Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

for

A Novel Protocol for Oxidative Degradation of Chitosan with Hydrogen Peroxide Catalyzed by Peroxomolybdate in aqueous Solution

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1. Experimental Section

1.1 Materials

$H_3PMo_{12}O_{40}$, $Na_3PMo_{12}O_{40}$ and K_2MoO_4 (AR) were purchased from Aladdin Industrial Corporation. H_2O_2 (Hydrogen peroxide, 30%) and Chitosan (DD≥90%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used was distilled.

1.2 Apparatus

The FT-IR spectra of samples were recorded on a NEXUS 670 FT-IR spectrometer with KBr pellets prepared by manual grinding. Raman spectra of samples were recorded on Renishaw RM1000 (λ =514.5 nm). Fluorescence spectra were acquired with an FLSP920 spectrofluorometer (Edinburgh Instruments Ltd, UK) at 20±1℃, equipped with a temperature-controlled circulator (Julabo, Germany). X-ray diffraction (XRD) patterns of samples were carried out on a PW 3040/60 X-ray diffractometer (Philips, Netherlands) with Cu Kα target at 40 kV and 40 mA. The samples were scanned from 5° to 70° of 2θ. The UV-vis absorption spectra of the samples were measured in the range of 100-800 nm on a UV-vis spectrometer (Nilcolet. Evolution 500 Thermo). The intrinsic viscosity is measured by the Ubbelohde viscometer with a 0.5mm capillary.

1.3 Synthesis of $(TBA)_3\{PO_4[MoO(O_2)_2]_4\}$

$(TBA)_3\{PO_4[MoO(O_2)_2]_4\}$ was prepared according to the literature.[1] Hydrogen peroxide (30%) (10mL, 100 mmol) was added to a solution of $H_3[PMo_{12}O_4]$ (1.65 g in 1 mL water). After 30 min, an aqueous solution of tetrabutylammonium chloride (1.6 mmol in 3 mL) was slowly added. The resulting pale yellow precipitate was filtered out, washed several times with water, and then air dried. IR (KBr): $\nu(PO_4)$：1072,1043 cm^{-1}, ν(Mo=O): 963 cm^{-1}, ν(O-O): 874 cm^{-1}, $\nu_{asym}[Mo(O)_2]$: 587 cm^{-1}, ν_{sym} $[Mo(O)_2]$: 543 cm^{-1}. Raman (in CH_3CN): $\nu(PO_4)$： 1131,1056 cm^{-1}, ν(Mo=O): 973 cm^{-1}, ν(O-O): 883 cm^{-1}, $\nu_{asym}[Mo(O)_2]$: 591 cm^{-1}, ν_{sym} $[Mo(O)_2]$: 563 cm^{-1}.

1.4 Synthesis of $K_2[Mo_2O_3(O_2)_4]$

$K_2[Mo_2O_3(O_2)_4]$ was prepared according to the literature.[2] A solution of K_2MoO_4 (5.0g in 10mL water) was placed in an ice-water bath. 30% H_2O_2 (14mL) was slowly

added. The solution turned dark red, to which dilute hydrochloric acid was added until the color just turned bright yellow at pH=4~5. Then the ethanol was added. The resulting yellow precipitate was filtered out, washed several times with ethanol and dried in air. IR (KBr): ν(Mo=O): 962 cm^{-1}, ν(O-O): 851 cm^{-1}, $\nu_{asym}[Mo(O)_2]$: 582 cm^{-1}, ν_{sym} $[Mo(O)_2]$: 533 cm^{-1}, $\nu_{asym}[Mo_2O]$: 714 cm^{-1}, $\nu_{sym}[Mo_2O]$: 449 cm^{-1}. Raman (solid): ν(Mo=O): 963 cm^{-1}, ν(O-O): 867 cm^{-1}, $\nu_{asym}[Mo(O)_2]$: 587 cm^{-1}, ν_{sym} $[Mo(O)_2]$: 537 cm^{-1}, $\nu_{asym}[Mo_2O]$: 684 cm^{-1}, $\nu_{sym}[Mo_2O]$: 454 cm^{-1}.

1.5 The typical procedure of Oxidative Degradation of Chitosan

In a typical reaction, a mixture of 0.200 g of chitosan, 4.2 μmol Mo in the catalyst, 5 mL of the distilled water, 1 mL of 30% H_2O_2, was stirred at the 50 mL round-bottomed flask for 20 min at different temperature. After the reaction, NaOH was added until reaching pH=7. The products were extracted with ethanol. The resulting white precipitate was filtered out, dried in vacuum and analyzed.

The degradation ratio of chitosan was defined as follows:

$$R\% = \frac{M_0 + M_{cat} - M_x}{M_0} \times 100$$
$$R\% = \frac{M_0 - M_x}{M_0} \times 100 \qquad (1)$$

Where R refers to the degradation ratio of chitosan, M_0 refers to the quantity of the original chitosan, M_{cat} refers to the quantity of the catalyst, M_x refers to the quantity of the collected solid after degradation at different conditions.

1.6 The viscosity average molecular weight (M_v)

The Ubbe-lodhe viscosimeter was used to determine the intrinsic viscosities at 303 K. Chitosan was dissolved in 0.1 mol/L CH_3COONa–0.2 mol/L CH_3COOH solution. The sample concentration was ca. 0.01mg/mL (w/v). The viscosity average molecular weight (M_v) was calculated according to the literature.[3]

$$[\eta] = \frac{\eta_{sp} + 3In\eta_r}{4C} \qquad (2)$$

$$[\eta] = 1.81 \times 10^{-3} M_v^{0.93} \qquad (3)$$

Here， η_{sp}, η_r refer to the incremental viscosity and the relative viscosity respectively, C is the concentration of chitosan or LMWSC (g/mL). M_v is the viscosity average molecular weight.

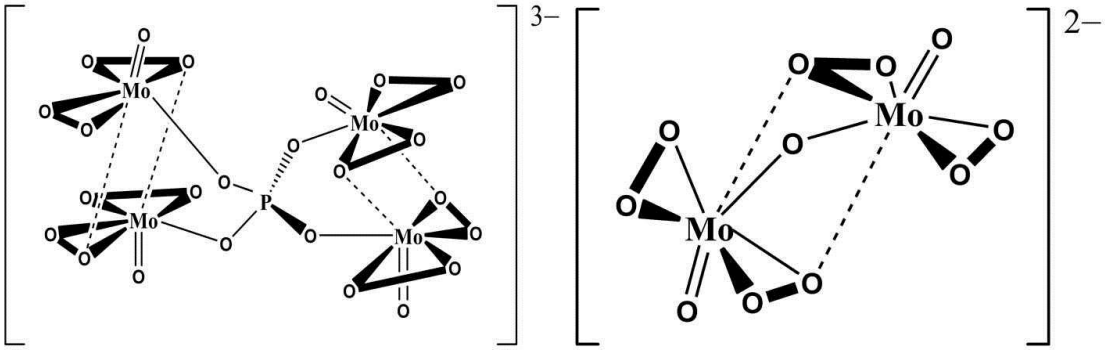

Fig. S1 the structure of the isolated peroxo species Ⅰ, $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ and $[Mo_2O_3(O_2)_4]^{2-}$

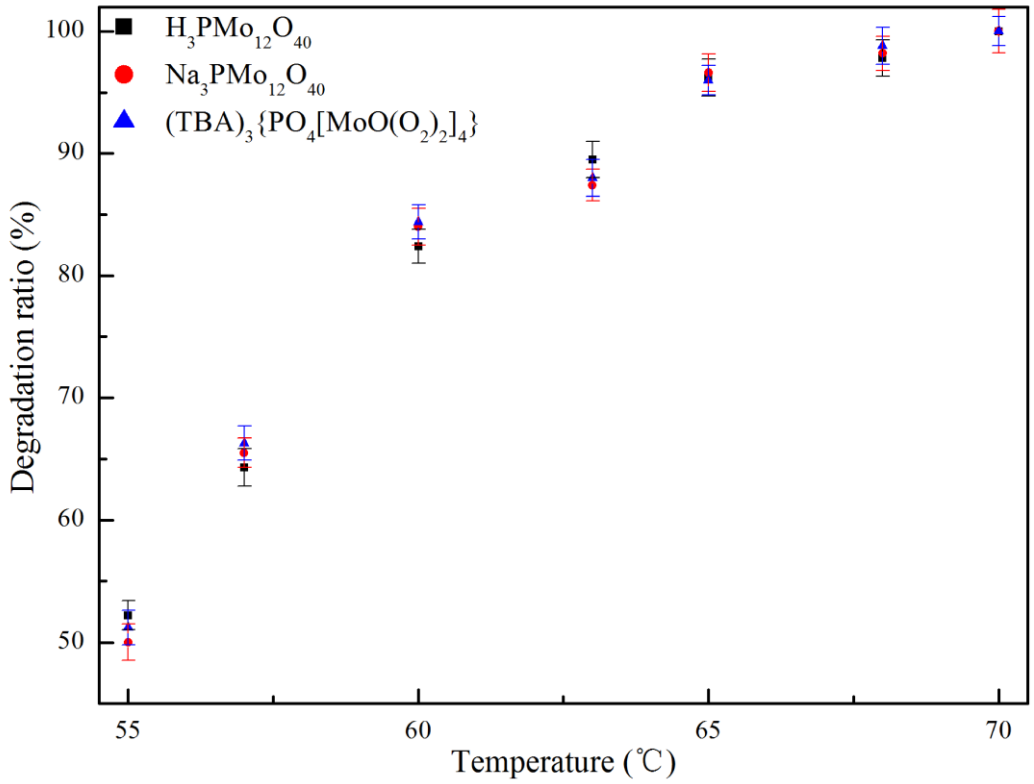

Fig. S2 The oxidative degradation of chitosan with H_2O_2 by $H_3PMo_{12}O_{40}$ (0.35 μmol), $Na_3PMo_{12}O_{40}$ (0.35 μmol) and $(TBA)_3\{PO_4[MoO(O_2)_2]_4\}$ (1.05 μmol), respectively. The reaction conditions: H_2O_2 (1mL), H_2O (5 mL), 20 min.

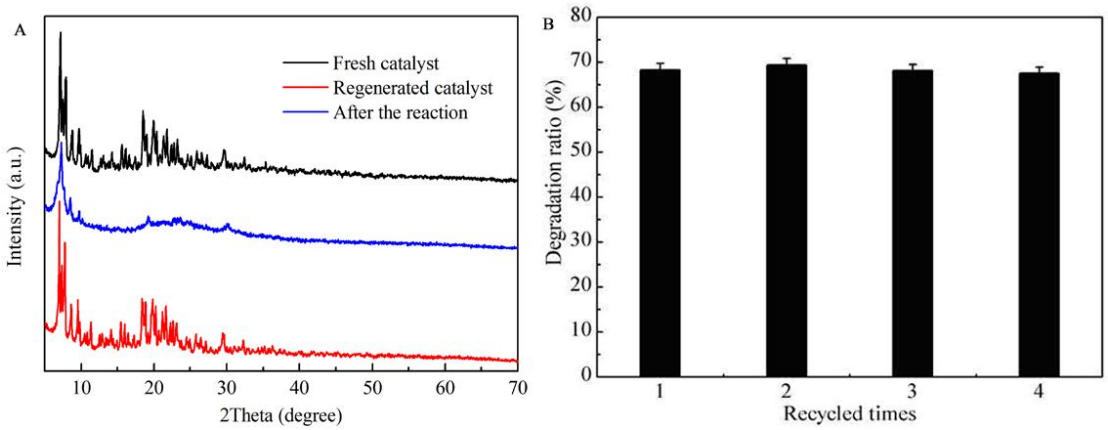

Fig. S3 (A) XRD pattern of the fresh catalyst, the used catalyst and the regenerated catalyst; (B) Recycled reaction, reaction conditions: 0.125 mmol $(TBA)_3\{PO_4[MoO(O_2)_2]_4\}$, 5 mL H_2O, 70 ℃, 20 min.

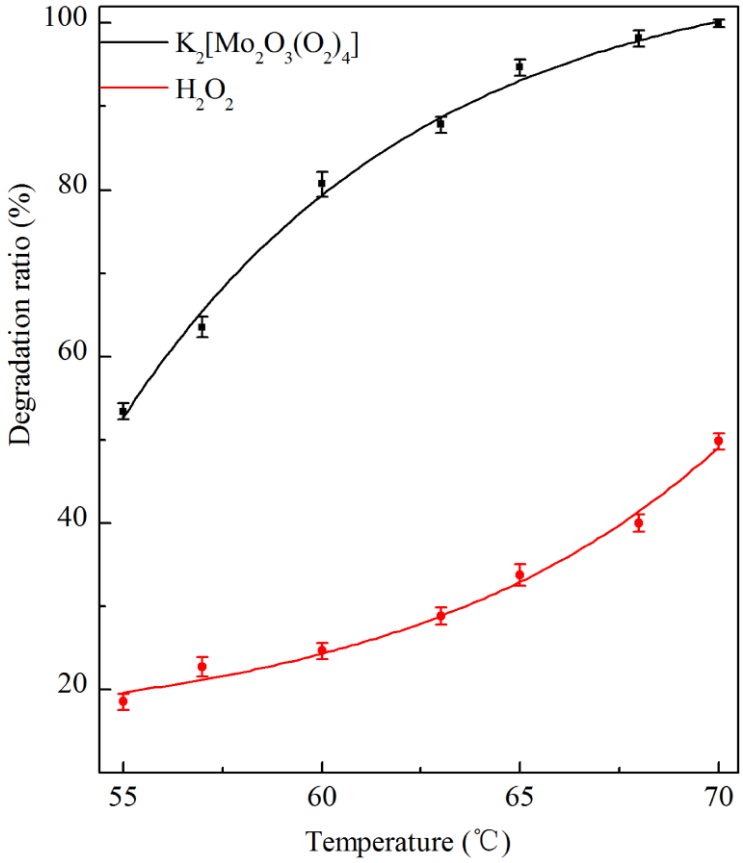

Fig. S4 The oxidative degradation of chitosan with H_2O_2 by $K_2[Mo_2O_3(O_2)_4]$ (0.7 μmol) and without any additives .The reaction conditions: H_2O_2 (1 mL), H_2O (5 mL), 20 min.

2. Characterization of the chitosan and LMWSC

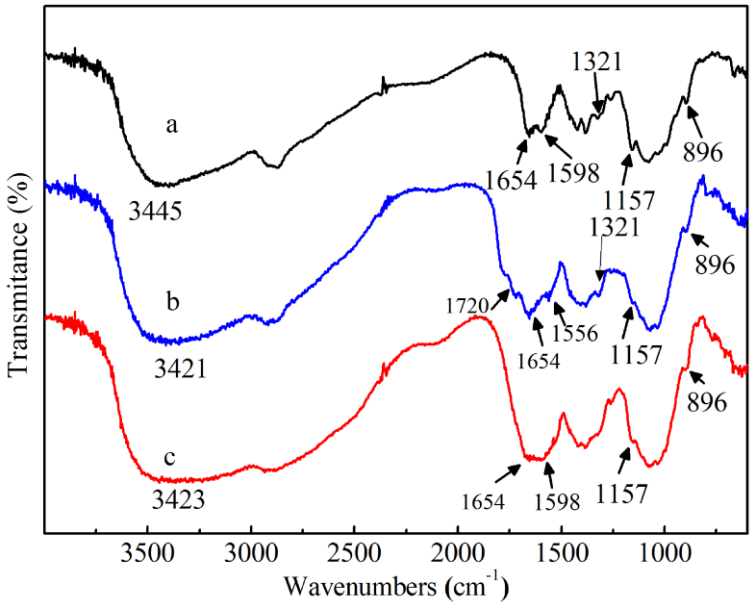

Fig. S5 FTIR spectra of original chitosan (a), LMWSC, pH=5~6 (b) and LMWSC, pH=8~9 (c).

Fig. S5 shows the FTIR spectra characterization of the original chitosan and the LMWSC . The main bands of original chitosan were as follows: the band at around 3445 cm^{-1} could be ascribed to the stretching vibration of O-H and N-H, the absorption peak at 1598 cm^{-1} corresponds to the binding vibration of the amido groups, an apparent carboxyl (-C=O) band at 1654 cm^{-1} is attributed to the residual acetyl. The band in the range 1157 cm^{-1} to 896 cm^{-1} belongs to the special absorb peaks of β-1,4 glucoside bond in chitosan.[4] The similar characteristics in the FTIR spectra of the LMWSC were also observed but with some differences. To confirm carboxylic group was formed in the process of degradation of chitosan. The products were collected at different pH. A new absorption peak at 1720 cm^{-1} was observed in the spectra of LMWSC (pH=5~6). However, it disappeared in the spectra of LMWSC (pH=8~9). Thus the absorption peak at 1720 cm^{-1} could be assigned to the absorption of carboxylic group (-COOH). And the absorption peak at 1598 cm^{-1} corresponded to $–NH_2$ disappeared in the spectra of LMWSC (pH=5~6) because it was formed $–NH_3^+$. The $–NH_3^+$ related band at 1564 cm^{-1} appeared in the spectra of LMWSC (pH=5~6). When the pH value was 8~9, the –COOH turned to $–COO^-$ and $–NH_3^+$ turned to $–NH_2$, the absorption peak 1720 cm^{-1} disappeared and the absorption peak 1598 cm^{-1} appeared.

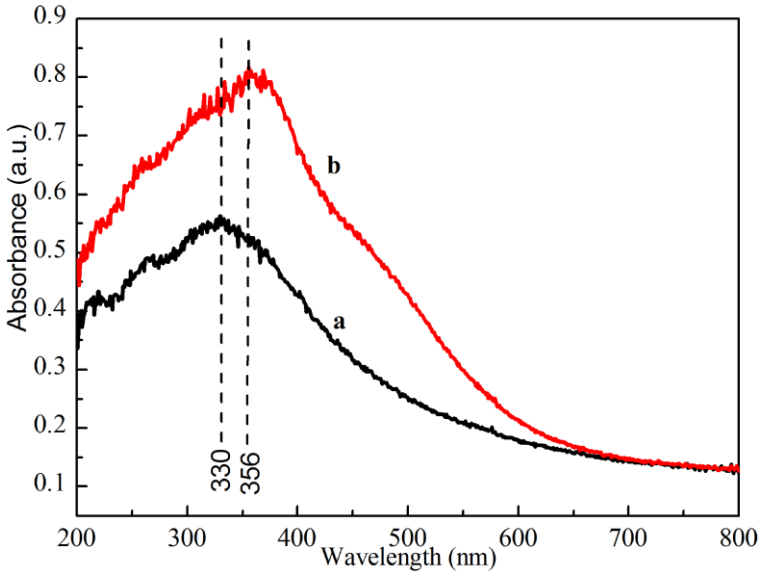

Fig. S6 DRS patterns of original chitosan (a) and LMWSC (b).

Further, to identify the carboxylic group of the LMWSC, DRS analysis are given in Fig. S6. There is an absorption band at 330 nm in the original chitosan, which is caused by the n→π* transition of residual acetyl. Compared with that of original chitosan, in the DRS pattern of LMWSC a new absorption band at 356 nm appeared, which might be caused by the n→π* transition of a carboxylic group in LMWSC. Consequently, the DRS patterns reflected that the carboxylic group was formed, which coincided with the analysis of the FTIR spectra.

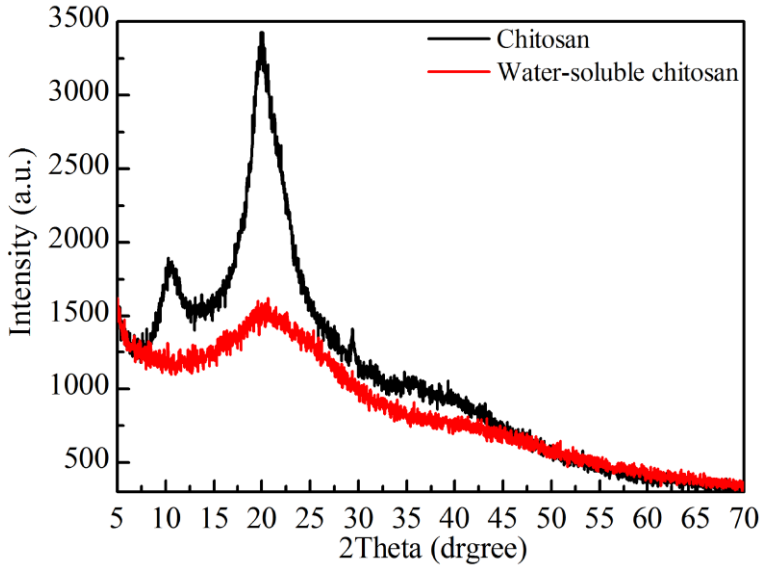

Fig. S7 XRD patterns of original chitosan and LMWSC.

The X-ray powder patterns of original chitosan and LMWSC are shown in Fig. S7. The pattern of original chitosan shows the characteristic peaks: the two peaks at 2θ = 10.4° and 20.02°correspond to (1 0 0) and (0 2 0) reflections of the L-2 polymorph of chitosan,[5] respectively. For LMWSC, the peak at 2θ = 10.4° disappeared and the peak at 2θ = 20.02° decreased. That reflected the crystalline structure of LMWSC was destroyed and the crystallinity decreased. LMWSC had only one major peak and became more amorphous than original chitosan.[6] Consequently, the degradation of chitosan occurred preferentially from the amorphous region to the water-soluble molecule, and dissolved in the water. With the deep degradation, the crystalline structure was destroyed thoroughly. As can be seen, the water soluble chitosan was obtained by breaking the β-1,4 glycosidic bonds of chitosan. And the hydroxymethyl (-CH_2OH) of chitosan was oxidized to carboxylic group (-COOH).

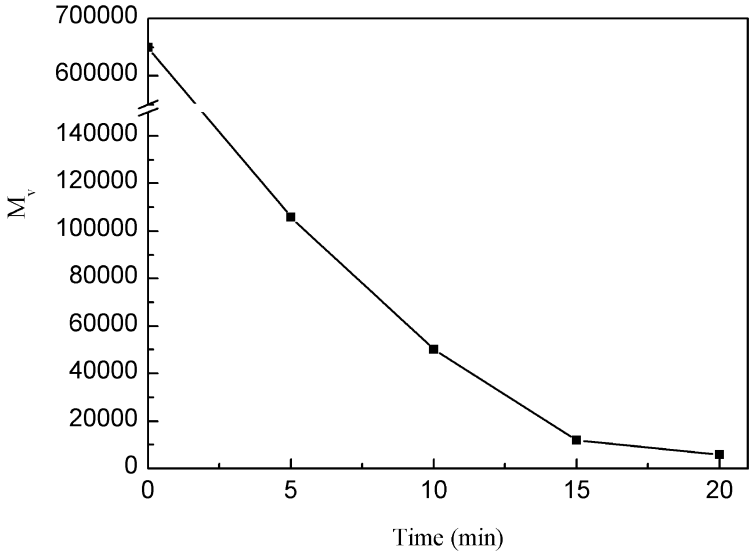

Fig. S8 The Mv of chitosan and LMWSC after different reaction time

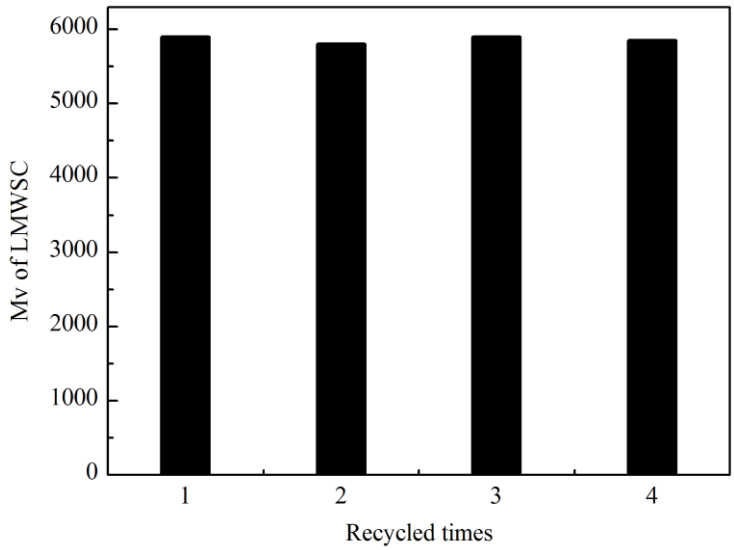

Fig. S9 The effect of the recycled catalyst on the Mv of LMWSC

In summary, the low molecular water-soluble chitosan was smoothly obtained. The structure of chitosan was still retained in the structure of the LMWSC, and formed carboxylic group (-COOH) increased the water solubility.

References:

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