Decolourization performance in C. I. Vat Yellow 1 aqueous suspension using hydrophobically modified poly(acrylic acid)

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ABSTRACT

A series of hydrophobically modified poly(acrylic acid) (PAA), poly(2-phenoxyethyl acrylate-co-acrylic acid) (poly(PHEA-co-AA)), have been synthesized and characterized by Ubbelohde type viscosity, Nuclear Magnetic Resonance (¹H NMR) spectrometry and Differential Scanning Calorimetry (DSC). The shear thinning Non-Newtonian fluid behavior of their aqueous solution and the dependence on pH and hydrophobic group contents were found through apparent viscosity and rheological property investigating. Decolourization performance in C. I. Vat Yellow 1 aqueous suspension was evaluated through visible absorbance data. Decolourization performance of hydrophobically associated polymer indicates two times better than that of PAA. The quantitative relationship was mainly studied.

Key words | decolourization performance, hydrophobic association, modified poly(acrylic acid), vat dye aqueous suspension

INTRODUCTION

Colour is a troublesome matter in the treatment of dyestuff industry effluent because of the low level of aerobic biodegradation (Games & Hites 1977). Physical, chemical and biological operations like flocculation (Moghaddam et al. 2010) and activated sludge methods (van Leeuwen et al. 2009) have become hot issues with advantages, however, there are drawbacks in application, such as low efficiency, expensive cost and partial decomposition of dyes which brings potentially further secondary pollution. Organic and inorganic flocculants have always attracted considerable attention. Synthetic polymers such as polyacrylamide (PAM) are effective due to their high molecular weights and reactive functional groups (Wong et al. 2006).

Hydrophobically associated water-soluble polymers have unique rheological properties in aqueous solution owing to intermolecular association by hydrophobic groups such as fluorocarbons (Chen et al. 1999; Zhuang et al. 2002), hydrocarbons containing from 8 to 18 carbon atoms (Zhuang et al. 2002) and polysiloxane (Hu et al. 2003), which brings extensive application in enhanced oil recovery, water treatment, personal care products and water-borne coatings (Bolto 1995). Hydrophobic groups help the interaction between polymer and particles, reduce the hydrophilicity of floc and enhance decolourization performance. In comparison with unmodified parent polymers (PAA), hydrophobically modified water-soluble polymers have particular properties such as enhanced viscosities and their obvious pH and shear dependence (Chen et al. 1999), promoting the flocculation efficiency in waste water treatment, especially in red or yellow dyeing effluents which are difficultly deal with. Hydrophobically modified polymeric flocculants is common in the purification of oily wastewater (Zhao et al. 2002), montmorillonite suspension (Dragan et al. 2002) and kaolin suspension (Ren et al. 2008), nevertheless, few refers to dye waste water.

Recently, we have successfully prepared hydrophobically modified poly(acrylic acid) (PAA) with 2-phenoxyethyl acrylate (PHEA) as the hydrophobic monomer through copolymerization in supercritical carbon dioxide. PHEA has applications in adhesives, inks, ultraviolet-curing coatings...
and photoresists electronics industries, however, few reports were about hydrophobically modified PAA. Apparent viscosities and rheological properties of their aqueous solution were studied. Decolourization with C. I. Vat Yellow 1 aqueous suspension has been quantitatively investigated. The influence of hydrophobic association is mainly discussed in this paper.

**METHODS AND MATERIALS**

**Materials**

Acrylic acid (AA, 99.5%, stabilized with 200 ppm hydroquinone monomethyl ether) purchased from Alfa Aesar company was purified to remove the polymerization inhibitor by distilling under reduced pressure and stored in a refrigerator before use. 2-Phenoxyethyl acrylate (PHEA, PHOTOMER® 4035, technical grade) supplied by Cognis Corp. was used as received. 2, 2’-Azobis(isobutyronitrile) (AIBN, Tianjin Fuchen Chemical Reagents Factory) as the initiator was recrystallized twice from methanol. The polymerization medium was carbon dioxide (Guangzhou Gas Factory Co., Ltd.) with the purity of no less than 99.9%. C. I. Vat Yellow 1 (Foshan Winhue Dyestuff Co., Ltd., technical grade) without further purification was utilized to simulate waste water of concentration 1 g/L with deionized water as a stock solution. All other chemicals used were analytically pure.

Characterization of poly(PHEA-co-AA)

The intrinsic viscosity, \([\eta]\), was determined in 2 mol/L sodium hydroxide (NaOH) aqueous solution at (30.0 ± 0.1)°C by an Ubbelohde type viscometer, while the viscosity-average molecular weight of poly(acrylic acid) was measured in 1, 4-dioxane at (30.0 ± 0.1)°C and calculated with the equation \([\eta] = K M^\alpha\), when Mark-Houwink parameters \(K\) and \(\alpha\) are \(8.5 \times 10^{-5}\) L/g and 0.50, respectively (Newman et al. 1954).

The constitution of products was characterized in 1 mol/L deuterated NaOH aqueous solution according to \(^1\)H NMR spectra using a Bruker DRX 400 MHz Nuclear Magnetic Resonance spectrometer at room temperature. Corresponding calculation shown by Equation (1) was based on the integrated areas (\(A\)) of resonance peaks of benzene ring (\(\delta, 6.7–7.2\ ppm\)) and methylene radical (\(\delta, 0.5–2.5\ ppm\)).

\[
cePHEA/ceAA (mol/mol) = \frac{(A_{(6.70–6.87) ppm} + A_{(7.05–7.19) ppm})/5}{A_{(0.50–2.45) ppm}^{3} \cdot (A_{(6.70–6.87) ppm} + A_{(7.05–7.19) ppm})/75} 
\]  

\[
T_g = x_{(PHEA)} \times T_g(PHEA) + x_{(AA)} \times T_g(AA) 
\]  

The glass transition temperature \((T_g)\), which was calculated followed by half delta specific heat (1/2 \(\Delta C_p\)) from the second-heating curve, was measured on a Q200 Differential Scanning Calorimeter (TA Instruments) at a heating rate of 20°C/min with a pure nitrogen gas flow of 50 mL/min. Equation (2) based upon Gibbs-DiMarzio Theory (He et al. 1990) was used to figure out \(T_g\) of poly(PHEA-co-AA) grounded on PHEA/AA mole ratios (\(x\)).

A rotary viscometer (Brookfield DV-II +, Brookfield Engineering Laboratories) with a No. 18 or 25 spindle was employed to investigate apparent viscosities and rheological
properties of 1 wt% poly(PHEA-co-AA) aqueous solution at 25°C. The rheological behavior was described by power law equation (Equation (3)) concerned with shear stress (τ), shear rate (Dr), viscosity coefficient (K) and flow index (n) (He et al. 1990). The logarithmic form (Equation (4)) was used to calculate K and n from the intercept and slope of the plot of Logτ versus LogDr, respectively.

\[ \tau = K \times Dr^n \]  
\[ \log \tau = \log K + n \log Dr \]  

**Decolourization performance of poly(PHEA-co-AA) in dye aqueous suspension**

Visible absorption spectra and absorbance data of dye were recorded on a Shimadzu UV-240 spectrometer in aqueous suspension. In a typical flocculating decolourization experiment, the polymer aqueous solution with pH 7 was introduced into 0.1 g/L C. I. Vat Yellow 1 homogeneous aqueous suspension. After the pH adjustment by adding hydrochloric acid (HCl) aqueous solution, the suspension was stirred at a speed of 200 rpm for 10 min. Followed with settling down for 2 hrs, the absorbance of the supernatant liquid was measured. The expression of decolourization rates (Equation (5)) was according to the concentration (c_0 and c_i denote the dye concentration in aqueous suspension before and after flocculation, respectively, g/L) of C. I. Vat Yellow 1 aqueous suspension, which was calculated by the linear Equation (6) fitted from the calibrated curve with absorbance ranged 0 to 3.5 at \( \lambda_{max} \) (424.3 nm).

\[ \text{Decoloured rate (\%)} = \frac{c_0 - c_i}{c_0} \times 100 \]  
\[ \text{Absorbance} = 0.129 + 9.63 \times c \text{ (g/L)}, \text{correlation coefficient (r)} = 0.999 \]  

**RESULTS AND DISCUSSION**

**Characterization of poly(PHEA-co-AA)**

The intrinsic viscosity in 1, 4-dioxane of PAA obtained in supercritical carbon dioxide is 0.0941 L/g, which is calculated to the viscosity-average molecular weight of over \( 1.2 \times 10^6 \) g/mol.

**Table 1 | Composition of poly(PHEA-co-AA)**

<table>
<thead>
<tr>
<th>No.</th>
<th>c PHEA/AA in feed (mol/mol)</th>
<th>c PHEA/AA in polymer (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0/100</td>
<td>0/100</td>
</tr>
<tr>
<td>(b)</td>
<td>0.651/100</td>
<td>0.644/100</td>
</tr>
<tr>
<td>(c)</td>
<td>1.41/100</td>
<td>1.42/100</td>
</tr>
<tr>
<td>(d)</td>
<td>2.00/100</td>
<td>2.01/100</td>
</tr>
<tr>
<td>(e)</td>
<td>2.51/100</td>
<td>2.47/100</td>
</tr>
<tr>
<td>(f)</td>
<td>3.00/100</td>
<td>2.94/100</td>
</tr>
<tr>
<td>(g)</td>
<td>10.0/100</td>
<td>9.95/100</td>
</tr>
<tr>
<td>(h)</td>
<td>16.1/100</td>
<td>15.5/100</td>
</tr>
<tr>
<td>(i)</td>
<td>24.3/100</td>
<td>23.8/100</td>
</tr>
</tbody>
</table>

The samples poly(PHEA-co-AA) with relative less PHEA/AA mole ratios are homogeneous loose powder and the homopolymer PPHEA is homogeneously aqueous suspension. After the pH adjustment by adding hydrochloric acid (HCl) aqueous solution, the suspension was stirred at a speed of 200 rpm for 10 min. Followed with settling down for 2 hrs, the absorbance of the supernatant liquid was measured. The expression of decolourization rates (Equation (5)) was according to the concentration (c_0 and c_i denote the dye concentration in aqueous suspension before and after flocculation, respectively, g/L) of C. I. Vat Yellow 1 aqueous suspension, which was calculated by the linear Equation (6) fitted from the calibrated curve with absorbance ranged 0 to 3.5 at \( \lambda_{max} \) (424.3 nm).

The samples poly(PHEA-co-AA) with relative less PHEA/AA mole ratios are homogeneous loose powder and the homopolymer PPHEA is homogeneously colloidal, however, a bit colloidal agglomeration can be found at the bottom of the reactor when PHEA/AA mole ratio is greater than 24/100. The monomer PHEA can swell PPHEA and partly dissolve poly(PHEA-co-AA). Excessive PHEA helps polymer dissolve and sink to the bottom, so the polymerization system is not homogeneous. The composition data of products are shown in Table 1. Polymeric activities of PHEA and AA in supercritical carbon dioxide at 60°C are approximately equal when PHEA/AA mole ratios are less than 24/100, because of the similarity of PHEA/AA ratios in feed and in the products.

It follows the point in Figure 1(A) that the polymerization of PHEA and AA is random copolymerization without homopolymer in the products. There is only one glass transition in each curve. Owing to the flexibility of hydrophobic side
chains (phenoxyethyl groups), \( T_g \) of poly(PHEA-co-AA) have an decreasing tendency as PHEA/AA ratio goes up. As exhibited in Figure 1(B), also worth mentioning is that calculated results resemble experimental ones, and \( T_g \) and PHEA/AA ratios have linear relationships except for PPHEA.

Polymerization through one step in supercritical carbon dioxide is simple to operate. Large amounts of hydrophobic group (-PHEA) could be easily introduced to PAA, which is beneficial to the property of products.

Rheological behavior of poly(PHEA-co-AA)

The solubility of poly(PHEA-co-AA) is pH sensitive. It separates out gradually when pH decreased. Besides, the introduction of too many hydrophobic groups (PHEA/AA mole ratio is more than 3/100) brings about the fact that polymer does not entirely dissolve in water (pH 7) with 1 wt% concentration.

Effect of pH. Because the flow index \((n)\) valued less than 1, the shear thinning Non-Newtonian fluid behavior can be seen in Figure 2. Clear pH sensitivity is displayed in poly(-PHEA-co-AA) compared with PAA. As pH increases, the viscosity coefficients curves peaked at pH 5.5. Flow indexes \((n)\) illustrate a negative peak with the similar change, which conveys that the greater pH deviates 5.5, the further it strays from the Newtonian fluid. It is explained by the balance between hydrophobic association and electrostatic repulsion through neutralization of carboxyl groups (Chen et al. 1999).

Effect of hydrophobic group contents on viscosity. It is shown in Figure 3 that the proportion of PHEA and AA exerts significant influence on viscosity properties of polymeric aqueous solution. Specifically, the viscosity coefficient of poly(PHEA-co-AA) (PHEA/AA mole ratio valued 2.94/100) is remarkably improved by 30 times compared with that of PAA. There is no distinct difference among molecular weights (intrinsic viscosities) of poly(PHEA-co-AA) with diverse amounts of hydrophobic groups. Hydrophobic association is the only cause of considerable distinction. Due to weak physical action such as Van der Waals Forces, the forming of network molecular structure in water obviously enlarges molecular weights, which is the root answer to the distinct viscosity increasing and an indispensable premise of flocculation and decolourization processes.

Decolourization performance in C. I. Vat Yellow 1 aqueous suspension

Water-soluble dyes have strong interaction with the medium, leading that the decolourization performance hardly occurs. For example, reactive dyes and cationic dyes water suspension are not decoloured with poly(PHEA-co-AA). But the interaction between water-insoluble dyes such as vat dyes and water is weak, which gives high probability of decolourization.

It is possible to speculate that the extension of macro-molecular chains and hydrophobically associated micro areas formed by exposed hydrophobic groups (-PHEA) allow easier surface contacting with dye particles. Owing to high-molecular-weight reticular molecule structure, it will have the property of more efficient precipitation after being flocculated. Also, the condition of deposition and separation process is more prone to be realized and controlled for its pH sensibility. Probably, several factors heavily affect the decolourization course, for example, polymeric hydrophobic association, physical interaction (Izumi & Hirata 1986; Dahlgren 1994; Bolto & Gregory 2007) between polymer and dye such
as Van der Waals forces, hydrogen bond and the affinity among benzene rings.

**Amounts of poly(PHEA-co-AA) and C. I. Vat Yellow 1.**

Based on the solubility of poly(PHEA-co-AA) in water and its better hydrophobically associated property, polymer with 2.94/100 PHEA/AA mole ratio was selected to do the decolourization experiments. The dosage of poly(PHEA-co-AA) produces obvious impacts on decolourization performance.

For one thing, Figure 4(A) depicts the common rule that along with the moderate rising of poly(PHEA-co-AA) dosage, decolourization rates skyrocket to above 90% and remain generally stable without any fluctuations with excessive dosages. The change is chiefly attributable to the fact that flocculating process is weak and rare with a small quantity of polymer, however, high dosage intake makes the interaction speeds up to much stronger. Continuous increase of polymer dosage hardly influences decolourization performance.

For another, to obtain the same decolourization results, dilute dye solutions required less dosage of polymer, while dense dye solutions needed more. Grounded on the assumption that added polymer is totally consumed for flocculation and sedimentation processes before adding excessive dosage, using the addition amounts of poly(PHEA-co-AA) as ordinate and the flocculated C. I. Vat Yellow 1 when 90% decolourization rates was selected to do the decolourization experiments. The dosage of poly(PHEA-co-AA) produces obvious impacts on decolourization performance.

**Effect of hydrophobic group contents on decolourization.**

Hydrophobic association plays an important role in the decolourization performance of poly(PHEA-co-AA), as is shown in Figure 5. PAA has certain effects for the water-soluble polymeric chains, however, it is not satisfying. The decolourization rate of hydrophobically modified polymer (92%) is improved two times higher than that of PAA (29%), which have been greatly contributed by a small number of hydrophobic groups among hydrophilic macro chains. Generally, stronger hydrophobic association promotes better decolourization performance. Also, due to network molecular structure, the increasing in molecular weights of poly(PHEA-co-AA) not only brings large viscosities in aqueous system, but also makes easier deposition in acidic medium. It is noteworthy that various decolourization performances of polymer with different hydrophobic group proportions well illustrate the existing of hydrophobically associating interactions in poly(PHEA-co-AA) aqueous solution.

**CONCLUSIONS**

The polymer poly(PHEA-co-AA) has been successfully synthesized in supercritical carbon dioxide. The aqueous solution shows the shear thinning Non-Newtonian fluid behavior, and when pH is close to 5.5, apparent viscosities are increased and it is near the Newtonian fluid. Hydrophobically associated polymers show more clear pH sensitivity than PAA. Effective decolourization performances in C. I. Vat Yellow 1 aqueous suspension with more than 92% decolourization rates were recorded. Hydrophobic association forms network molecular structure, promoting not only the apparent viscosity enhancing of aqueous solution but also decolourization performance. The mechanism of flocculation and the effect of hydrophobic group and dye structures will be included in further studies.
REFERENCES