ELSEVIER

Colloids and Surfaces A: Physicochem. Eng. Aspects 264 (2005) 114–119

COLLOIDS AND SURFACES A

www.elsevier.com/locate/colsurfa

Synthesis and electrorheological characterization of polymer containing amino and carboxy groups

Xinrong Song *, Yuanbin Lin

Institute of Polymer Science and Engineering, Xiangtan University, Xiangtan 411105, China

Received 11 May 2004; received in revised form 12 January 2005; accepted 11 February 2005
Available online 10 August 2005

Abstract

A new polymer (poly[*N*,*N*′-(2-amino-5-carboxy-1,3-phenylenedimethylene)-2,2′-diamino-4,4′-bithiazole], PACPDMDABT) containing amino and carboxy groups was synthesized. This polymer can be used as a disperse phase to prepare excellent electrorheological (ER) fluids. Several ER fluids were prepared (1) with the polymer in different type of disperse mediums (bromodiphenylmethane and silicone oil) and (2) with different polymer concentration in each type of the disperse medium. Rheological properties of the fluids were measured. Impact of the strength of the applied electric field, disperse phase concentration and different disperse mediums to the ER properties of the materials were measured and discussed. The results showed that ER properties of the fluids were improved as increase in the disperse phase concentration and as increase in the electric field strength. We also found that ER properties of the fluids depended on the densities of both polymer and disperse medium. Based on the results measured from two disperse mediums, the disperse medium with a closer match in density to the polymer showed better ER properties. Several key physical properties of the polymer were also measured by FTIR, thermogravimetric analysis and scanning electron microscopy.

Keywords: Synthesis; Electrorheological fluid; *p*-Aminobenzoic acid; Bithiazole; Disperse medium

1. Introduction

In general, electrorheological (ER) fluids are heterogeneous colloidal suspensions. Their electrorheological properties strongly depend on strength of the applied electric field. In the presence of an electric field, a characteristic fibrillation with the strings of particles oriented along the direction of electric field could be formed. The process of fibrillation of particles is usually reversible when the electric field is removed. The fibrillation of particles results in a drastic increase in apparent viscosity [1–3]. And the change of viscosity is also reversible when subjected to the application and removal of an electric field [4,5]. Various types of ER materials have been investigated including hydrous materials such as corn starch, cellulose and mesoporous particles with small amounts of absorbed water [6,7]. However, semiconducting polymers, biopolymer and polymer/clay nanocomposite systems [8–14], anhydrous ER materials have been drawn more attention due to their thermal stability and potential use as engineering materials such as for dampers and brake systems [15].

In this paper, we report our methods to synthesize a new polymer (poly[*N*,*N*′-(2-amino-5-carboxy-1,3-phenylenedimethylene)-2,2′-diamino-4,4′-bithiazole], PACPDMDABT) using 2,2′-diamino-4,4′-bithiazole (DABT) [16] condensed with *p*-aminobenzoic acid and paraformaldehyde and we discuss electrorheological effect and key physical properties of PACPDMDABT.

2. Experimentation

2.1. Synthesis of poly[N,N′-(2-amino-5-carboxy-1,3-phenylenedimethylene)-2,2′-diamino-4,4′-bithiazole]

2,2′-Diamino-4,4′-bithiazole (0.02 mol) and *p*-aminobenzoic acid (0.02 mol) with paraformaldehyde (0.02 mol) were

* Corresponding author.
E-mail address: songxinrong@vip.sina.com (X. Song).

0927-7757/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.colsurfa.2005.02.023

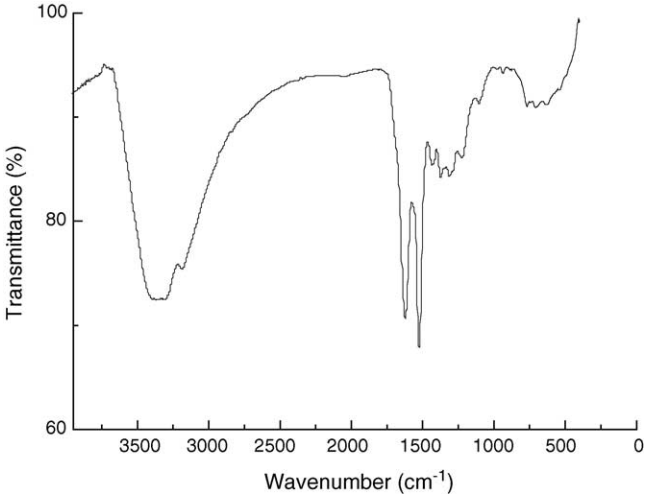


Fig. 1. IR spectrum of PACPDMDABT.

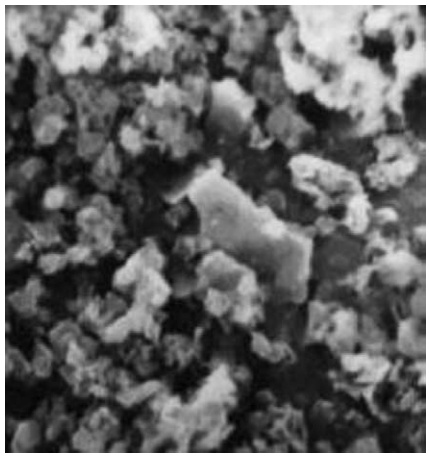
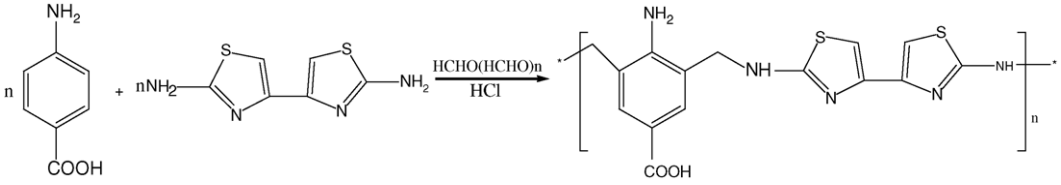


Fig. 2. SEM photograph of PACPDMDABT particles.

added into a 250 mL three-necked flask. The flask was equipped with a spherical condenser and filled with nitrogen gas. The reaction mixtures were gently stirred at 100 °C for 8 h in the presence of 2 mol L^{-1} HCl as catalyst. Brown precipitates (PACPDMDABT) were formed. PACPDMDABT was filtered and then washed successively with water, ethanol and ether, and finally dried under vacuum at 60 °C for 48 h.



2.2. Synthesis of bromodiphenylmethane

Four hundred millilitres of bromobenzene and 20 g anhydrous aluminium chloride were added into a 1000 mL three-necked flask equipped with a spherical condenser and agitator; 185 mL benzyl chloride was slowly added into the flask during a period of 3 h. The reaction mixture was gently stirred for 24 h at room temperature and then washed with 600 mL of 2 mol L^{-1} NaOH solution followed by distilled water, and finally separated by a separating funnel. The remainder containing the product was further purified by distillation to remove bromobenzene and was then distilled at 150 °C and at 20 mmHg. The bromodiphenylmethane has a density of 1.45×10^3 kg m^{-3} and viscosity of 1.5×10^{-2} Pa s at 20 °C.

2.3. Infrared spectrum

Infrared spectrum of PACPDMDABT was measured by FTIR (Fig. 1). The broad band observed at 3680–3200 cm^{-1} is due to stretching of NH and NH_2. Another broad band at 3190–2500 cm^{-1} is the characteristic band of Ar–H and COOH group in the solid state. The peak at 1623 cm^{-1} is due to stretching of C=C and C=N, and the peak at 910 cm^{-1} is the 1,3,4,5-tetrasubstituted aromatic C–H out-of-plane deformations. The bithiazole ring and skeletal stretching were observed at 1523, 1438, 1374, 1298, 1218 and 1090 cm^{-1}. The FTIR spectrum measured from PACPDMDABT was synthesized and is in well agreement with the proposed structure groups [17].

2.4. Density

Apparent density of PACPDMDABT particles was measured. Proper amount of PACPDMDABT particles was added into a 100 mL volumetric flask. The volumetric flask was then filled with water. The result showed that the apparent density of PACPDMDABT was about 1.56×10^3 kg m^{-3}.

2.5. Particle size

Surface morphology of PACPDMDABT particles was studied with a scanning electron microscope (SEM, S-570, Japan). PACPDMDABT particles were found irregular in physical shape (Fig. 2) with a size distribution about 15–32 μm in diameter.

2.6. Thermal analysis

Thermogravimetric measurements were performed with a WRT-3 thermal analyzer at a heating rate of 10 °C min^{-1}. The sample chamber was filled with nitrogen gas during the