Synthesis and Characterization of Electrorheological Copolyaniline

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NOTES

SYNTHESIS AND CHARACTERIZATION OF ELECTRORHEOLOGICAL COPOLYANILINE

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ABSTRACT

Copolyaniline containing phenyl sulfonic acid sodium salt pendent, was chemically synthesized and used for its characterization as an electrorheological (ER) fluid. Its chemical structure and particle shape were analyzed using an FT-IR, ^{13}C-NMR, and SEM. Copolyaniline particles have irregular and lamellar morphology. This ER fluid was prepared by dispersing polymer particles in silicone oil and was characterized by a rotational Haake rheometer with a high voltage generator. Typical ER behavior was found in the copolyaniline suspension.

INTRODUCTION

Electrorheological (ER) fluids are known as the fluids which show a large increase in apparent viscosity and recovery to the original viscosity by the application and removal of an external electric field, respectively. When an electric field is imposed, this fluid's rheological properties vary by showing a characteristic fibrillation, with the strings of the particles oriented along the electric field direction. This particle structuring is caused by the dielectric constant mismatch of the particles and the suspending oil [1].

Polyaniline is generally recognized as an air-stable organic conducting polymer. The following figure is a chemical structure of the polyaniline (emeraldine base) with the combination of both a reduced unit(x) and an oxidized unit(y), where x+y=1, and x is known to be ~ 0.5 under general polymerization conditions.

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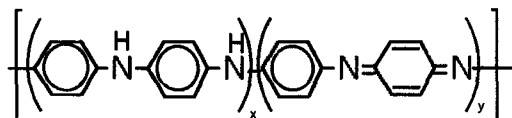
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Polyaniline has good thermal properties and a relatively high solubility in general organic solvents than other conducting polymers. Due to these characteristics, it has been widely investigated as a conducting polymer. Furthermore, it has been also adopted recently as dispersing particles to prepare ER fluids [2,3]. It has the advantages of a relatively low density, a controllable conductivity, and a thermal stability comparable to any other conventional hydrous ER fluid system. Nonetheless polyaniline is difficult to process. In order to develop better processibility of polyaniline, many researchers have investigated polyaniline dispersions [4], the synthesis of copolyaniline, introduction of a side group into the main chain [5], and different kinds of dopants [6]. Among various copolymers, SO_3^- and alkyl sulfonate substituents are often substituted into the polymer backbone. In this type of polymer, the sulfonate ion acts as a self-dopant. Thus, conductivity of the polymer is affected minimally by pH. The value of the conductivity, however, is lower than that of homopolymers, due to the disturbance of the conjugation of the electrons through the main chain. Recently, Chapman et al. [7] synthesized soluble polyaniline copolymers containing N-substituted benzene sulfonic acid groups. They also concluded that the conductivities of these copolymer samples are rather low due to the disruption of the conjugated backbone by the bulky aromatic sulfate groups.

In this study, N-substituted copolyaniline was synthesized and used as the dispersing particles in the ER fluid. Its molecular chain structure is hypothesized as follows:
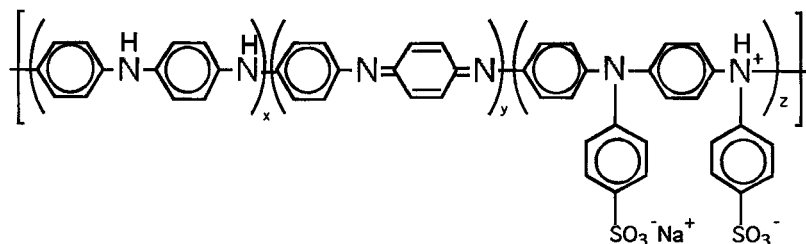
EXPERIMENTALS

To synthesize N-substituted copolyaniline [7], a monomer mixture of aniline (Junsei Chemical Co., Japan, used as purchased) and diphenyl-4-sulfonic acid sodium salt (Aldrich, used as purchased) (molar feed ratio = 3 : 1) were mixed into a 1-neck flask of 1M HCl. $FeSO_4$ was also added as a catalyst according to a published procedure [9]. The flask was kept in a controlled thermostatic bath (0°C ± 0.1°C). With vigorous stirring, a prechilled $(NH_4)_2S_2O_8$ solution in 1M HCl was then added dropwise to the mixture of aniline and 1M HCl for one hour in a nitrogen environment. The system was stirred for approximately 2 hours to complete the reaction. The solution was then allowed to precipitate, and the product was separated using a glass filter. The pH of the product was adjusted to 8.26 by adding either a NH_4OH or HCl solution. The synthesized polymer was washed 3 times using distilled water to remove the initiator (oxidant), the unreacted monomer, and the oligomer. It was then further washed with ethanol and cyclohexane, sequentially, in order to make the surface of the synthesized particles hydrophobic [2]. This process is advantageous for wetting between the particles
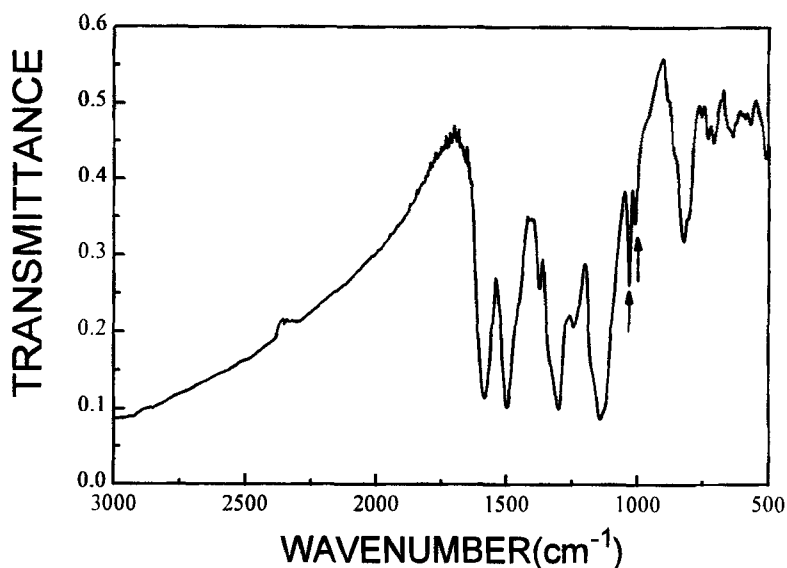
Figure 1. FT-IR spectrum of copolyaniline. Arrows indicate characteristic peaks of sulfonate ion vibration (1029 and 1004 cm^{-1}).

and oil during the ER fluid preparation. The product was finally put into a vacuum oven for approximately two days to dry. The polymers thus obtained were free-flowing, dark, green/blue powders.

The conductivity of the particles was measured to be 2.33×10^{-6} S/cm by using the 2-probe method with a pressed disk of the polymer. The particle size was controlled by a 38μm sieve, and the size of the particles was measured by a particle analyzer (Malvern), using ethanol as the dispersant (average diameter : 15.4μm, median : 7.3μm).

The shape of the polymer particles was also identified by using a scanning electron microscope (SEM). The structural analysis of copolyaniline was performed by using both an FT-IR (BIO-RAD, FRS-40) and a solid state ^{13}C NMR (Varian, Unity+300).

The ER fluid was prepared by dispersing copolyaniline particles in silicone oil, and the resulting particle concentration was 0.5 wt %. The viscosity of the silicone oil was 30 cS, and its density was 0.955 g/cm^3. The rheological properties were measured by a rotational Haake rheometer(VT 500) equipped with a DC high voltage generator.

RESULTS AND DISCUSSION

Figure 1 presents the FT-IR spectrum that is determined by using KBr pellets. The peaks at 1586 and 1490 cm^{-1} arise from aromatic C-C stretching vibrations, those at
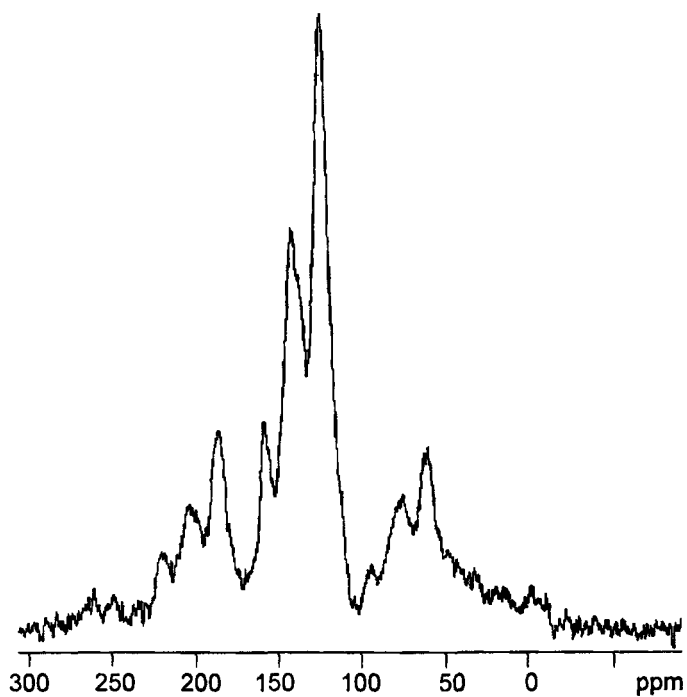
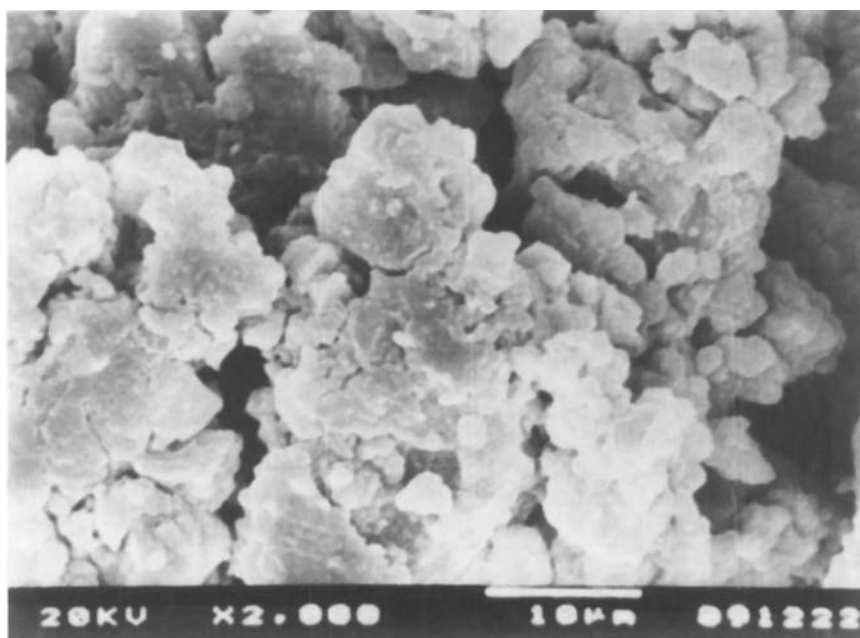Figure 2. Solid state ^{13}C-NMR spectra of copolyaniline.
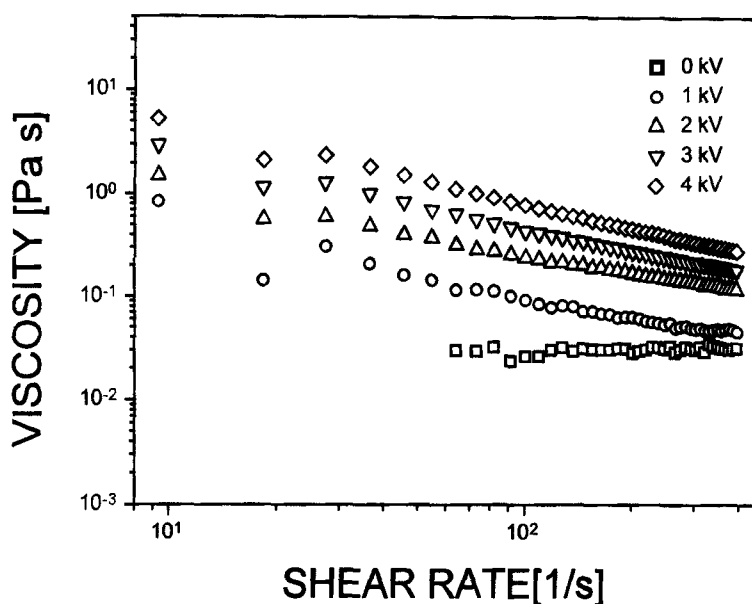

Figure 3. SEM photograph of copolymer particles.

Figure 4. Viscosity versus shear rate of 0.5 wt% copolyaniline in silicone oil with various electric fields.

1309 and 1144 cm^{-1} are from aromatic amine stretching, and the peak at 824 cm^{-1} is from the out-of-plane H deformation for aromatic rings, which occur because of the homopolymer unit. In addition, the characteristic peaks of the copolymer occur at 1029 and 1004 cm^{-1} , which are caused by the vibration of the sulfonate ion.

Copolyaniline is insoluble in general organic solvents, so we attempted another structural analysis using solid ^{13}C NMR. Figure 2 is the result from solid ^{13}C NMR and the peaks at 123.4, 141.7 and 158.1 ppm are the characteristic peaks of the polyaniline homopolymer [8]. Peaks of aromatic carbons in phenyl sulfonate are located between 126 - 130 ppm. In this result, these peaks seem to be contained within those of the homopolymer.

Particle shape is also observed by using SEM. Figure 3 indicates that copolyaniline particles have a irregular and laminar structure. This type of structure seems to arise from the rigid molecular structure of the copolymer.

Figure 4 gives the results of steady shear experiments using a Haake rheometer for copolymer ER systems. This shows the typical behavior of ER fluids under various applied electric fields. The viscosity increases with increasing applied electric fields and decreases with shear rate, similar to shear thinning polymer melts or solutions. We expect that at an extremely high shear rate, the viscosities reduce to those in an absent electric field. These trends of viscosity are due to the microstructural change in the suspension; the broken chains are continuously reformed in the low shear rate region, while small clusters become dominant in the high shear rate region.

We further expect that ER properties of the copolyaniline system might be better than those of the polyaniline homopolymer system. This is possibly due to the fact that the counter ion, Na^+, attached to the sulfonate anion, enhances the polarization of the polymer particles.

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