

New Phase Transfer Agent for Dye: Application for Hyperbranched Poly (ester-amine)

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Abstract: Hydrophilic hyperbranched poly(ester-amine) (HPEA) synthesized from diethanolamine and methyl acrylate was used as phase transfer agent for the first time to transfer methyl orange (MO) from water into chloroform. This process was quantified by UV-Vis spectra. A possible mechanism was put forward based on the formation of amphiphilic aggregates.

Keywords: Hyperbranched poly(ester-amine), phase transfer agent, dye.

It has been well reported that dendrimers with regular global molecular structures showed micelle-like properties and were used as phase transfer agents^{1,2}. A modified hyperbranched polymer with large amount of hydrophobic end-groups has also been used as phase transfer agent³. However, the modifying reaction was rather complicated and the transfer mechanism needs to be explored. In this work, we discovered that hydrophilic hyperbranched poly (ester-amine) (HPEA), synthesized from diethanolamine and methyl acrylate, can be used as phase transfer agent directly to transfer methyl orange (MO) from water into chloroform in high efficiency.

HPEA was synthesized by pseudo one-step procedure similar to that reported in the literature⁴. The ideal formula for a 3-generation molecular was shown in **Scheme 1**. HPEA had good solubility in water and dissolved slowly in unrefined chloroform.

Suitable amount of HPEA was firstly dissolved in chloroform and the solution was poured into a separating funnel. The aqueous solution of MO was then added into the funnel to obtain a two-phase system. Without stirring the colorless chloroform layer turned yellow gradually. A new absorbance peak for MO in chloroform phase in UV-Vis spectrum was clearly observed (**Figure 1**). After the equilibrium was reached in about 16~20hr, the upper layer was replaced by pure water. The aqueous layer remain colorless even for a long time. These phenomena indicated that MO molecules had been transferred into chloroform with the assistance of HPEA and the process was irreversible.

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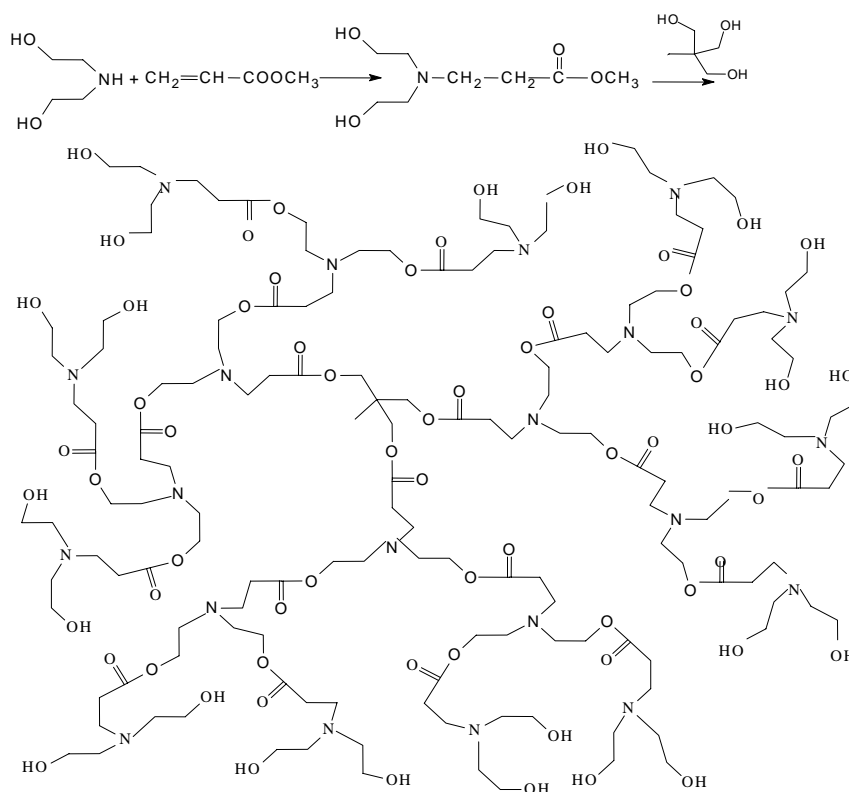
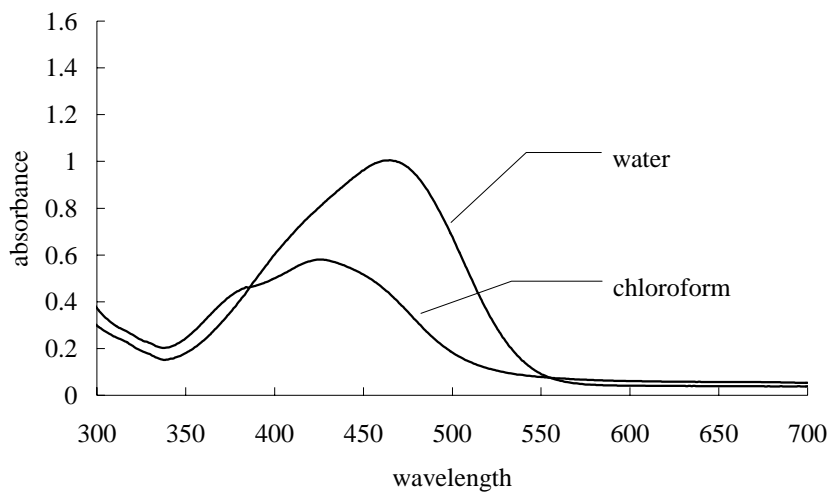
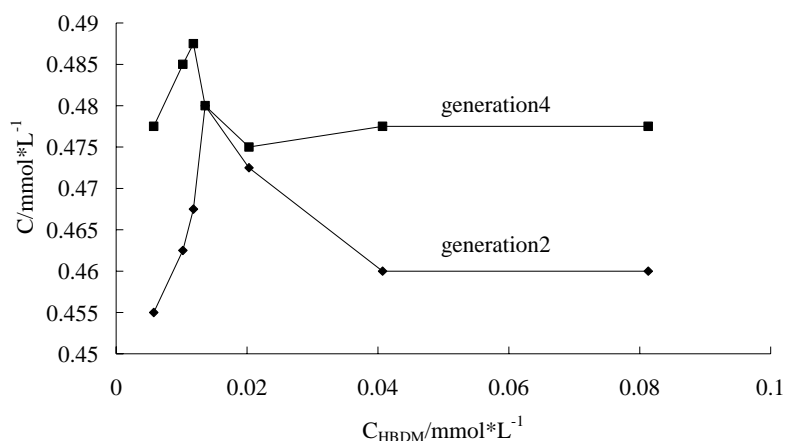
Scheme 1 The synthesis of 3-generation hyperbranched poly (ester-amine)**Figure 1** The UV-Vis spectra for MO in water and chloroform

Figure 2 The relationship between the polymer concentration and the amount of MO transferred into chloroform

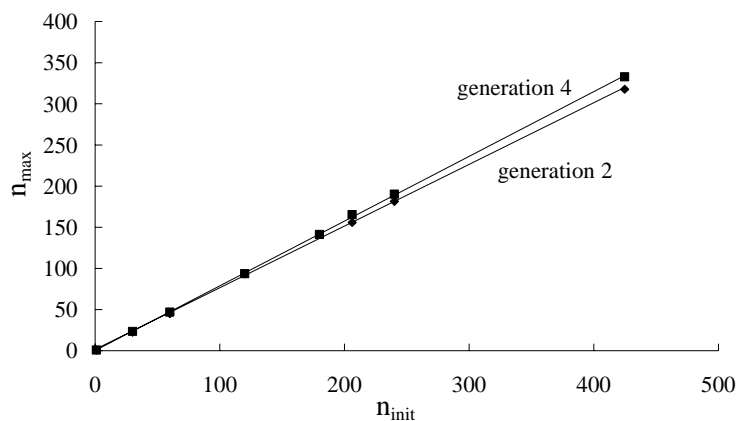


The initial concentration of MO in aqueous phase was 0.96mmol/L

Figure 2 shows the relationship between the polymer concentration and the amount of MO transferred into chloroform detected by UV-Vis spectra. It was obvious that the polymer with higher generation had a stronger phase transfer efficiency under the same concentration and an optimal concentration existed in both cases. Shown in **Figure 3**, the loading of dye molecules per macromolecule kept increase with increasing the initial molar ratio between MO and HPEA, quite different to the behavior of hydrophobic modified global molecules with a saturated value⁵.

As HPEA is highly hydrophilic, it has the tendency to migrate from organic phase into water and interact with dye molecules at phase interface based on the interaction between sulfonic acid groups in the dye molecule and tertiary amine groups within the hyperbranched molecule⁶. The acid-base interaction resulted in some interim amphiphilic aggregates with hydrophobic shell, which would diffuse gradually into the whole chloroform phase and made hydrophilic MO being successfully transferred. This process was noticed by careful observation and was confirmed by TEM. But the existence of such aggregates was transient. After the aqueous phase was removed and the organic phase was kept still for 6hr, the final obtained chloroform solution was yellowish and transparent. When the polymer concentration came to high, some aggregates would be formed from the macromolecules themselves, and only the tertiary amine near the surface could react with MO molecules, thus resulted in a decreased phase transfer capability. This result demonstrates new application for hyperbranched polymers as phase transfer agent.

Figure 3 The loading of dye molecules per macromolecule (n_{\max}) increase with increase the initial molar ratio of MO and HPEA (n_{init})



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