Polymer 117 (2017) 243–248

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Short communication

Electrophoretic non-ionic nano-spheres (latexes) for structural coloring

Daiki Mokude, Akinori Takasu*, Masahiro Higuchi

Department of Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

ARTICLE INFO

Article history:
Received 15 January 2017
Received in revised form
8 March 2017
Accepted 6 April 2017
Available online 12 April 2017

Keywords:
Latex
Electrodeposition (EPD)
Structural color

ABSTRACT

Electrophoretic deposition (EPD) is one of the most important coating methods. This method has various advantages, such as being able to make a coating as a uniform film, even on a complex surface. Recently, we found that non-ionic poly(ester-sulfone) materials show anode selective electrophoretic behavior. In this paper, we performed electrophoresis of non-ionic nano particles (diameter: ca. 300 nm), prepared via soap-free emulsion copolymerization of vinyl monomers containing a sulfide linkage with styrene and subsequent oxidation to a sulfonyl group. After EPD, a structural color was observed, indicating that the monodisperse spheres had attached to the surface and exhibited specific light diffraction, in which the wavenumber is dependent on the incident angle.

1. Introduction

Electrophoretic deposition (EPD), or electrodeposition, is one of the most important coating methods and is now applied for coating many metals as a rustproofing layer before painting, ex., in automobile, electronics, and buildings (Fig. 1) [1–10]. This conventional procedure has typical advantages, such as forming a uniform film even on complex surfaces and being operable as both cationic and anionic depositions, in which the coating is charged positively and negatively, respectively. Although the use of non-ionic paints for electrodeposition has a unique advantage from the viewpoint of rustproofing for facilities of electrodeposition, too, there have been no reports dealing with electrophoretic non-ionic polymers for this purpose, except for a report concerning conjugated polymers [11]. Recently, we found that non-ionic poly(ester-sulfone) shows anode selective electrophoretic behavior (Fig. 2) [12]. This enabled us to coat bioactive glass [12] and titanium (IV) oxide (TiO_2) [13] anode-selectively, and further, fabricate electrophoretic poly(ester-sulfone) gels [14]. In turn, this prompted us to explore why the poly(ester-sulfone) is deposited only onto the anode, and what part of the sulfone-containing polymer is responsible for this unusual electrophoretic behavior. Therefore, we synthesized a new poly(2-oxazoline) [15] and poly(methacrylate) [16] containing pendent sulfones via ring-opening polymerization and atom-transfer radical polymerization (ATRP) procedures, and investigated their electrophoretic behavior. A dispersion of these polymers in *N,N*-dimethylformamide (DMF)/ethanol also moved to the anode, suggesting that the sulfonyl groups are key to this phenomenon, and we concluded that partial charge separation of protic alcohols is induced by the pendent sulfonyl group at the interface under the influence of the electric field [17]. The speculation fits well with Uematsu's new theory [18] that electrophoresis of electrically neutral porous spheres can be induced by selective affinity of ions.

Our next target was the preparation of electrophoretic nanoparticles, which gave us stable dispersion, uniform surface, and structural coloring based on a specific light diffraction by deposited nano-particle layers (Fig. 3). Although there are some reports dealing with electric field-induced assembly of ionic colloidal spheres displaying structural color [19–21], there are no reports of nonionic colloidal crystals displaying structural color to the best of our knowledge. In this paper, we report the synthesis of electrophoretic non-ionic latexes by emulsion polymerization using a methacrylate containing a pendent sulfide linkage. After oxidation of the pendent sulfide to a sulfonyl group, we performed coating of monodisperse latex on a metal surface by the electrophoretic deposition (EPD) method, aiming at producing a structural color (Fig. 3).

Electrophoresis is employed in numerous engineering applications such as the separation of polyelectrolytes and coating by

* Corresponding author.
E-mail address: takasu.akinori@nitech.ac.jp (A. Takasu).

http://dx.doi.org/10.1016/j.polymer.2017.04.019
0032-3861/

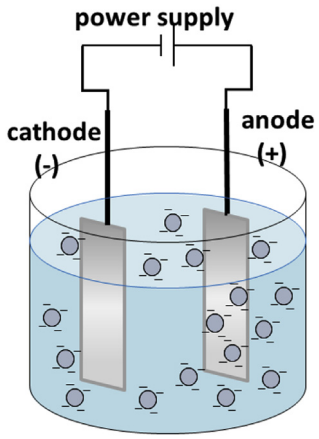

Fig. 1. Schematic representation of EPD of poly(ester-sulfone).

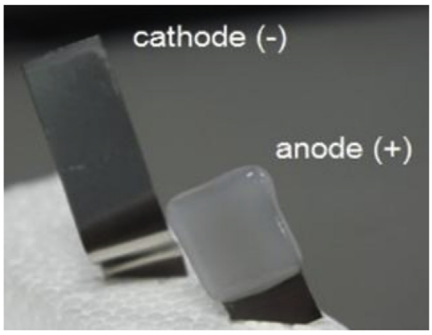

Fig. 2. Anode selective deposition of poly(ester-sulfone) after EPD.

electrophoretic decomposition. Smoluchowski presented the best known model wherein he argued that the mobility of a charged spherical colloid is given by $\mu = \varepsilon\zeta/(4\pi\eta)$ in the thin-double-layer limit (where μ is the mobility, ε is the dielectric constant of the solution, ζ is the electrostatic potential at slip surfaces, and η is the viscosity of the solution) [22]. In this article, we used protic solvents including water as various dispersion media to explore the EPD behavior of these non-ionic nano particles, and further investigated the relationship between the electrophoretic behavior and observed structural color.

2. Experimental section

2.1. Materials and methods

Materials. 2-(Ethylthio)ethanol and methacryloyl chloride, ethyl 2-bromoisobutyrate (EBiB), ascorbic acid, and hexadecane were purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). Triethylamine, copper(II) bromide ($CuBr_2$), and styrene were obtained from Wako Pure Chemical Industries, Ltd (Osaka, Japan). Commercially available dichloromethane (Kanto Chemical Co, Tokyo, Japan), tri-(2-pyridylmethyl)amine (TPMA) and polyoxyethylene (20) oleyl ether (Brij98) (Aldrich) were used in this study. Potassium hydroxide (KOH), potassium dihydrogenphosphate (KH_2PO_4), and potassium persulfate ($K_2S_2O_8$) were purchased from Nacalai Tescque Inc. (Kyoto, Japan). Other chemicals were obtained from commercial sources and used without further purification. ^{1}H NMR spectra were acquired at 27 °C using a Bruker Analytik DPX200 spectrometer (200 MHz) or a Bruker Analytik DPX400 spectrometer (400 MHz). Tetramethylsilane was used as an internal standard (0 ppm). FT-IR spectra of the polyesters in KBr disks were obtained using a JASCO/IR-430 spectrometer. The number average molecular weight (M_n) and polydispersity indexes (M_w/M_ns) for the polyesters were estimated using a size exclusion chromatography (SEC) system consisting of a Tosoh DP8020 pump system, a Tosoh RI-8020 differential refractometer, and Tosoh TSK-gel α-3000 and α-5000 columns (Tosoh, Tokyo, Japan). The eluent used was 0.05% (w/v) LiBr and 100 mM tetramethylethylenediamine in DMF. The flow rate was 0.5 mL/min, and the temperature was 40 °C. Zeta potential (ζ) measurements were performed using a Zetasizer Nano ZS (Malvern Instruments, UK) employing the electrophoretic light scattering method, with literature η values. The latex was visualized via scanning electron microscopy (SEM) (dual-stage JSM-6010LA; JEOL Ltd., Tokyo, Japan). Elemental composition was also investigated via energy-dispersive X-ray spectroscopy (EDX). The elemental distribution was determined using Smart Map, which simultaneously acquires X-ray data from each pixel in an image (JEOL Ltd., Tokyo, Japan). Transmission electron microscopy (TEM) combined with energy dispersive X-Ray analysis (EDX) mapping was performed using a JEM-z2500 (JEOL). Reflection spectrum of the structural colored film deposited on transparent glass electrode was measured using UV–vis spectrometer V-770 (JASCO, Japan) equipped with automated absolute reflectance system ARMN-920 (JASCO, Japan), and the measurement angle is parallel to that of the incident that of the incident and reflective light.

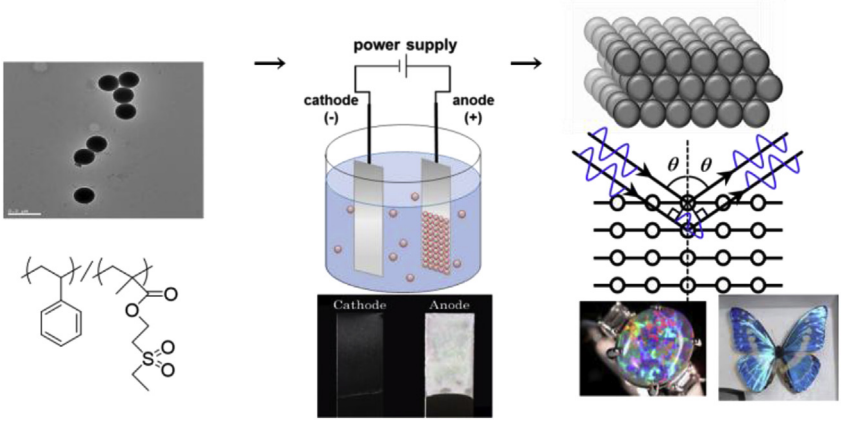

Fig. 3. Schematic of structural color induced by electrodeposition of sulfone-containing nano-latexes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)