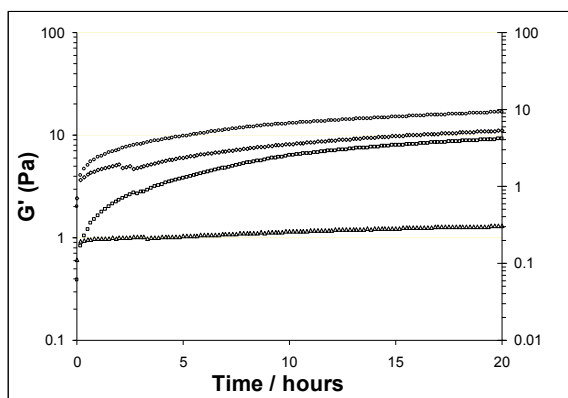


Figure 4. Storage modulus as a function of time from BBL20 (\square), BBL20-PEO17 (\circ) and BBL10-PEO17 (\diamond), BBL20-PEO45 (\triangle). The BBL concentrations of the samples are 1 mg/ml.

The strength of the gels were studied by oscillatory stress sweeps after the time sweep, see Figure 5. It can be seen how the dispersion made from BBL has lower onset of gel breaking.

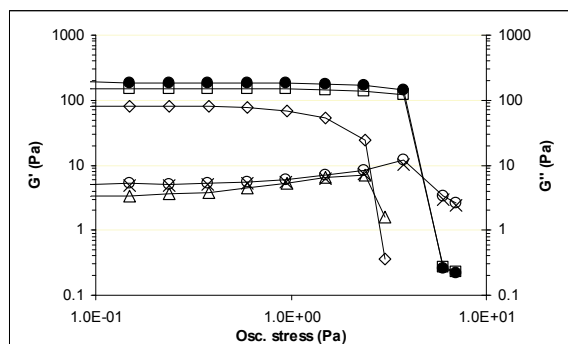


Figure 5. Storage and loss moduli of BBL20-PEO17 (G' \square , G'' \times), BBL10-PEO17 (G' \bullet , G'' \circ) and BBL20 (G' \diamond , G'' \triangle). BBL concentration 5 mg/ml.

The gel strength correlates well with the gel modulus observed after time sweep – the BBL-PEOs having PEO DP of 17 show also the highest gel strengths.

The flow curves of the dispersions were measured after the samples were allowed to reach plateau value in the gelling. It was

found that all dispersions were strongly shear thinning, see Figure 6. The low-shear viscosities are decreasing with decreasing BBL content of the samples. The sudden steep decrease in viscosity at low shear rates at low polymer concentrations to the breakage and orientation of loose aggregates as the shear rate is increased. This is the case also at higher concentrations (data not shown) as some larger aggregate structures break down by increased shear rate. The shear thinning is most prominent with the sample having the most PEO incorporated because the concentration of BBL is the lowest and so are the attractive interactions between the insoluble aromatic units.

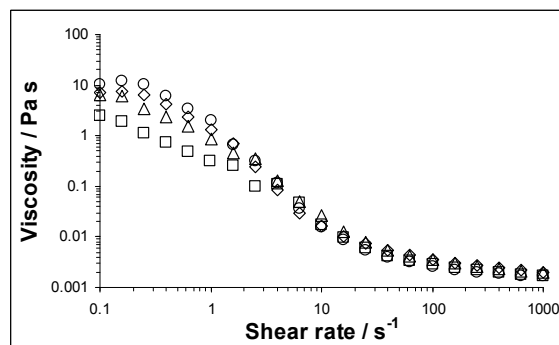


Figure 6. Flow viscosity of BBL dispersions as function of shear rate at a total polymer concentration 1.00 mg/ml. BBL20 (\circ), BBL20-PEO17 (\triangle), BBL10-PEO17 (\diamond) and BBL20-PEO45 (\square).

CONCLUSIONS

Dilute aqueous BBL and BBL-PEO dispersions form aggregates and, with increased concentration, form gels after the samples have been sonicated and allowed to rest. The gel strength increases with increasing the proportion of BBL of the total polymer concentration. Of samples with constant BBL content the strongest gels are formed from BBL-PEOs with short PEO chains. The gel strength was also found to increase as the BBL block size increases.

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