Ambient Cross-linking System Based on the Knoevenagel Condensation Reaction between Acetoacetylated Sucrose and Aromatic Dicarboxaldehydes

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ABSTRACT: An ambient cross-linking system based on the Knoevenagel condensation reaction between acetoacetylated sucrose and aromatic dicarboxaldehydes was demonstrated. In this study, we use a rheological instrument to measure the gel time to predict and elucidate the likely reaction mechanism of the system, and we prepare films based on the mechanistic results. Acetoacetylated sucrose and 4,4′-biphenyldicarboxaldehyde were used as raw materials, piperidine was used as the catalyst, and nonvolatile dimethyl sulfoxide (DMSO) was used as the solvent. After mixing 4,4′-biphenyldicarboxaldehyde and piperidine for 30 min, the acetoacetylated sucrose was added, thus producing the shortest gel time. Then, the gel was characterized by Fourier transform infrared spectroscopy. In addition, three films were prepared by this approach with different aromatic dicarboxaldehydes, and the properties of the coatings were characterized by differential scanning calorimeter, dynamic mechanical analysis, thermogravimetric analysis, and swelling ratio. It was found that these films have high Young’s modulus, high glass transition temperatures, high pencil hardnesses, and low swelling ratios.

INTRODUCTION

Since the Knoevenagel condensation reaction was first reported by Emil Knoevenagel in 1894,1 the Knoevenagel condensation reaction has been increasingly used and has become an important C−C bond formation reaction.2−5 It has been used to obtain a variety of compounds, such as synthetic natural products,6 drugs,7 fine chemicals,8 functional polymer materials,9 and so forth.

In a Knoevenagel condensation reaction, in the dehydration condensation of compounds, compounds containing active methylene groups is used with aldehydes or ketones under weak base catalysis to produce α, β-unsaturated carbonyl compounds and their analogues.10 Currently, the following two kinds of mechanisms consistent with the Knoevenagel condensation reaction are known (Scheme 1): in the first mechanism, aldehyde compounds are combined with catalysts and then react with acetylacetate to form an addition product, as was first proposed by Emil Knoevenagel11(Scheme 1a); in the second mechanism, the catalyst first reacts with acetyl acetate and then attacks the aldehyde to obtain an addition product12 (Scheme 1b). These two mechanisms are the subject of some agreement, but theoretical investigations of the mechanism of the Knoevenagel condensation reaction have been rare.13,14 The Knoevenagel condensation reaction is a good cross-linking method because it can be carried out at room temperature with a high yield. Therefore, it is widely used in the synthesis of polymer materials, such as fluorescent materials,15 conductive polymer materials,16 and coatings.17

Paint has become an indispensable material for our society.18 However, the production of paint is still based on petrochemical products. With the increasing importance of environmental issues, the need for sustainable resources and new approaches has gradually increased. As a renewable resource, sucrose is cheap, easily available, and has multiple hydroxyl groups, and it can be modified to produce a large number of coatings such as epoxy coatings,19 polyurethane coatings,20 and UV curing coatings.21 However, there has been only one report in the literature on the preparation of the acetoacetylated sucrose coating which was used for the preparation of the coating for acetoacetylated sucrose and diamine.22 Recently, our group23 reported a Knoevenagel condensation reaction between plant groups and aromatic dicarboxaldehydes, but the possible reaction mechanism of the system was not studied.

In this work, we used the gel time to study the possible mechanism for the reaction between acetoacetylated sucrose and aromatic dicarboxaldehydes via the Knoevenagel condensation reaction at room temperature (25 °C) and elucidated the likely mechanism of the reaction. We then used this mechanism as guidance in the study of the coating properties.
RESULTS AND DISCUSSION

NMR Characterization of Acetoacetylated Sucrose.
The structure of acetoacetylated sucrose was confirmed based on the results of its $^1$H NMR and $^{13}$C NMR spectral analyses. Figure 1a shows the $^1$H NMR spectra of acetoacetylated peaks at 3.58–3.54 and 2.29–2.24 ppm, while the $^{13}$C NMR spectra of acetoacetylated sucrose show peaks at 199, 165, 48, and 20 ppm (Figure 1b). In addition, a significant decrease in the absorbance at 3380 cm$^{-1}$ (–OH stretching frequency) and in the stretching vibration band of C$\equiv$O of –COCH$_2$COCH$_3$ at 1746 and 1704 cm$^{-1}$ is observed in Fourier transform infrared (FTIR) spectra (Figure 2). These results demonstrate that sucrose and t-butyldiacetate undergoes a transesterification reaction.

Characterization of Gel Time. Figure 3 and Table 1 show the different gel times of the system for different orders of the addition of acetoacetylated sucrose, 4,4′-biphenyldicarboxaldehyde, and piperidine in the Knoevenagel condensation reaction. At the gel point, the storage modulus ($G'$) is equal to the loss modulus ($G''$), and the viscosity ($\eta$) increases.

Scheme 1. Two Mechanisms of the Knoevenagel Condensation, (a) the Catalyst First Reacts with Aldehyde Compounds and (b) the Catalyst First Reacts with Acetyl Acetate
dramatically. As observed from Figure 3 and Table 1, after mixing 4,4′-biphenyldicarboxaldehyde (B) with the catalyst piperidine (C) for 30 min prior to adding the mixture to acetoacetylated sucrose (A), the gel time is the shortest (Figure 3b and Table 1, entry 1). When acetoacetylated sucrose (A) and 4,4′-biphenyldicarboxaldehyde (B) are mixed for 30 min prior to the addition of piperidine (C) for the cross-linking system of the Knoevenagel condensation reaction, an intermediate gel time was obtained (Figure 3c and Table 1, entry 2). When acetoacetylated sucrose (A) was mixed with piperidine (C) for 30 min prior to adding the mixture to the 4,4′-biphenyldicarboxaldehyde (B), the gel time was the longest (Figure 3d and Table 1, entry 3). The rheological complex viscosity results also prove that mixing 4,4′-biphenyldicarboxaldehyde with the catalyst piperidine followed by the addition of the mixture to the acetoacetylated sucrose (A) obtains the shortest gel time.

An examination of the gel time data indicates that the mechanism of the Knoevenagel condensation reaction of acetoacetylated sucrose and 4,4′-biphenyldicarboxaldehyde under the piperidine catalyst may involve the reaction of piperidine with 4,4′-biphenyldicarboxaldehyde, followed by the reaction with acetoacetylated sucrose. The likely mechanism of this reaction is the mechanism proposed by Knoevenagel in Scheme 1a.

The FTIR spectra of acetoacetylated sucrose, 4,4′-biphenyldicarboxaldehyde, and the gel after reaction are shown in Figure 4. Significant peaks due to the −CHO

Table 1. Gel Time for Different Orders of Addition of Raw Materials and Catalysts

| entry | adding order | G’ = G’’ (s) | η increase (s) |
|-------|--------------|---------------|----------------|
| 1     | BC-A         | 2142          | 2131           |
| 2     | AB-C         | 2600          | 2721           |
| 3     | AC-B         | 4364          | 4461           |

Figure 3. Rheological properties of gel time for different orders of the addition of raw materials and catalysts: (a) raw materials and catalysts; (b) order of addition: mix B and C for 30 min, then add to A; (c) order of addition: mix A and B for 30 min, then add to C; and (d) order of addition: mix A and C for 30 min, then add to B.
stretches at 2828 and 2753 cm\(^{-1}\) were observed to decrease after cross-linking, and the insoluble material showed the characteristic absorption peaks of benzene rings at 1510 and 1380 cm\(^{-1}\); these results indicate that the acetoacetylated sucrose has reacted with 4,4′-biphenyldicarboxaldehyde.\(^{23,27}\)

**Characterization of the Films.** After exploring the reaction mechanism by rheological testing, we prepared the coating using the optimum cross-linking time. According to the above-mentioned cross-linking system, as shown in Table 2, volatile THF was used as the solvent, and 4,4-biphenyldicarboxaldehyde and piperidine (10 wt %) were mixed for 30 min; then, this mixture was added to the acetoacetylated sucrose to cure the film. We found that this system produced many insoluble substances after 10 min, but this method cannot form a uniform membrane. The main reason for this may be that the amount of catalyst is too large and the system cured too fast. When we add the mixture to the piperidine in 2.5 wt %, the film could be cured in 3 h, and the film was retracted and could not form a flat membrane. Encouraged by this result, we further decreased the catalyst amount and found that 1 wt % of piperidine resulted in the best performance with the curing time of 5 h and gel content of 96%.

FTIR spectra of acetoacetylated sucrose, an acetone-swollen substance after curing (P1) and 4,4′-biphenyldicarboxaldehyde are shown in Figure 5. A comparison with Figure 1 shows that the cross-linked insoluble material and the film insoluble material were similar. Both showed the –CHO stretching frequency decreases at 2828 and 2752 cm\(^{-1}\), and for both, the benzene ring peaks at 1510 and 1380 cm\(^{-1}\) were produced.\(^{23,27}\)

**Table 2. Optimization of the Curing Reaction Conditions**

| entry | piperidine (catalyst) (wt %) | cure time (h) | pencil hardness | solvent-swelling (%) | Ggel content (%) |
|-------|-----------------------------|---------------|----------------|----------------------|-----------------|
| 1     | 10                          |               |                |                      |                 |
| 2     | 2.5                         | 3             |                |                      |                 |
| 3     | 1                           | 5             | 5H             | 22                   | 96              |
| 4     | 0.5                         | 8             | 5H             | 21                   | 95              |

*Dry through cure time of the film.*

**Table 3. Films of Different Cross-Linking Aromatic Dicarboxaldehydes**

| sample | cure time (h) | set to touch | tack free | dry hard | dry through | pencil hardness | pendulum hardness (s) | acetone-swelling (%) | gel content (%) |
|--------|---------------|--------------|-----------|----------|-------------|----------------|----------------------|---------------------|-----------------|
| P1     | 1.2           | 2.5          | 3.8       | 5        |             | 5H             | 41.2                 | 22                  | 95              |
| P2     | 0.8           | 2.1          | 3         | 4.5      |             | 5H             | 39.5                 | 19                  | 96              |
| P3     | 1.3           | 2.8          | 4.2       | 6        |             | 4H             | 33.1                 | 17                  | 91              |

**Table 4. M_c, Cross-Link Density, and Density of These Films**

| sample code | P1 | P2 | P3 |
|-------------|----|----|----|
| M_c (g/mol) | 7579 | 12,731 | 18,425 |
| \(v_c \times 10^{-4} \text{ (mol/cm}^3\) | 1.702 | 1.041 | 0.691 |
| density (g/cm^3) | 1.290 | 1.325 | 1.273 |

molecular weight increased gradually from 7579 to 18 425 g/mol, while the cross-link density of these films was reduced from 1.702 to 0.691 mol/cm.\(^3\) This was due to the steric hindrance of benzene rings.

**Dynamic Mechanical Analysis.** The stress–strain behaviors of these coating films are shown in Figure 6 and Table 5. Compared to P1, P2, and P3, it is obviously seen that three films have higher Young’s modulus and the film of P1, the best extension ratio. The main reason may be, that is, the high cross-linking density of P1.

**Differential Scanning Calorimeter Analysis.** The glass-transition temperatures \(T_g\) were obtained from the differential scanning calorimeter (DSC) curves, as shown in Figure 7 and Table 5. Three films have higher glass-transition temperature and their \(T_g\) values were in the 71–79 °C range. The main reason for this result is the high cross-linking density of P1.\(^{30}\)

**Thermogravimetric Analysis.** Figure 8a shows the thermogravimetric analysis (TGA) curves for three films; the DTGA curve is presented in Figure 8b, and the \(T_{10}, T_{50}\) and \(T_{\text{max}}\) data are summarized in Table 5. Based on Figure 8a, two distinct degradation stages were observed for all three films. The degradation at the first stage in the range of 169–320 °C can be attributed to the dissociation of the modified ester bonds and carbon groups to form \(\text{CO}_2\). At the second stage,
when the temperature reaches 350 °C, the polymer skeleton is obtained.31 According to the Table 5, the $T_{10}$, $T_{50}$, and $T_{max}$ decomposition temperatures of the three films were similar.

**Solvent Swelling.** Figure 9 shows the swelling ratio of the three films. After soaking for 30 h, the film swelling ratio reached the maximum values. Compared with the swelling ratio of the three coatings, P1 has the largest swelling ratio and P3 has the smallest swelling ratio. This result may be obtained because the aromatic dicarboxaldehyde cross-linking agent has the longest chain in the P1 structure.32

**CONCLUSIONS**

An ambient cross-linking system of acetoacetlated sucrose and aromatic dicarboxaldehydes was demonstrated. The possible mechanism for the synthesis of this system was explored by the rheological evaluation of gel time measurements. It was determined that the shortest gel time was obtained during the mixing of aromatic dicarboxaldehydes and the catalyst (piperidine) for 30 min, which was followed by the addition of acetoacetated sucrose. In addition, three films were prepared by the procedure with the shortest gel time, and it was found that the films have high Young’s modulus, higher

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**Table 5. Thermal and Mechanical Properties of the Three Films**

| codes | Young’s modulus (MPa) | stress at break (MPa) | elongation at break (%) | TGA in nitrogen (°C) | DSC $T_g$ (°C) |
|-------|-----------------------|----------------------|------------------------|----------------------|----------------|
| P1    | 1402 ± 26             | 3.05 ± 0.5           | 0.31 ± 0.02            | 183                  | 275            |
| P2    | 1229 ± 33             | 1.39 ± 0.3           | 0.17 ± 0.05            | 183                  | 271            |
| P3    | 1045 ± 39             | 1.37 ± 0.4           | 0.23 ± 0.01            | 183                  | 268            |

$T_{10}$, $T_{50}$, and $T_{max}$ represent the temperatures at the mass losses of 10, 50 wt %, and maximum mass loss, respectively.
glass transition temperature, higher hardness, and lower acetone swelling ratio.

# EXPERIMENTAL SECTION

## Materials
Sucrose, 1,4-phthalaldehyde, 1,3-benzenedialdehyde, t-butylacetoacetate, and 4,4′-biphenyldicarboxaldehyde were obtained from Sigma-Aldrich, China. Piperidine dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) were purchased from Beijing Chemical Works. All the materials were used as obtained without further purification. The water used in this study was deionized and doubly distilled.

## Preparation of Acetoacetylated Sucrose
The synthesis of acetoacetylated sucrose was carried out according to a previously reported study, and the detailed synthesis method was as follows (Scheme 2). In a 250 mL round-bottomed flask equipped with a magnetic stir bar and a condenser, a mixture of sucrose (40 g, 0.0538 mol) and t-butylacetoacetate (147.7 g, 0.936 mol) was stirred at 130 °C for 3 h, and the mixing was stopped when no more liquid evolved. Finally, 63 mL of the liquid was removed, and a yellow oil was obtained. \[\text{H NMR (CDCl}_3\text{, 400 MHz): } \delta (\text{ppm}) 5.61 (m, 1H), 5.49 (m, 1H), 5.29 (m, 1H), 5.12 (m, 1H), 5.06 (m, 1H), 4.99 (m, 1H), 4.89 (m, 1H), 4.39 (m, 6H), 4.28 (m, 1H), 3.58–3.54 (m, 16H), 2.29–2.24 (m, 24H). \[\text{C NMR (CDCl}_3\text{, 400 MHz): } \delta (\text{ppm}) 199.85, 165.34, 102.24, 89.18, 88.08, 73.67, 69.14, 69.32, 63.23, 52.58, 48.49, 29.13, 20.16. Calculated molecular weight = 1015; GPC: \[M_n = 931, M_w = 1121, \text{PDI} = 1.20.  

## Gel Time Study Using a Rheometer
Two sample bottles (30 × 50 mm) were used to study the gel time. Acetoacetylated sucrose (A, 0.25 g, 0.247 mmol) and DMSO (1.5 mL) were added to the first bottle, and 4,4′-biphenyldicarboxaldehyde (B, 0.156 g, 0.743 mmol) and DMSO (2.5 mL) were added to the second bottle for backup; the ratio of acetoacetylated sucrose and 4,4′-biphenyldicarboxaldehyde was 1:0.75, which was based on our previous report. (BC-A). Piperidine (52.5 μL, 0.478 mmol) was added to the dissolved sample bottle of 4,4′-biphenyldicarboxaldehyde (B) for 30 min; then, the dissolved acetoacetylated sucrose (A) was mixed by stirring for 2 min. Afterward, the mixing solution (20 drops) was added to the rheometer plate. (AB-C). The solution of acetoacetylated sucrose (A) and 4,4′-biphenyldicarboxaldehyde (B) was mixed for 30 min, and piperidine (52.5 μL, 0.478 mmol) was added with stirring for 2 min. Then, the mixing solution (20 drops) was added to the rheometer plate. (AC-B). Piperidine (52.5 μL, 0.478 mmol) was added to the dissolved sample bottle of acetoacetylated sucrose (A) for 30 min, and the dissolved 4,4′-biphenyldicarboxaldehyde (B) was mixed by stirring for 2 min. Then, the mixing solution (20 drops) was added to the rheometer plate.

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modulus, and viscosity monitored at room temperature (25 °C) were reported. The gel time was set as the time when the storage modulus was equal to the loss modulus or when the viscosity increased dramatically.

Coating Formulation. The method used for the preparation of the films is described in Scheme 3 and Table 6, and the detailed experimental procedure was as follows: aromatic dicarboxaldehydes (2.958 mmol) and piperidine (1 wt %) were dissolved in THF (5 mL), and after mixing for half an hour, acetocetylated sucrose (1 g, 0.986 mmol) was added to the mixture. Then, the mixture was stirred for 15 min and poured into a poly (tetrafluoroethylene) (PTFE) mould (8 cm × 8 cm × 8 mm). Then, the films were cured at ambient temperature to obtain a dry film (100–200 microns thick).

Coating Characterization. The viscosity of acetocetylated sucrose was determined using a TA Discovery HR-2 rheometer. 1H NMR and 13C NMR spectra were obtained with a Bruker AV-400nmr instrument using tetramethyl silane as an internal reference. FT-IR spectra were obtained using a Bruker-Veretex70 spectrometer in the attenuated total reflection mode with the reported values obtained as averages of 32 scans for each sample in the 4000–400 cm⁻¹ range. The drying times of the coatings were determined using a BK Drying Recorder, and the results were analyzed according to the ASTM D5895-2013 standard. The pencil hardness was measured using a BK D4366 pendulum hardness tester (Sheen Instrument Ltd., UK).

Differential scanning calorimetry (DSC) employed a TA Instruments calorimeter (TA-Q200). The sample of films which at nitrogen atmosphere underwent the temperature raised from 60 to 100 °C at a rate of 10 °C/min. TGA was performed using a TGA-Q50 system obtained from TA Instruments at a heating rate of 10 °C/min. The gel content was measured by immersion of a film (2 cm × 2 cm) in acetone for 48 h and dehydrated for 48 h at 60 °C to obtain weight W₂, and the gel content M was assessed according to the eq 1

\[ M(\%) = \frac{W_2}{W_1} \times 100\% \]  

Acetone swelling was performed by the immersion of a film with a known weight (W₁) in an acetone bath, after which the towel-dried sample weight (W₂) and the oven-dried sample weight (W₃) were obtained; then, the acetone swelling (M %; amount of acetone absorbed by the film) of the films was calculated according to the eq 2

\[ M(\%) = \left(\frac{W_3}{W_1}\right) \times 100\% \]  

The cross-link density (νₑ) of the films was obtained by calculating the volume fraction of the swollen polymer with eq 3 by the Flory–Rehner relation

\[ ν_e = \frac{-[\ln(1 + ν_2) + ν_2 + χ V_2^2]}{V_1 (V_2^{1/3} - V_2/2)} = \frac{ρ_2}{M_c} \]  

where νₑ is the cross-link density, V₂ is the volume fraction of the polymer in the swollen specimen, V₁ is the molar volume of the solvent, χ is the interaction parameter between the polymer and the solvent, and M_c is the relative average molecular weight of the polymer.

The V₂ from eq 1 can be calculated according to eq 4

\[ V_2 = \frac{W_2/ρ_2}{W_2/ρ_2 + W_1/ρ_1} \]  

where ρ₁ and ρ₂ are the densities of the solvent and the polymer, respectively.

The interaction parameter (χ) between the polymer and the solvent was determined by eq 3

\[ χ = 0.34 + V_3/RT(δ_p - δ_s)^2 \]  

where R is the gas constant and T is the absolute temperature. δ_p and δ_s were the solvent and the solubility parameters of the polymer, respectively. The solubility parameter δ_p of the polymer could be determined by the swelling method.

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Notes
The authors declare no competing financial interest.

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