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Nano cellulose particles covered with block copolymer of cellulose and methyl methacrylate produced by solid mechano chemical polymerization

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ABSTRACT

Nano cellulose particles covered with a block copolymer of microcrystalline cellulose and poly(methyl methacrylate) (MCC-*block*-PMMA) were produced by a solid mechano-chemical polymerization. The polymerization of methyl methacrylate was initiated by chain-end-type microcrystalline cellulose (MCC) radicals (i.e., MCC mechano radicals) on the surface of MCC that were induced by mechanical fracture of β-1,4 glycosidic linkages. The chemically modified cellulose particles with MCC-*block*-PMMA were fractionated by Soxhlet extraction with chloroform, and resulted in MCC-*block*-PMMA residue from residue on the filter and MCC-*block*-PMMA filtrate from filtrate solution. The surface of the MCC particles chemically modified with MCC-*block*-PMMA in MCC-*block*-PMMA residue was partially covered with PMMA chains of the MCC-*block*-PMMA. In contrast, the surfaces of the MCC nanoparticles chemically modified with MCC-*block*-PMMA in MCC-*block*-PMMA filtrate were fully covered with PMMA chains of the MCC-*block*-PMMA. A dispersion of the chemically fully modified MCC nanoparticles in chloroform was optically transparent. The average diameter of the chemically fully modified MCC nanoparticles in chloroform was estimated to be 52 nm. These were confirmed by electron spin resonance, Fourier transform infrared, and ^{1}H nuclear magnetic resonance spectroscopy, by gel permeation chromatography and dynamic light scattering.

1. Introduction

Cellulose is the most abundant biological resource on Earth and is a carbon-neutral material. To achieve its widespread use, novel chemical modifications of cellulose are desired. Conventional chemical modifications have been limited to the hydroxyl group on the glucopyranose ring, which comprise the main chain of cellulose, because the β-1,4 glycosidic linkages that connect the main chain of cellulose are very rigid due to intra- and inter-molecular hydrogen bonding. Recently, we reported a novel main chain modification of bacterial cellulose involving the production of a block copolymer of bacterial cellulose and poly(methyl methacrylate) by mechano-chemical polymerization of methyl methacrylate [1].

Here, we report that the mechano-chemical polymerization was applied to the synthesis of a block copolymer of microcrystalline cellulose (MCC) and poly(methyl methacrylate (PMMA) (MCC-*block*-PMMA). The characterization of the products shows that MCC nanoparticles fully covered with PMMA chains of MCC-*block*-PMMA were obtained, and the dispersion of these modified MCC nanoparticles in chloroform was optically transparent.

2. Experimental

2.1. Mechanical fracture of MCC

A glass ball mill containing MCC (1.28 g, Aldrich) was evacuated under 0.6 Pa at 373 K for 7 h, sealed, and placed in a Dewar filled with liquid nitrogen. The MCC in the glass ball mill was then mechanically fractured using a homemade vibration ball mill apparatus [2] for 7 h at 77 K under vacuum. After milling, the fractured MCC was dropped into an electron spin resonance (ESR) sample tube attached to the top of the glass ball mill by quickly turning the mill over in the liquid nitrogen.

2.2. Synthesis of MCC-block-PMMA

Methyl methacrylate (MMA; Wako Pure Chemical Industries, Ltd) was purified twice by distillation in vacuum before use. The

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oxygen gas incorporated in MMA was eliminated by three repeated freeze-pump-thaw cycles. The purified MMA (2.13×10^{-3} mol) was introduced into the glass ball mill containing the vacuum-dried MCC (1.41 g), and the glass ball mill was sealed off from the vacuum line, set on the homemade vibration ball mill, and milled under vacuum at 77 K for 7 h.

2.3. Acetylation of fractured MCC and MCC-block-PMMA

The acetylation was based on the reported method [3]. A mixture of acetic acid (0.570 mol) and trifluoroacetic acid anhydride (0.436 mol) was held at 323 K for 20 min. Then, MCC (0.023 mol) was introduced and the solution was acetylated at 323 K for 12 h. The acetylated MCC (MCCTA) was precipitated with methanol, filtered, and dried under vacuum at 343 K for 6 h. Acetylated MCC-*block*-PMMA (MCCTA-*block*-PMMA) was produced using the same procedure.

2.4. ^{1}H nuclear magnetic resonance (^{1}H NMR) measurements

^{1}H NMR spectra were recorded on a JEOL ALPHA-500 NMR spectrometer at 500 MHz in $CDCl_3$. TMS was used as the internal reference.

2.5. ESR measurements

ESR spectra were observed at a microwave power level of 2 μW to avoid power saturation with 100 kHz field modulation using a Bruker EMX Plus spectrometer (X-band) equipped with a helium cryostat (Oxford ESR 900) and a temperature controller (Oxford ITC4).

2.6. ESR spectral simulations

The computer program was developed by author (M.S.). We have modified Heinzer's method to calculate a line-shape equation of ESR spectra in the solid state having anisotropic g and hyperfine splitting tensors A [4,5].

2.7. BET measurements

Nitrogen adsorption isotherms were obtained at 77 K on a Quantachrome Autosorb-1 system. All samples were degassed at 298 K for over 5 h before measurement. The surface areas were calculated using the BET method in the relative pressure (P/P_0) range of 0.13–0.27.

2.8. Gel permeation chromatography measurements

Number and weight average molecular weights (M_n and M_w) and polydispersity index (M_w/M_n) were estimated by gel permeation chromatography (GPC) (SCL-10Avp, SIL-10A, LC-10Ai, CTO-10ACvp, RID-10A, Shimadzu) in chloroform at 40 °C. Shodex columns (K-806M, K-802) were used, and the flow rate was 0.8 ml/min. A calibration curve was obtained using polystyrene standards (Shodex).

2.9. Fourier transform infrared (FT-IR) measurements

FT-IR spectra were observed on a JASCO FT/IR 4200 using solid KBr pellets.

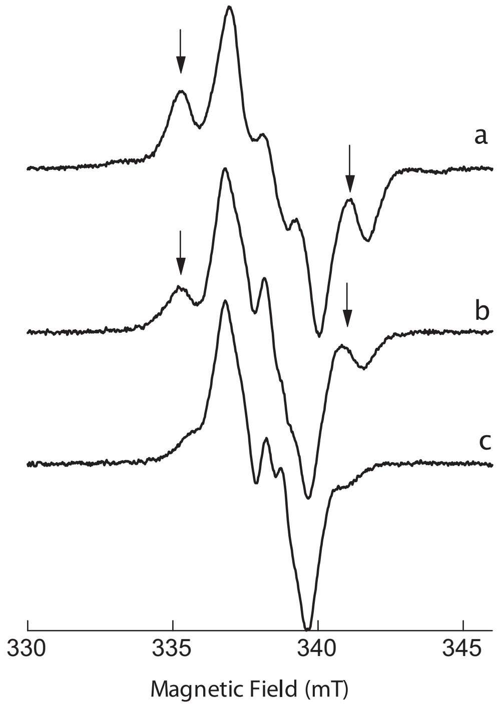

Fig. 1. ESR spectra of (a) fractured MCC, (b) fractured MCC annealed at 262 K, and (c) fractured MCC annealed at 304 K. All ESR spectra were observed at 77 K.

2.10. Dynamic light scattering measurements

Dynamic light scattering (DLS) measurements were performed using a nano Partica SZ-100 (HORIBA Co. Ltd.) in chloroform at 298 K.

3. Results and discussion

3.1. Mechanical fracture of MCC and radical pair formation

MCC was fractured in vacuum at 77 K for 7 h. The ESR spectrum of the fractured MCC was observed at 77 K (Fig. 1a). This spectrum revealed that the mechanical fracture of MCC induced covalent bond scission to produce free radicals. To elucidate the effect of temperature on the ESR spectrum, the fractured MCC was annealed at an elevated temperature (262 K) for 10 min, cooled to 77 K, and then the ESR spectrum was determined at 77 K. The intensity of the humps decreased (shown with arrows) in the resultant spectrum (Fig. 1b) as compared with that of the MCC annealed at 77 K. By sequentially annealing at 304 K, the humps disappeared from the spectrum (Fig. 1c) and were replaced by a broad doublet. Although the shape of the broad doublet did not change by annealing at 342 K, the ESR intensity decreased. These results indicate that the fractured MCC annealed at 304 K (Fig. 1c) consisted of a single radical species whereas the fractured MCC before annealing (Fig. 1a) consisted of several radical species.

Fig. 2 shows the relative ESR intensity of the fractured MCC with respect to the annealing temperature. To obtain these results, the sample was annealed at each temperature for 10 min and stored at 77 K for 10 min; then, the spectrum was measured at 77 K. The intensity was obtained by double integration of the ESR spectrum and was normalized to that of the fractured MCC before annealing. The intensity did not change below 120 K then decreased with increasing annealing temperature to 53.9% at 304 K. This indicates that the doublet spectrum (Fig. 1c) is caused by a single radical