

# Material Science and Engineering with Advanced Research

# Synthesis and Characterization of Copolymer of Styrene / Maleic Acid-Dicyclopentadiene Monoester

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#### Abstract

Dicyclopentadiene-maleic acid monoester (DCPDMA) was synthesized and was used as monomer to synthesize the styrene /DCPDMA copolymer (poly-St / DCPDMA) by solution polymerization. Reaction conditions including esterification temperature, reaction time, and molar ratio of starting materials, polymerization temperature and time were investigated and optimized. DCPDMA and poly-St / DCPDMA were obtained in 93% and 87% yields respectively under the optimal conditions. The synthesized DCPDMA and copolymer (poly-St / DCPDMA) were characterized by MS and IR. Gel Permission Chromatography (GPC) showed that the DCPDMA has average molecular weight of 61200 g/mol and polydispersity index (*D*) of 1.3.

**Keywords:** Maleic anhydride; Dicyclopentadiene; Monoester; Styrene; Copolymer.

#### Introduction

With the rapid development of petrochemical industry, the comprehensive utilization of  $C_5$  resources arouses interest among industrial and academic communities [1-5]. In this context, the utilization of  $C_5$  resources such as dicyclopentadiene which is about 15%~20% of  $C_5$  has become paramount important. The main focus is to develop value added materials.

The design and synthesis of functional materials with interesting properties has become an active area in this field [6-10]. Dicyclopentadiene has been used as reaction injection film, adhesives, coatings, optical materials, resin monomers, etc [11]. Recently Ring Opening Polymerization turned out to be a versatile technique for the synthesis of dicyclopentadiene derivatives and copolymerization of dicyclopentadiene and maleic anhydride [12-16]. Maleic anhydride (MA) is an important unsaturated organic acid and often is used to form graft polymer [17-21].

Styrene-maleic anhydride copolymer could be material with excellent heat resistance and rigidity, so it was widely used in paints, adhesives, printing inks, textile auxiliaries, emulsifying agent and composites, etc [22-25]. In order to improve the thermal stability and rigidity, the dicyclopentadiene-maleic acid monoester (DCPDMA) was synthesized and used as monomer with styrene to synthesize the copolymer of styrene and DCPDMA (poly-St / DCPDMA) by solution polymerization.

#### **Experimental Section**

#### Materials

Dicyclopentadiene (97%, Nanjing Petroleum & Chemical Co., Ltd.) and maleic anhydride (99%, Shanghai Shanpu Chemical Co., Ltd.) were used. Styrene (98%, Tianjin Chemical Technology, Ltd.) that was firstly washed with 4% NaOH solution to the colorless, then washed with distilled water to neutral, and finally dried fully with anhydrous sodium sulfate was used. Benzoyl peroxide (BPO) (98%) and carboxymethyl cellulose (98%) were obtained from Shanghai Shanpu Chemical Co., Ltd. All other materials were purchased as reagent grade.

#### **Analytical Methods**

For acid value (in units of milligrams of KOH per gram) was determined according to method ASTM D1639. Esterification yield was calculated according to the changes of acid value and its formula was that esterification yield (%) =  $(1-a/a_0) \times 100\%$ , in which was acid value after reaction, and  $a_0$  was acid value before reaction. The yield of poly-St / DCPDMA was the weight (poly-St / DCPDMA) / the weight of total materials (including styrene and DCPDMA). ISO 14855-2005 (Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions-Method by analysis of evolved carbon dioxide) was used to determine the biodegradability of poly-St / DCPDMA.

#### Characterization

**Mass Spectrum (MS):** The Q STAR Elite high resolution mass spectrometer (AB SCIEX Corporation, USA) was used to determine the chemical structure of MACO. MS conditions: ionization mode, electron impact ionization (EI); ion source temperature, 250 °c; electron energy, 70 eV.

**GelPermeation Chromatography (GPC):** The average molecular weight  $(M_n)$  and the molecular weight distribution (D) of the copolymers were measured by Gel Permeation Chromatography (GPC) (Shimadzu LC-20AT HPLC Pump, Shimadzu RID-10A Refractive Index Detector, Tskgel G3000PW column). The samples were dissolved in N,N-dimethylformamide (DMF) and then filtered. Other operating conditions: mobile phase, DMF with HPLC grade; flow rate, 1 mL/min; column temperature, 35 °c. The molecular weights and Ds were derived from a calibration curve based on a polystyrene standard.

**Fourier transform infrared spectrometry (FT-IR):** The Fourier transform infrared (FT-IR) spectrometry of FTS-165 (BIO-RAD) was used in an infrared spectrum analysis. A certain amount of sample was grinded with potassium bromide in a mortar box. And then using the tablet machine, the grinding mixture of the sample and potassium bromide were pressed for subsequent IR analysis. The measuring range was 400–4000 cm<sup>-1</sup>.

**Thermal Gravity Analysis (TGA):** The TGA measurements were performed using the STA449F3GA TG-DSC analyzer (NETZSCH Corporation, Germany) in the temperature range from 30 to 1000  $^{\circ}$ c under a nitrogen atmosphere. The mass of the samples varied from 4 to 10 mg. The nitrogen flow was 50 mL/ min and heating rate of 10 K /min.

#### Procedure

Measured quantities of dicyclopentadiene 8.81 g (0.067 mol), maleic anhydride 7.85 g (0.08 mol), anhydrous sodium acetate 0.2 g and xylene17.6 mL were added to a three-neck 250 mL flask fitted with a condenser, a thermometer and a stirrer. The reaction mixture was kept at 120 °c and 1.44 g (0.08 mol) water was added to the reaction mixture drop wise to obtain dicyclopentadienemaleic acid monoester (DCPDMA). The reaction was monitored by testing the acid values of the reaction mixture. The reaction mixture was cooled to room temperature. Finally, the unreacted dicyclopentadiene and maleic anhydride were removed by evaporation under reduced pressure to give the final product of dicyclopentadiene-maleic acid monoester (DCPDMA).

Then measured quantities of DCPDMA 7.45 g (0.03 mol), styrene 3.75g (0.036 mol), 0.034g benzoyl peroxide (BPO) as initiator and toluene14.9mL were added to the reaction flask for solution polymerization. The reaction mixture was kept at 110 °c for 3 h. Then the toluene was removed and 11.2 mL methanol was used as aid-precipitant to obtain the styrene/dicyclopentadiene-maleic acid monoester (poly-St / DCPDMA) by filtering and drying. The syntheses of the DCPDMA and poly-St / DCPDMA are shown in Scheme 1.



## Results and Discussion

#### **Esterification Temperature**

Appropriate esterification temperature was necessary to obtain a product with satisfactory esterification yield. In the experiments, we studied the effects of different esterification temperature on the esterification yield of DCPDMA. Results obtained are shown in Figure 1.



As shown in Figure 1, as the esterification temperature was increased, the esterification yield first increased and then decreased. Generally, low temperature may induce longer reaction time. However, high temperature often induce the decomposition of DCPD occur and the esterification yield of DCPDMA decrease. The esterification yield was satisfactory when the esterification temperature was 120°c -125°c, therefore, it is feasible that the optimal esterification temperature of DCPDMA was 120°c -125°c.

#### Molar Ratio of Materials (maleic anhydride:water: dicyclopentadiene) and Esterification Time

The effects of different molar ratio of material and esterification time on the esterification yield of DCPDMA are shown in Figure 2. The experiments were conducted in triplet and the average results were taken.

As shown in Figure 2, in the same time, the esterification yield of DCPDMA was highest when the molar ratio of material ((maleic anhydride:water: dicyclopentadiene) was 1.2:1.2:1.0. In addition, as the esterification time was increased, the esterification yield of DCPDMA first increased and the decreased. This is probably because that too high temperature induced more dicyclopentadiene-maleic acid diester was formed. Therefore, the appropriate esterification time was 2 h.



# Effects of Different Reaction Conditions on the Yield of Poly-St /DCPDMA

The effects of different reaction conditions (including molar ratio of styrene to DCPDMA, polymerization temperature and polymerization time) on the yield of poly-St / DCPDMA are shown in Table 1.

**Table 1:** Effects of different reaction conditions on the yield of P[St/DCPDMA]

Styrene/ DCPDMA (molar ratio)	Т (°с)	Time (h)	Yield (%)
1.0:1	110	3	63±1.5
1.1:1	110	3	80±2.0
1.2:1	110	3	87±1.9
1.3:1	110	3	84±2.1
1.2:1	100	3	72±1.1
1:2:1	120	3	85±1.5
1.2:1	110	2	78±1.2
1.2:1	110	5	86±1.4

As shown in Table 1, as the polymerization temperature was increased, the yield of poly-St/DCPDMA first increased and then decreased slightly. Generally, high temperature can accelerate the reaction; however, an extremely high temperature may increase the occurrence of a side reaction, such as self-polymerization of monomer as well as coking. Thus, the polymerization temperature of 110 °c was feasible. In addition, sufficient polymerization time was necessary to obtain a product with high yield. As the polymerization time was increased, the yiled of the product increased. And the yield of poly-St/DCPDMA attained the highest value when the molar ratio of styrene to DCPDMA was 1.2:1. Therefore, the appropriate reaction conditions were as

follows: molar ratio of styrene to DCPDMA, 1.2:1; polymerization temperature, 110 °c; polymerization time, 3 h.

### Characterization of DCPDMA and Poly-St / DCPDMA

The mass spectrum was used to determine the structure of DCPDMA (Figure 3). As shown in Figure 3, the molecular ion peak of the DCPDMA (247.3) demonstrated the molecular weight of measured DCPDMA was 247.3, which was consistent with its theoretical molecular weight (248.3). Therefore, the MS result showed the resulting product was dicyclopentadiene-maleic acid monoester.



The infrared spectrum of poly-St/DCPDMA is shown in Figure 4. It can be seen that there were C-H stretching vibration absorption bands of benzene ring ( $3032 \text{ cm}^{-1}$ ,  $3064 \text{ cm}^{-1}$  and  $3085 \text{ cm}^{-1}$ ) and carbon-carbon vibration absorption bands of benzene ring ( $1452 \text{ cm}^{-1}$ ,  $1496 \text{ cm}^{-1}$  and  $1603 \text{ cm}^{-1}$ ); the absorption bands at 699 cm<sup>-1</sup> and 732 cm<sup>-1</sup> showed there was single substituted benzene group in poly-St/MACO; 1783 cm<sup>-1</sup> was the characteristic absorption band of carbonyl group of COOH; 1713 cm<sup>-1</sup> was the characteristic absorption band at  $1643 \text{ cm}^{-1}$ (alkene double bond) was evidence for the complete conversion of alkene double bond. The above demonstrated the formation of the poly-St/DCPDMA copolymer.



The number average molecular weight  $(M_n)$  and weight average molecular weight  $(M_w)$  were measured with GPC. The polydispersity index  $(\mathcal{D})$  can be calculated. For poly-St / DCPDMA,  $M_n$  was measured as 61200 g/mol, and  $M_w$  was measured as 82200 g/mol,  $\mathcal{D}$  was the calculated as  $M_w/M_n = 1.3$ .

In Figure 5, the peaks between 7.00-7.27 ppm belong to aromatic protons on the benzene ring. The signals at 5.43 ppm and 5.79 ppm belong to the unreacted double bond in dicyclopentadiene. The peaks at 2.42-2.68 ppm belong to the methyne protons adjacent to carboxylate group. Based on NMR data it is implied that the synthesis of Poly-St/DCPDMA was successful.



To examine the thermal stability of the poly-St/DCPDMA, the TGA measurement has been carried out (Figure 6). It was observed that the initial weight loss temperature of the poly-St/DCPDMA was 150 °c, and then the weight loss increased gradually as the temperature was increased. When the temperature was 350 °c, the residual mass of poly-St/DCPDMA was less than 50%. Thus, the poly-St/DCPDMA has excellent thermal stability.



**Biodegradability of Poly-St / DCPDMA** 

The biodegradability of poly-St / DCPDMA was investigated according to method ISO 14855-2005, and results are shown in Figure 7.

As shown in Figure 7, as the incubation time was increased, the biodegradability of poly-St / DCPDMA also increased. The biodegradability of poly-St / DCPDMA was 15% at 90 day, which demonstrated the poly-St / DCPDMA has decent biodegradability.



# Conclusions

In this study, the DCPDMA first was synthesized using dicyclopentadiene and maleic anhydride as raw material, and then using it and styrene as monomers, the copolymer of poly-St/DCPDMA was obtained by solution polymerization. Under suitable reaction conditions (esterification temperature, 120 °c; dicyclopentadiene (molar ratio), 1.2:1.2:1.0; esterification time, 2 h), the DCPDMA with esterification yield of 93% can be obtained. For the polymerization of poly-St/MACO, under the suitable reaction conditions (molar ratio of styrene to DCPDMA, 1.2:1; polymerization temperature, 110 °c; polymerization time, 3h), the resulting copolymer with the following properties (yield, 87%; M, 61200 g/mol; molecular weight distribution, 1.3) could be obtained. The MS results showed the DCPDMA was dicyclopentadiene-maleic acid monoester. The FT-IR result demonstrated the final product was the copolymer of styrene and DCPDMA.

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