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Synthesis of conductive microspheres by radiation polymerization

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Abstract

A conductive monodisperse microspheres consisting of poly(ethylene glycol)dimethacrylate and methyloxycarbonyl-bicyclo[2.2.1]hepta-2,5-diene was synthesized by radiation induced polymerization. Ionic conductivity and relative dielectric constant were found to be greatly dependent on the content of poly(ethylene glycol)methacrylate in the copolymer. The diameter of the microspheres was 0.48–0.86 μm, in which the irradiation was carried out without stabilizer at a dose rate of 20 kGy/h with ^{60}Co γ-ray.

Keywords: Conductive microspheres; Radiation polymerization; Poly(ethylene glycol)dimethacrylate containing copolymer

1. Introduction

The applications of polymer microspheres have increased in various fields, e.g. chemical industry, biotechnology, electronics, and medicine [1–9]. The conducting microspheres has been successfully prepared in our laboratory by radiation-induced polymerization. The advantages of this preparation method are that the synthesis is carried out in a single step and without any surfactant or stabilizer. Ionizing radiation can initiate the polymerization at any temperature and in the absence of chemical initiators. It is also possible to co-polymerize poly(ethylene glycol)dimetacrylate (PEGDMA) with a range of monomers, thus varying the hydrophobicity and the size of the microspheres.

The mechanism of the formation of the conductive microspheres in the present method is proposed as follows: the initiation radical formed by irradiation of monomer should react with the monomer by a chain reaction in which the nucleus of the polymer is isolated because the polymer is entirely insoluble in the solvent phase. This nucleus of the polymer grows to a stable particle according to a propagation reaction. The small particles with propagation radicals on their surfaces become larger as the polymerization proceeds. This polymerization reaction process occurs in the solvent phase, and then the microspheres of larger sizes are precipitated. Immediately after irradiation the precipitated microspheres of larger sizes were observed at the bottom of the vessel and those of a small size, in the solvent phase. Thus, this method can be referred to as a radiation precipitation polymerization.

The purpose of this paper is to aim at the application of conductive paste for liquid crystal display panel. To improve this property, a new polymer/$LiClO_4$ microspheres were prepared using a matrix polymer with poly(ethylene glycol) substituents and an alkali metal salt.

In this paper, the effect of radiation crosslinked of the microspheres, and of matrix polymer on the ionic conductivity and relative dielectric constant was investigated.

2. Experimental

2.1. Materials

Methyl propiolate, PEGDMA and $LiClO_4$ were purchased from Aldrich Chemical Co. and used without further purification. 2-Methyloxycarbonyl-bicyclo-2,5-diene (MOCBCHD) was prepared according to the literature [10].

2.2. Measurements

Proton NMR spectra was obtained using a Bruker AM-300 FT NMR spectrometer in $CDCl_3$. Infrared spectra were obtained using a Bruker EQUINOX 55. The weight-average molecular weight (M_w) was determined in tetrahydrofuran (THF) by a Waters GPC-150C calibrated with polystyrene standards. Morphology was observed using a scanning

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Table 1
Irradiation induced polymerization of MOCBCHD with PEGDMA

Monomer feed ratio[a]		Content of PEGDMA (mol%)	M_w[b] (10^4)	T_g[c] (°C)
MOCBCHD	PEGDMA			
4	1	17	2.8	107
10	1	9	5.4	131
20	1	3	6.5	158

[a] Polymerizations were carried out in MOCBCHD/PEGDMA molar feed ratios.
[b] Weight average molecular weights were measured by GPC in soluble fraction of THF and estimated relative to the polystyrene standards.
[c] T_g was measured with a Perkin–Elmer TA 7 system at a heating rate 10 °C/min.

electron microscope (Hitachi S-4100). DSC measurements were made at a heating rate of 10 °C/min in nitrogen.

2.3. Radiation polymerization

A mixture of MOCBCHD (0.6 g, 0.004 mol), PEGDMA (0.36 g, 0.001 mol) and $LiClO_4$ was dissolved in ethyl propionate. The mixed monomer solution (5 v/v% monomer concentration) was transferred into a glass vessel, and then nitrogen gas was bubbled through. The vessel was sealed. The irradiation of the vessel was carried out to polymerize at room temperature for 2 h at a dose rate of 20 kGy/h with ^{60}Co γ-ray. After irradiation, the polymer was isolated by precipitation in petroleum ether, and dried in vacuo. ^1H NMR ($CDCl_3$, ppm): 3.6 (1H, s), 2.3–1.4 (7H, m). FTIR (cm^{-1}): 3422 (OH), 2951 (aliphatic CH), 1719 (C=O).

2.4. Cell preparation of conductivity and dielectric constant

The ionic conductivity of the microspheres was measured by complex impedance analysis using a Solartron 1255 frequency response analyzer coupled to an IBM PS/2 computer over a frequency range of 20–10 MHz. The real and imaginary parts of the complex impedance were plotted, and the ionic conductivity could be obtained from the bulk resistance (R_b) found in the complex impedance diagram. The electrical impedance, Z^*, was converted to the complex dielectric permittivity using the equation.

$$\varepsilon^* = l\left(i\omega\varepsilon_0 A Z^*\right)^{-1} = \varepsilon' - i\varepsilon'$$

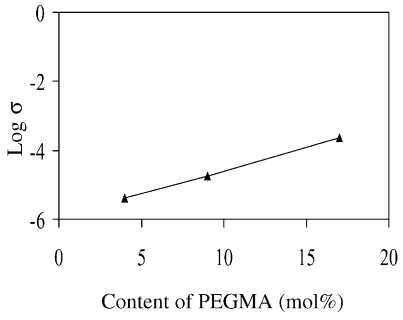

Fig. 1. Ionic conductivity of poly(MOCBCHD-*co*-PEGDMA)/$LiClO_4$ as a function of PEGDMA content at 25 °C.

where ε_0 is the dielectric permittivity of free space, A the surface area of the electrode, and l is the thickness of the film. In our study, the molar ratio of $LiClO_4$ and ethylene oxide unit in PEG in all the microspheres was fixed to be 0.05.

3. Results and discussion

Irradiation induced polymerizations of MOCBCHD with PEGDMA were carried out with various molar feed ratios in the absence of stabilizer and catalyst by using γ-ray source at a rate of 20 kGy/h in air and the results are summarized in Table 1. The PEGDMA content of the copolymer was calculated by comparing the integral areas of the proton NMR. Ionic conductivities of the poly(MOCBCHD-*co*-PEGDMA)/$LiClO_4$ for various content of PEGDMA are given in Fig. 1. The ionic conductivity of the system increased with the increase of content of PEGDMA. The conductivities at room temperature are measured to be in the range 3.8×10^{-4} to 7.2×10^{-6} S/cm. To investigate frequency dependence of the relative dielectric constant on the microspheres, the dielectric relaxation studies of the poly(MOCBCHD-*co*-PEGDMA)/$LiClO_4$ system were carried out. The relative dielectric constant ($\varepsilon'/\varepsilon_0$) vs. frequency plots are shown in Fig. 2. The $\varepsilon'/\varepsilon_0$ was increased with increasing content of PEGDMA. The size of the microspheres was studied by addition of concentration of MOCBCHD monomer. The relationship between the diameter of the microspheres and the concentration of

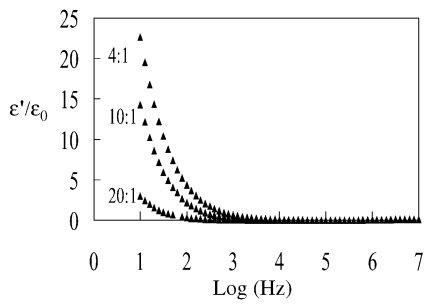

Fig. 2. Frequency dependence of the relative dielectric constant for poly(MOCBCHD-*co*-PEGDMA)/$LiClO_4$ as a function of PEGDMA content at 25 °C.

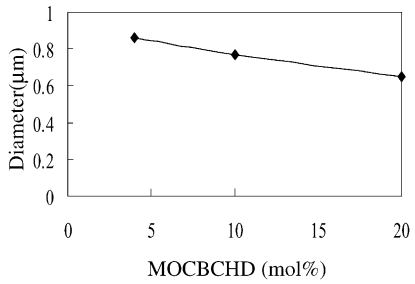

Fig. 3. Relationship between the diameter of the microspheres and the concentration of MOCBCHD monomer.

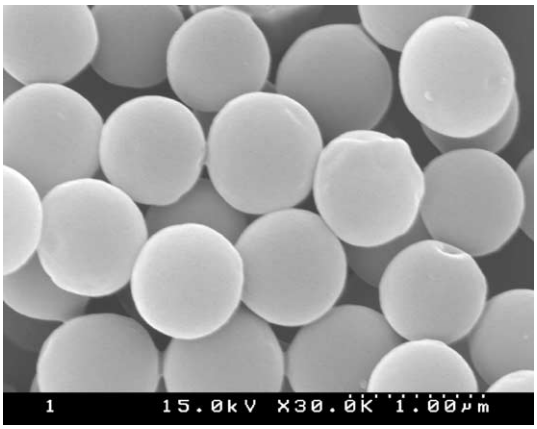

Fig. 4. The scanning electron micrograph of the microspheres in the poly-(MOCBCHD-*co*-PEGDMA) (4:1)/$LiClO_4$.

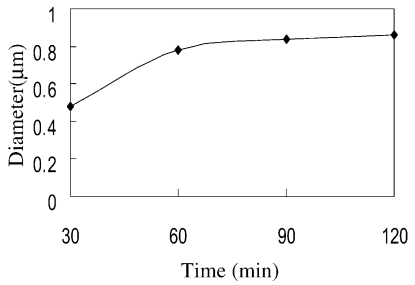

Fig. 5. Relationship between the diameter of the microspheres and the irradiation time for the poly(MOCBCHD-*co*-PEGDMA) (4:1)/$LiClO_4$.

MOCBCHD monomer in the mixture solution is shown in Fig. 3. The diameter of the microspheres was decreased by increasing the addition concentration of MOCBCHD monomer, leading to the formation of uniform microspheres. The scanning electron micrograph of the microspheres from PEGDMA to MOCBCHD monomer system is shown in Fig. 4. As can be seen in Fig. 4, radiation polymerization of the poly(MOCBCHD-*co*-PEGDMA)/$LiClO_4$ system was able to form monodisperse microspheres. This formation would be due to a uniform propagation rate of the polymer chains in the nucleus during irradiation. The size of the microspheres increased with increasing irradiation time as

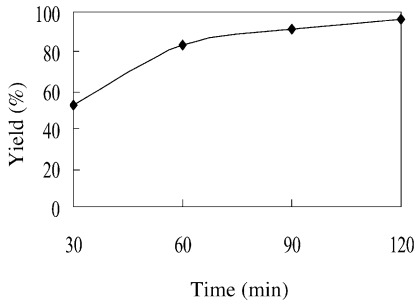

Fig. 6. Relationship between polymerization yield and the irradiation time for the poly(MOCBCHD-*co*-PEGDMA) (4:1)/$LiClO_4$.

shown in Fig. 5. The polymerization yield was increased with irradiation time to form the microspheres, in which the polymerization was completed within 2 h at room temperature as shown in Fig. 6. The size of the microsphere increased with increasing content of PEGDMA in the PEGDMA-*co*-MOCBCHD monomer system. The oxyethylene units with a hydrophilic property contributed to an interaction between the microsphere and solvent. This interaction should be related to an affinity of microspheres to solvent. The affinity of the microsphere was increased with increase of the content of PEGDMA resulting in an increase in the size of microsphere. The formation of the microspheres in MOCBCHD monomer was impossible, owing to a high affinity of MOCBCHD monomer, in which the polymer of MOCBCHD monomer is dissolved in solvent. In the present method, the control of the size of microspheres is related to a relative density of the microspheres and affinity to solvent because precipitation of the microsphere is dependent on the relative density of the microspheres. Additionally, PEGDMA monomer increased density and controlled the solubility of the microsphere.

Conductive paste of this microspheres as a liquid crystal display panel system is in progress, and the results will be published.

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