

Synthesis and properties of new water-soluble copolymers based on methyl acrylic acid sucrose ester and methyl acrylic acid

Yan Chen,¹ Jin Liu,^{1,2} Zhen Li²

¹Department of Polymer Materials, Anhui Key Laboratory of Advanced Building Materials, Anhui Jianzhu University, Hefei 230022, China

²Department of Polymer Materials, School of Materials Science and Chemical Engineering, Anhui Jianzhu University, Hefei 230022, China

Correspondence to: J. Liu (E-mail: liujin910@yeah.net)

ABSTRACT: The new series of copolymers were obtained based on free radical solution copolymerization by mixing self-made methyl acrylic acid sucrose ester (MASE) and methyl acrylic acid (MAA) with different ratios. Copolymerization behavior and properties of the new copolymers was investigated with the reaction time, temperature, monomer ratios and characterized by Fourier transform infrared spectra (FT-IR), carbon nuclear magnetic resonance (¹³C NMR), and intrinsic viscosity. The results indicated that sucrose was successfully grafted onto poly (methyl acrylic acid). Further, it was demonstrated that low temperature benefited the esterification of MASE. Importantly, the copolymers were founded to have good compatibility with polymethyl methacrylate (PMMA), polytetrafluoroethylene (PTFE), and polyethylene (PE). © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43627.

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INTRODUCTION

Coal, oil, and natural gas are the main source of modern synthetic polymer materials. With the depletion of fossil resources, as well as the emphasis of environmental protection, people are forced to turn to the use of biomass raw materials instead of the fossil materials. Sucrose is a renewable natural biomass resource which is abundant in nature mainly for the sweetener.¹ Sucrose has eight hydroxyl groups, each hydroxyl group can participate in the reaction to give different degrees of substitution of water-soluble or amphipathic sucrose esters.^{2–6} With safe, nontoxic, biodegradable, and environment friendly features the sucrose esters are used in medicine,⁷ food,⁸ detergent, and cosmetics.^{9,10} Sucrose instead of synthetic chemicals used in various studies is being widely explored and applied, such as Olestra and other brands.¹¹ At present, the sucrose added to the water-soluble polymer materials has been scarcely reported. Carrying out the synthesis and research of sucrose and its macromolecular derivatives has important theory and application value.

Methacrylic polymer is an important kind of water-soluble polymer which can be easily copolymerized with other monomers¹² for the design of products with desired properties. Such polymers are very valuable chemicals or additives,¹³ whether it is the acid form, salt form, or ester group-containing products. In this paper, the new copolymerization, taking self-made

MASE and MAA as comonomer, was obtained containing sucrose short side chains in free radical solution polymerizations, hoping to provide sufficient new green materials for the water-soluble polymer.

EXPERIMENTAL

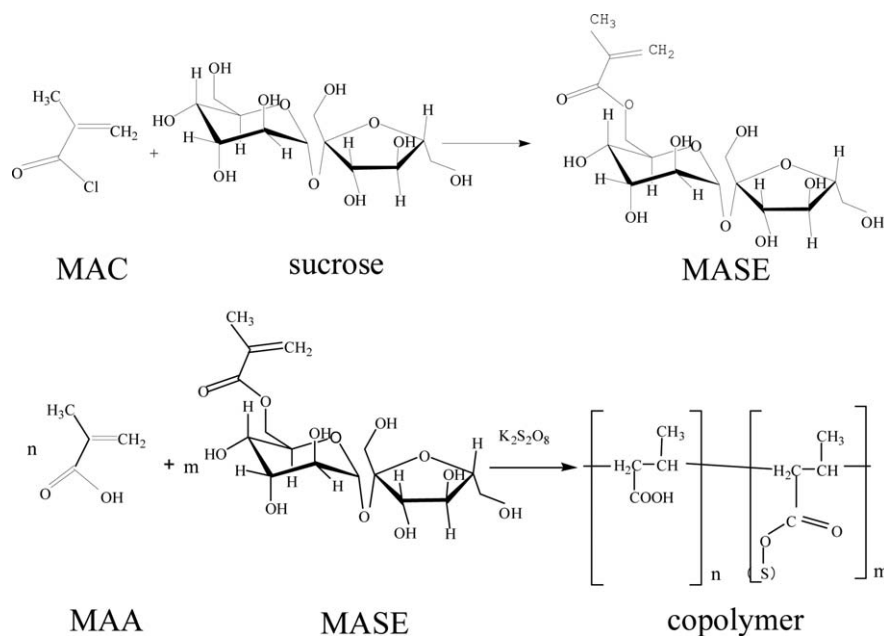
Materials

Methyl acrylic acid (MAA, CP, Sinopharm Chemical Reagent Co., Ltd.); potassium persulfate (KPS, AR, Yixing Second Chemical Reagent Factory, recrystallized); NaOH (AR, Xilong chemical Co., Ltd); ethanol (AR, Sinopharm Chemical Reagent Co., Ltd), sucrose (Suc, AR, Sinopharm Chemical Reagent Co. Ltd.); self-made methyl acrylic acid sucrose ester (MASE).

Synthesis of MASE and its Copolymer

MAA was first changed into methacryloyl chloride (MAC). MASE were obtained by the reaction of sucrose and MAC according to references.^{14–16} As showed in Scheme 1. The esterification also occurs between MAC and primary alcohol of glucose or fructose units in the order of 6'-OH, 6-OH > 4-OH > 1'-OH. In this article, we take glucose ester as an example, and fructose esters are also included in the esters.

To prepare the copolymer of MASE and MAA, a 250 mL four-necked flask equipped with nitrogen inlet, mechanical stirrer, condenser was charged with MASE solution and potassium



Scheme 1. The reaction processes for synthesizing MASE and the copolymer.

persulfate. After the reactants were heated to a certain temperature in a constant temperature silicone oil bath, MAA solution was added and the reaction was carried out for a given time. Then the crude product were completely neutralized with NaOH solution and precipitated in ethanol. Finally, the copolymer product was obtained by filtering and steaming. The reaction processes for synthesizing MASE and the copolymer are shown in Scheme 1. When the amount of MASE is 0, the copolymer is completely PMAA.

Measurements

Intrinsic Viscosity. 1 g copolymer was dissolved in 1 mol L⁻¹ NaCl solution, yielding 0.02 g mL⁻¹ solution. The intrinsic viscosity was measured in dilution method by Ubbelohde viscometer under the constant temperature of 30 ± 0.1 °C.

Characterization. MASE and copolymer products spectrum were recorded by using a Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc.) with 32 scans and 4 cm⁻¹ resolution at the range 4000–400 cm⁻¹. The ¹³C NMR spectra of copolymer dissolved in 0.5 mL D₂O (for signal lock) were recorded with a Bruker Avance 400 NMR spectrometer. Dynamic/static contact angle meter (SL200A/B/D, Solon (Shanghai) technology Science Co., Ltd.) was used to measure the contact angles.

Infrared Spectrum Quantitative Analysis. Generally, when carrying out the quantitative analysis of the polymer chain structure, it always selects a characteristic peak as the molecular bands to qualitatively calculate. According to Beer–Lambert's equation $c = A/kL$, $A = \lg(I_0/I)$, where A is the absorbance, k as the molar absorption coefficient, L as the thickness of sample cell, C as the sample concentration, I_0 and I is the intensity of incident light and transmitted light, respectively. So C is proportional to A . The relative amount of carboxyl, ester and hydroxyl groups in different copolymers can be got by analyzing A .

RESULTS AND DISCUSSION

Characterization of MASE and its Copolymer

Figure 1(A) shows FT-IR spectra of MASE (trace a). The peaks at 3327 cm⁻¹, 1717 cm⁻¹, and 1654 cm⁻¹ are shown in the FT-IR spectrum, which are assigned to O–H, C=O, and C=C of the main characteristic group peaks of MASE, respectively. Therefore, the FT-IR spectra suggest that the hydroxyl group of sucrose and carboxylic acid group of methyl acrylic acid are involved in esterification. The double bond of methyl acrylic acid still exists after esterification. As shown in Figure 1(A) (trace b), the peak that appeared at 1543 cm⁻¹ is assigned to carboxylic acid salt of two C=O groups, and the other peaks at 2988 cm⁻¹ and 2933 cm⁻¹ are assigned to the methyl C–H group. 1694 cm⁻¹ is the carboxyl group of two aggregates C=O stretching vibration. In Figure 1(A) (trace c), 3312 cm⁻¹ corresponds to O–H groups, while 1056 cm⁻¹ corresponds to C–O–C bands. The above results suggest that the sucrose is successfully grafted PMAA chain.

Figure 1(B) is the ¹³C NMR of copolymer 2. 171.9 ppm and 164.9 ppm are the C chemical shifts of ester and carboxyl groups, respectively. 10–50 ppm was the C chemical shifts in the main chain of the copolymer. The chemical shifts of 55–100 ppm are the C in the sucrose molecule. The NMR results confirm once again the successful copolymerization of MASE and MAA.

Influence of Monomer Molar Ratio on the Intrinsic Viscosity of the Copolymer

Figure 2 shows that, when the monomer molar ratio is 0.1, the maximum intrinsic viscosity of the copolymer is obtained. The change of intrinsic viscosity of the copolymer not only related to the molecular weight, but also to the stretching state of the copolymer chain structure and the radius of rotation of the fluid in the solvent. On the one hand, under the same reaction conditions, with gradually increasing amount of MASE, the

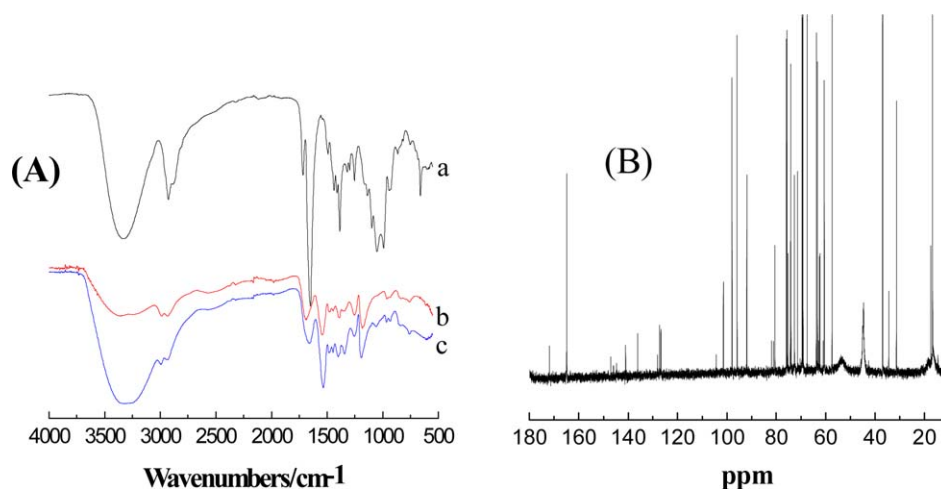


Figure 1. (A) FT-IR spectra of MASE (a), PMAA salt (b), and copolymer 2 (c). (B) The ^{13}C NMR of the copolymer 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

intrinsic viscosity of the copolymer is increased first and then decreased rapidly. This may be due to that, the molecular volume of MASE is too larger, and hinder its effective participation in the copolymerization reaction, with the increasing of sucrose ester content, increasing the steric hindrance effect and decreasing the reaction activity, the reaction becomes difficult to proceed, and may lead to a decrease in the molecular weight of the copolymer. On the other hand, with the change of the proportion of polymer monomer, the composition of the copolymer molecular chain is also changing, and the stretching state of the copolymer chain and the radius of rotation of the fluid in the solvent is very different. From Table I can also be seen, along with the continuous increasing of the proportion of monomers, the $A_{\text{Ester}}/A_{\text{Carboxyl}}$ is increased, the relative content of sucrose monoester in copolymer is increased, meanwhile, the intrinsic viscosity of the copolymers decreased, may be indicating that the MASE was not favorable for MAA to participate in the copolymerization. So we assume that with the increase of sucrose ester monomer content, if the molecular weight of the copolymer is almost constant, but the copolymer chains with different compositions tend to form different chain extension structure in the solvent system, which may lead to the contraction of the molecular chain in aqueous solution. Thus, there

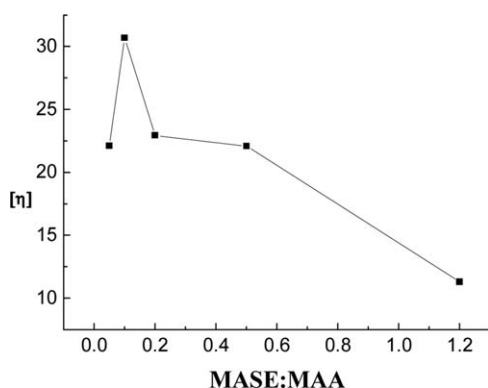


Figure 2. Influence of monomer molar ratio on the intrinsic viscosity of the copolymers.

will be appeared a change intrinsic viscosity of the copolymer as Figure 2. For this purpose, we measure copolymer molecular chain size in 0.02 mol L^{-1} NaCl solution and under 30°C through molecular simulation by Materials Studio software, and we obtained the results as followed: When the copolymer is connected with 8 MASE monomer chain, the aggregation scale of the copolymer is 77.32 \AA , and the scale of the 16 MASE is 55 \AA . The results showed that molecular chain segment curl with the increasing of MASE monomer content, the size of copolymer molecular chain decreases due to the curling causing by sugar molecules, which means the intrinsic viscosity of the copolymer decreases. Under the condition of the invariable of $n_{\text{MASE}}:n_{\text{MAA}}$, the copolymer molecular chain size increases with the increasing of monomer content under the same simulation conditions. The intrinsic viscosity of the copolymer increases with the growth of the copolymer molecular chain. So as the $n_{\text{MASE}}:n_{\text{MAA}}$ increases, the intrinsic viscosity of the copolymer decreases sharply.

Effect of Reaction Time on the Intrinsic Viscosity of the Copolymer

Under the condition of reaction temperature of 80°C and monomer molar ratio of 0.1 to study the effect of reaction on the intrinsic viscosity of the copolymer by changing the polymerization time, the test results shown in Figure 3(A).

Figure 3(A) shows that the intrinsic viscosity of copolymer increases with the increasing of reaction time. When the reaction time was 24 h, the highest intrinsic viscosity was obtained. When the reaction time was further extended, the intrinsic viscosity of copolymer decreased slightly. This may be due to that the free radical reaction process was also accompanied by trace amounts of hydrolysis reaction of MASE. In the initial stage of the reaction, the molecular weight increased slowly. The radical reaction occurred auto-acceleration into the middle stage of the reaction, while the hydrolysis of MASE has little effect on the molecular weight of the copolymer. So the molecular weight increased, the intrinsic viscosity increased gradually. Since then, the radical polymerization rate turned slowly into the post-radical reactions gradually because of the influence of glass

Table I. The Relative Content of Functional Groups of the Copolymers Synthesized at Various Preparative Conditions

No.	$\eta_{\text{MASE}}/\eta_{\text{MAA}}$	T/°C	t/h	Absorbance				
				A_{Ester}	A_{Hydroxyl}	A_{Carboxyl}	$A_{\text{Ester}}/A_{\text{Carboxyl}}$	$A_{\text{Hydroxyl}}/A_{\text{Carboxyl}}$
1	0.05	80	24	0.003	0.160	0.106	0.028	-
2	0.1	80	24	0.009	0.265	0.160	0.056	1.656
3	0.2	80	24	0.008	0.128	0.092	0.087	-
4	0.5	80	24	0.022	0.135	0.103	0.214	-
5	1.2	80	24	0.080	0.232	0.110	0.727	-
6	0.1	80	6	0.012	0.192	0.119	0.101	1.613
7	0.1	80	12	0.013	0.142	0.094	0.138	1.511
8	0.1	80	30	0.004	1.273	0.066	0.061	-
9	0.1	65	24	0.022	0.127	0.079	0.278	1.608
10	0.1	75	24	0.009	0.163	0.119	0.076	1.370
11	0.1	85	24	0.011	0.191	0.117	0.094	1.632

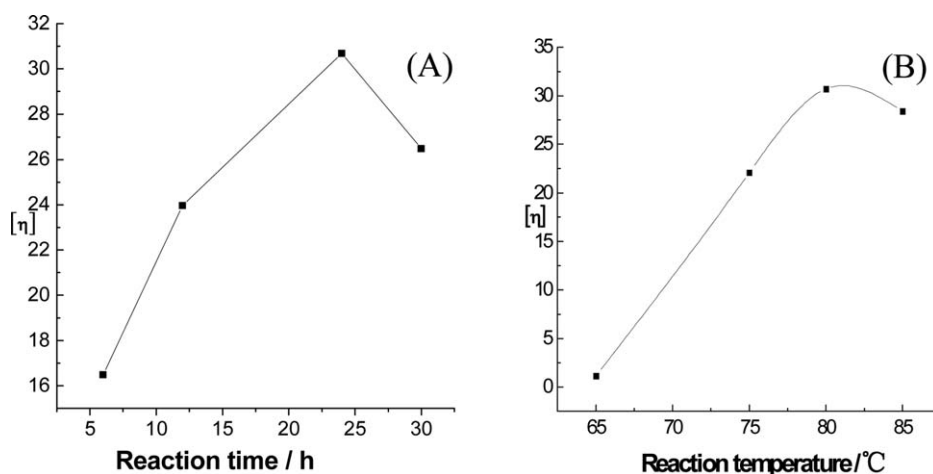
effect. In this case a low monomer concentration, the molecular weight of the polymer increased slowly or even not increased. Hydrolysis of MASE has a certain effect on molecular weight at this time. When using Ubbelohde-viscometer-measurement, the friction between the molecules reduced, indicating the intrinsic viscosity of the copolymer decreased. The same can be seen from Table I, with the increasing of reaction time, the $A_{\text{Ester}}/A_{\text{Carboxyl}}$ increased first and then decreased, leading to a minimum at 24 h. That is the relative content of the ester group at 24 h is the least.

Effect of Reaction Temperature on the Intrinsic Viscosity of the Copolymer

In the radical polymerization reaction, the reaction temperature also has an effect on the rate of polymerization. Generally, higher temperature will accelerate the decomposition of the initiator, thereby increasing the rate of polymerization. The polymerization rate is one of important indicators of the free radical polymerization. In other conditions remaining unchanged, the monomer molar ratio was 0.1, the reaction time

was 24 h, and we studied the effect of reaction temperature on the intrinsic viscosity of the copolymer, the test results shown in Figure 3(B).

Figure 3(B) shows that the intrinsic viscosity of copolymer is the maximum when the reaction temperature is 80 °C. From the Arrhenius $k = A \cdot e^{-E/RT}$ of the relationship between the polymerization rate constant k and temperature of polymerization can be seen, an increase in temperature will make the rate of polymerization (constant) improved. The intrinsic viscosity of copolymer was relatively small at 65 °C, for which the reason may be that, in low temperature, potassium persulfate cannot be decomposed effectively, and the reaction rate was low, so the molecular weight was small. With the increasing of the reaction temperature, effectively decomposing of potassium persulfate, and constantly increasing of the reaction rate, the molecular weight of the copolymer also increased significantly. But when the temperature is higher than 80 °C, the molecular weight of the copolymer is reduced slightly. This may be due to that at a certain temperature, chain polyaddition polymerization and depolymerization (either growth or negative growth) usually

**Figure 3.** Effects of reaction time (A) and reaction temperature (B) on the intrinsic viscosity of the copolymer.

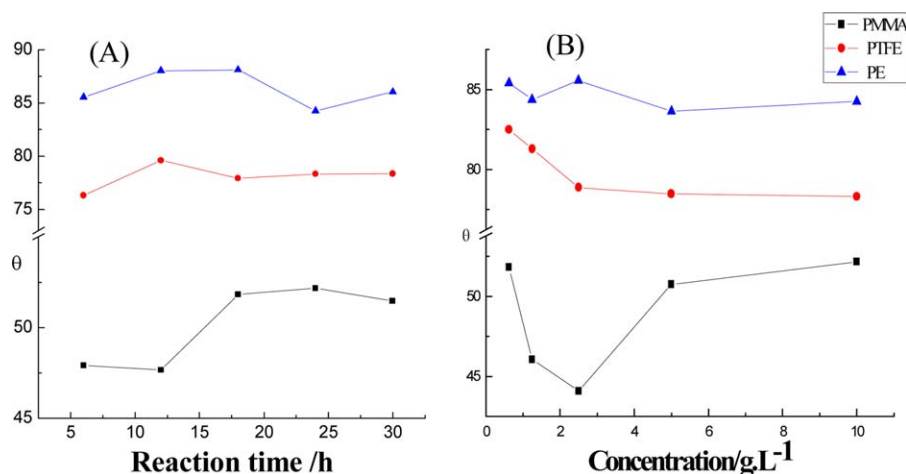


Figure 4. Effects of reaction time (A) and reaction temperature (B) on the contact angle of the copolymer on different substrates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

constitute a balance, and the balance moves with the temperature, and there is the corresponding equilibrium monomer concentration.

When the degree of polymerization is large, the equilibrium constant K and equilibrium monomer concentration $[M]_e$ are following reciprocal relationship: $K = kp/kdp = 1/[M]_e$. Equilibrium monomer concentration depends on the temperature. Polymerization reaction is exothermic, heating-up is conducive to depolymerization. When the reaction temperature is 80 °C, the synthesis of the copolymer is more conducive. When the reaction temperature is higher than 80 °C, the molecular weight of the copolymer decreased. In Table I, the $A_{Hydroxyl}$ and $A_{Carboxyl}$ are increased first and then decreased with the increasing of the reaction temperature. The maximum absorbance is at 80 °C which also shows that the relationships between the polymerization reaction and temperature. The maximum absorbance of ester group is at 65 °C, indicating low temperature is favorable to the synthesis of MASE.

Surface Properties of the Copolymer

The copolymers prepared with different reaction times were dissolved into 10 g L⁻¹ solutions, and the contact angles were measured in the polymethyl-methacrylate (PMMA), polytetrafluoroethylene (PTFE) sheet, and polyethylene (PE) film, respectively. Figure 4(A) shows that with increasing reaction time, that is to say, with the increasing of molecular weight of the copolymer, the contact angle of the polymer is increased first and then changed a little. The copolymer surface tension is increased with the increasing of molecular weight of polymer, when the molecular weight reaches a certain amount, the effect of molecular weight on the surface tension can be ignored. This is because the hydrophilic groups of copolymer molecules close to the interface of the carrier, the surface is slightly hydrophobic. With the molecular weight of copolymer gradually increasing, the solid-liquid interfacial tension is gradually increased, until the interfacial tension reached a balance. In addition, among the three kinds of carriers, PMMA was wet better.

Figure 4(B) shows that the concentration effect (10 g L⁻¹, 5 g L⁻¹, 2.5 g L⁻¹, 1.25 g L⁻¹, 0.625 g L⁻¹) on the contact angle of copolymer 2 on PMMA, PTFE plate, and PE film. From the figure we can see with the increasing of polymer concentration, the contact angles of copolymer in PE film and PTFE plate were sharp decreased first and then remained unchanged basically, while in the PMMA the contact angle was a minimum value at 2.5 g L⁻¹. PE film was better wetting while the copolymer concentration in the 5 g L⁻¹, and the surface of PTFE plate and PMMA were also better wetting at the concentration of 2.5 g L⁻¹.

CONCLUSIONS

The new water-soluble copolymers based on methyl acrylic acid sucrose ester and methyl acrylic acid is successfully synthesized. With the $n_{MASE}:n_{MAA}$ increases, the intrinsic viscosity of the copolymer showed a downward trend after the first increase. The copolymer with the maximum intrinsic viscosity is at 0.1 of the monomer molar ratio of $n_{MASE}:n_{MAA}$. The synthesized copolymer solution has good wetting effect on PMMA PTFE and PE, the order of the wetting action is as follows: PMMA is greater than PTFE and PE. In this study, the sucrose molecules derived from biomass materials were reacted into the polymer structure are of great significance for the synthesis and application of the rich water soluble polymers.

ACKNOWLEDGMENTS

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