Original Research Article

Synthesis and Characterization of Pentaerythritol Diacrylate

Abstract

Pentaerythritol diacrylate (PEDA) is synthesized by the esterification of pentaerythritol (PER) with acrylic acid (AA) using p-toluenesulfonic acid (PTSA) supported on silica as a catalyst. Fourier transform infrared spectrometer (FT-IR), and carbon nuclear magnetic resonance spectroscopy (^{13}C-NMR) were used to characterize the product of PEDA purified by utilizing column chromatography. The effects of various operating conditions such as the catalyst concentration(w_{cat}), the reactants mole ratios (N_{AA}/N_{PER}), the reaction temperature (T) and time (t) on the yield of PEDA are investigated. The results show that the yield of PEDA increases sharply with increase in w_{cat} until w_{cat} is 2.0 wt% and then increases gently. The highest yield (64.5%) is obtained when the operation conditions are as follows: w_{cat}=2.0 wt%, N_{AA}/N_{PER} =2.7, T=403 K and t =240 min.

KEYWORDS: Pentaerythritol diacrylate, Pentaerythritol, Acrylic acid, PTSA-Silica catalyst, Esterification

1. Introduction

Pentaerythritol diacrylate (PEDA) is an important intermediate, and can be used to synthesize some special purpose copolymers, such as the poly (PEDAS-co-TPTM) monolithic column [1], the waterborne polyurethane-acrylate (WPUA) [2], and the acrylate chemical grouting materials [3], which can be applied in proteome analysis, UV-curing resins, and concrete construction works, respectively. Additionally, PEDA is widely used as photoinitiator in the UV-curing field [4,5,6]. Especially, because it contains two hydroxyl groups，PEDA can be incorporated in reactive hot melt polyurethane adhesives (PURs) by replacing a portion of the polyols [7,8]. Meanwhile, as a dihydroxy-terminated acrylic monomer, PEDA can increase the initial bond strength of PURs, to enhance the green strength of PURs [9-12].

PEDA can be synthesized by esterification from pentaerythritol (PER) with acrylic acid (AA) catalyzed by p-toluenesulfonic acid (PTSA) [3,7]. However, it is very difficult to separate PTSA from PEDA products, which will reduce the product purity of PEDA. So, it is necessary to develop a new catalyst which can be easily separated from the reaction system. The supported catalyst can be easily removed by filtration [13-15].

In this work, a supported catalyst (PTSA-Silica) was prepared by loading PTSA on silica gel, and PEDA is synthesized by direct esterification using PTSA-Silica as a catalyst. The effects of various reaction variables on the esterification conversion are investigated, including the reaction temperature (T) and time (t), the mole ratio of acrylic acid to pentaerythritol（N_{AA}/N_{PER}）and the amount of catalyst (w_{cat}, defined as the mass percentage of the catalyst to the total reactants). The product of PEDA purified by chromatography and distillation in the sequence is characterized by infrared spectroscopy (FT-IR), and ^{13}C nuclear magnetic resonance spectroscopy (C-NMR).

2. Materials and methods

2.1. Reagents

Pentaerythritol is purchased from Shanghai Titan technology co. LTD. Acrylic acid, sodium chloride, sodium hydroxide and anhydrous copper sulfate are obtained from Shanghai Chemical Co., Ltd. Hydroquinone, anhydrous copper sulfate, toluene, sodium chloride, sodium hydroxide and p-toluenesulfonic acid are bought from Shanghai Macklin Biochemical Co., Ltd. All the chemicals are analytical grade. The silica gel was obtained from Tsingdao Shuoyuan Chemical Co., Ltd. (Tsingdao, China), with a particle diameter of 0.20 ±0.02 mm, and its detailed physical parameters are shown in Table 1[16].

Table 1. Physical Parameters of Silica Gel.

Parameters	Value
BET surface area, m^2/g	254.7
Volume of pores, cm^3/g	0.68
Pore diameter, Å	97
Apparent density, g/cm^3	1.02

2.2. Preparation of the PTSA-Silica catalyst

The procedure for preparing the PTSA-Silica catalyst is similar to the literature[17] and is briefly described as follows: To a solution of 0.04 mol PTSA·H_2O + 40 mL H_2O in a 100-mL beaker containing a stir bar was added 20 g of silica gel, and the mixture was stirred for 15 min and then gently heated on a hot plate, with intermittent swirling, until a free-flowing white solid was obtained. The catalyst was further dried by placing the beaker in an oven maintained at 120 °C for at least 48 h before use.

2.3. Synthesis of PEDA

The esterification reaction between an acrylic acid (AA) and pentaerythritol (PER) catalyzed by PTSA-Silica is a series of reactions that will generate pentaerythritol monoacrylate(PEMA) and PEDA in succession and in some cases even pentaerythritol triacrylate (PETA). The final reaction equations can be described as follows：

$$CH_2CHCOOH + C(CH_2OH)_4 \longrightarrow PEMA + H_2O$$

$$PEMA + CH_2CHCOOH \longrightarrow PEDA + H_2O$$

$$PEDA + CH_2CHCOOH \longrightarrow PETA + H_2O$$

Therefore, to obtain a high yield of PEDA products, it is necessary to systematically study the process conditions of the esterification reaction. In this work, PEDA is synthesized by PTSA-Silica catalyzed the direct esterification of PER with AA using hydroquinone/anhydrous copper sulfate as the inhibitor and toluene as the solvent. The procedure is briefly described as follows: A certain amount of pentaerythritol (~ 30 g) and a small amount of hydroquinone -anhydrous copper sulfate (~ 1.2 g, w/w, 1:1) are dissolved in toluene (~150 mL) in a three-necked flask (500 mL) equipped with a mechanical stirrer, a thermocouple and a fractional distillation column (for separating water produced in the system). The mixture is heated to a specific temperature, and then acrylic acid (~33- 46 g) and PTSA-Silica (~0.9-4.8 g) is added to the flask to start the reaction and maintain the reaction at the temperature for 50 ~ 300

minutes. After the reaction is completed, the reaction mixture is filtered to remove the catalyst. The filtrate was cooled to room temperature and then separated into two layers (organic/water) by adding saturated sodium chloride solution to it. The organic phase was collected, and its pH value was adjusted to 7 by adding sodium hydroxide solution. The sodium salt generated was removed by water washing, and the organic solvent was removed by reduced pressure distillation. The remainder was the crude product of PEDA, and the purity was analyzed by high-performance liquid chromatography(HPLC). The specific analysis method is described in section 2.3. The yield of PEDA can be calculated by the analysis result. We conduct a series of experiments in the flask in the temperature range of 373~403K, with the value of w_{cat} changing from 0.5% to 2.0 wt% and the value of N_{AA}/N_{PER} from 2.1 to 2.9. Figure 1 presents a typical HPLC chromatogram of the crude product.

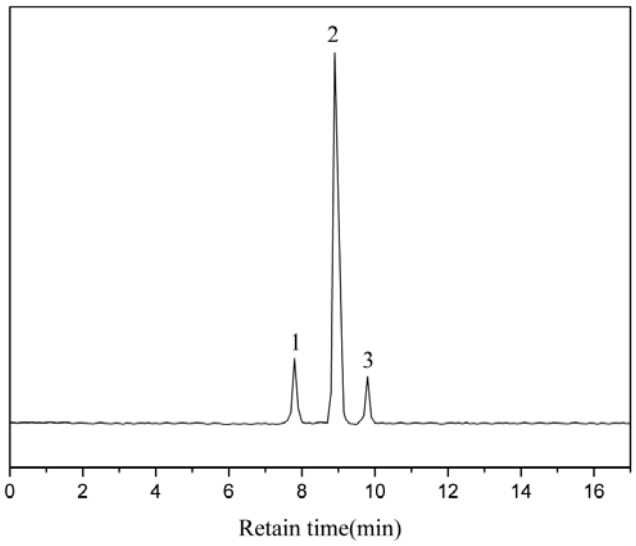

Fig.1. HPLC chromatogram of the crude product (1-PEMA, 2-PEDA, 3-PETA).

In order to determine whether the main product obtained is the target product, it is necessary to obtain a small amount of pure product. The pure product of PEDA was obtained by utilizing column chromatograph (Eluent, V(CH_3OH)/V(CH_2Cl_2), 1:20) and its purity was analyzed by HPLC to be 99%. Figure 2 presents a typical HPLC chromatogram of the pure product.

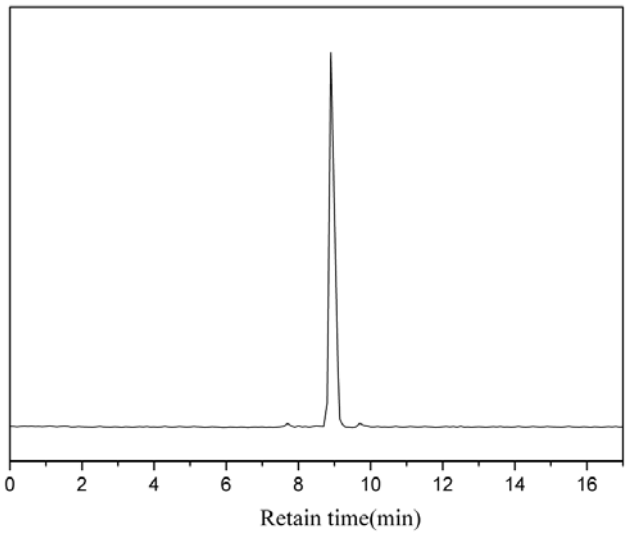

Fig. 2. HPLC chromatogram of the pure product.

2.3. Analytic method

The concentrations of PEDA, PEMA, PETA in the sample are determined by high-performance liquid chromatography (HPLC, Waters Breeze 1515) with refractometer 2414 as a detector. According to the analysis results of HPLC, the yield of PEDA at a certain time can be calculated. The column used is Sun Fire C_{18} stainless steel (4.6mm×250 mm). The optimum operation conditions of HPLC are: column temperature, 313K; flow phase, menthol(A)-potassium dihydrogen phosphate buffer solution (B, 0.2 $mol \cdot L^{-1}$) (V_A ∶ V_B = 10 ∶ 90); flow rate, 1.0 $ml \cdot min^{-1}$; sample volume, 10 μl.

3. Results and discussion

3.1 Characterization of the PEDA product

The synthesized product of PEDA is characterized by FT-IR (NICOLET 6700 IR spectrometer), and the result is shown in Figure 3. From Figure 3, bands with peak maximums at 3498 cm^{-1}(O-H stretching), 1727 cm^{-1}(C=O stretching), 1635 cm^{-1}(C=C stretching) and 1187 cm^{-1}(C-O-C stretching) all correspond to motions associated with PEDA.

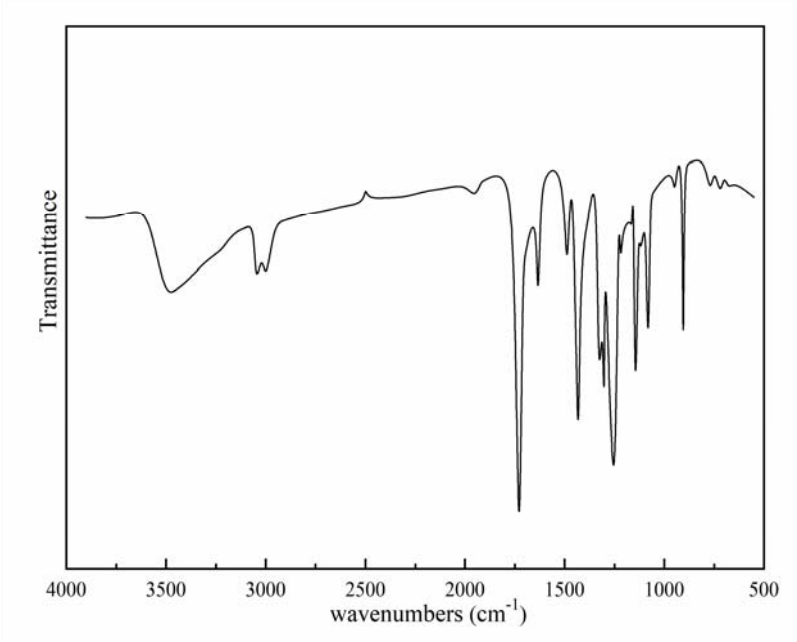

Fig. 3. FTIR spectra of PEDA.

^{13}C nuclear magnetic resonance spectroscopy, ^{13}C-NMR spectra were recorded with a 400-MHz spectrometer (Bruker, 400MHz/AVANCE 400). Figure 4 represents the ^{13}C-NMR spectra of the synthesized product dissolved in dimethylsulfoxide-d_6 (DMSO-d_6). The peaks interpretation is explained as following: a peak at ~ 167 ppm is attributed to the ester carbons attached to the vinyl group. Two peaks at ~ 130 ppm are attributed to the carbons of the vinyl group attached to the ester carbon. A peak around ~ 65 ppm is attributed to the cabon attached to the hydroxyl group, and its intensity can be used to calculate the proportion of alcoholic hydroxyls contained in the product. A peak around ~ 62 ppm is attributed to carbons attached to the acrylate group, and its intensity can be used to calculate the proportion of acrylate contained in the product. A peak at ~ 44 ppm is attributed to the quarter carbon atom. The results show that there are two alcoholic hydroxyls in the formula of the product. Thus, we can conclude that the product is PEDA.

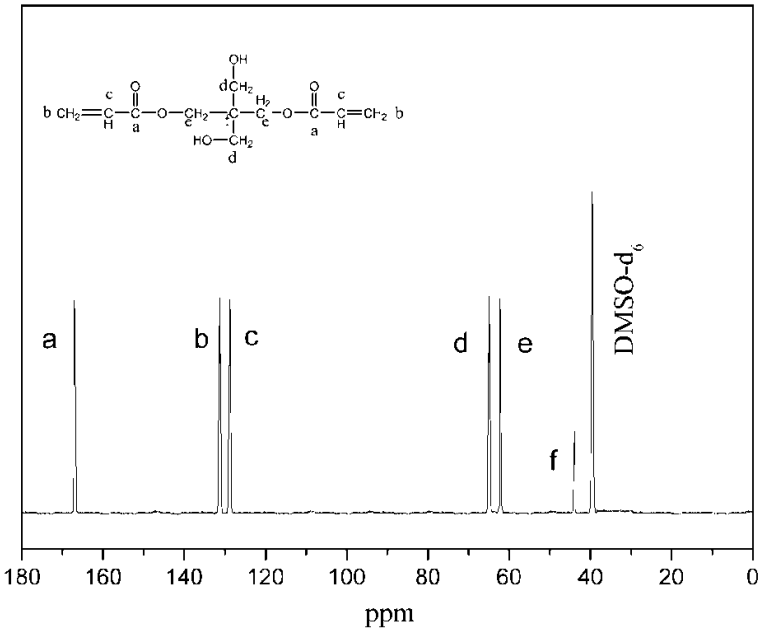

Fig. 4. ^{13}C-NMR spectra of PEDA.

3.2. Effect of Catalyst Concentration

The effect of catalyst concentration (w_{hat}) on the yield of PEDA was investigated by varying w_{cat} from 0.5wt% to 2.5wt% when the reaction conditions were as follow: T=393 K, N_{AA}/N_{PER}=2.7 and t = 240 mim. The relationship between the yield of PEDA and w_{cat} is presented in Figure 5. From Figure 5, it can be seen that the yield of PEDA increases from ~20% to ~ 52% when the value of w_{cat} changes from 0.5 wt% to 2.0 wt%. However, when w_{cat} >2.0 wt%, there no significant increase in yield of PEDA, this may be because the higher catalyst concentration will increase the chance of PEDA reacting with AA to generate PETA.

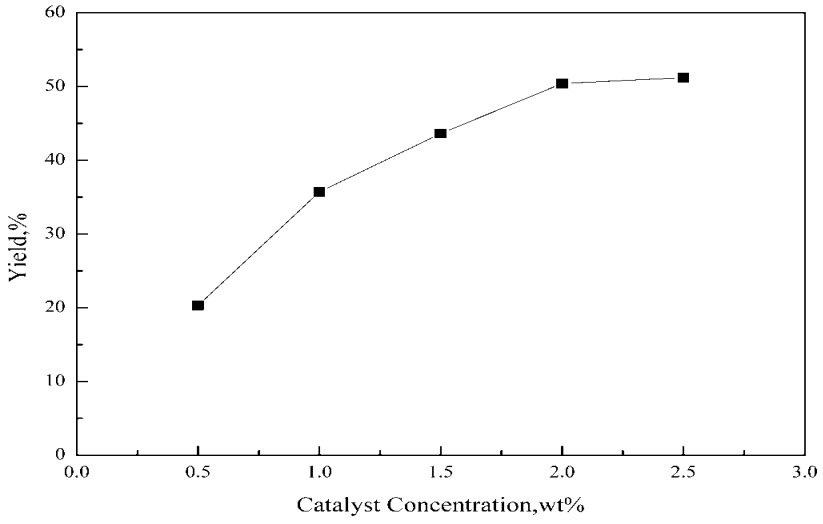

Fig. 5. The effect of the catalyst concentration on the yield of PEDA
(T=393 K, t=240 min, N_{AA}/N_{PER}=2.7)

3.3 Effect of mole ratio of reactants

When the reaction temperature is 393 K, and the value of w_{cat} is 2.0%, the effect of mole ratio of reactants on the yield of PEDA at a reaction time of 240 minutes was investigated by varying N_{AA}/N_{PER} from 2.1 to 2.9, and the results are shown in Figure 6. From Figure 6, it can be seen that the yield of PEDA increases with increasing in N_{AA}/N_{PER} until N_{AA}/N_{PER} =2.7 (yield, 52.6%), and then decreases slightly. This may be because the higher concentration of AA is beneficial to the formation of PEDA, however, when the value of N_{AA}/N_{PER} is larger than 2.7, a portion of PEDA will be converted to PETA by reacting with AA.

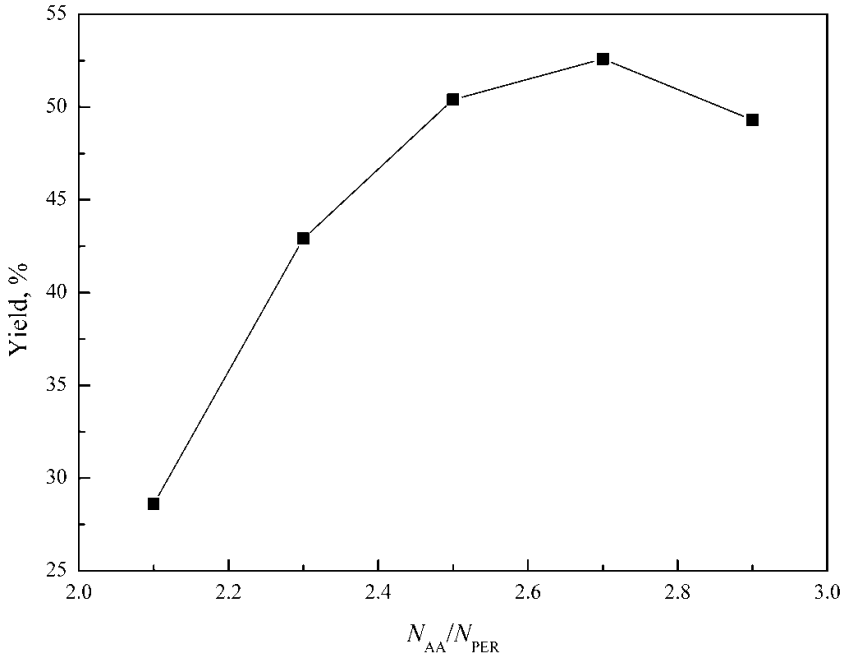

Fig. 6. The effect of molar ratio of reactants on the yield of PEDA
(T=393 K, t=240 min, w_{cat} =2.0 wt%)

3.4 Effect of reaction temperature and reaction time

The chemical reaction rate is strongly affected by the reaction temperature [21]. Therefore, the effect of reaction temperature and reaction time on the yield of PEDA was investigated a period of 50 to 300 min when the reaction conditions are as follows: N_{AA}/N_{PER} =2.7, T =373 ~ 403 K and w_{cat}=2.0 wt%. The results were shown in Figure 7. From Figure 7, the following conclusions can be drawn: (1) At the same reaction time, the higher the temperature, the greater the yield of PEDA. For example, the yield of PEDA at 240min increases from 28.9% to 64.5% when the temperature changes from 373 K to 403 K. The reason is that the reactant molecules at higher temperature have higher energy and the probability of collision between the molecules is larger; (2) At the same reaction temperature, the yield of PEDA increases with increaseing in reaction time for the lower temperatures (373K and 383K) , however, when the reaction temperature reaches or exceeds 393 K, the yield of PEDA increses with reaction time until ~250 min, and then decreases. This may be because a small amount of PEDA turns into PETA when the concentration of PEDA in the reaction mixture is sufficiently large.

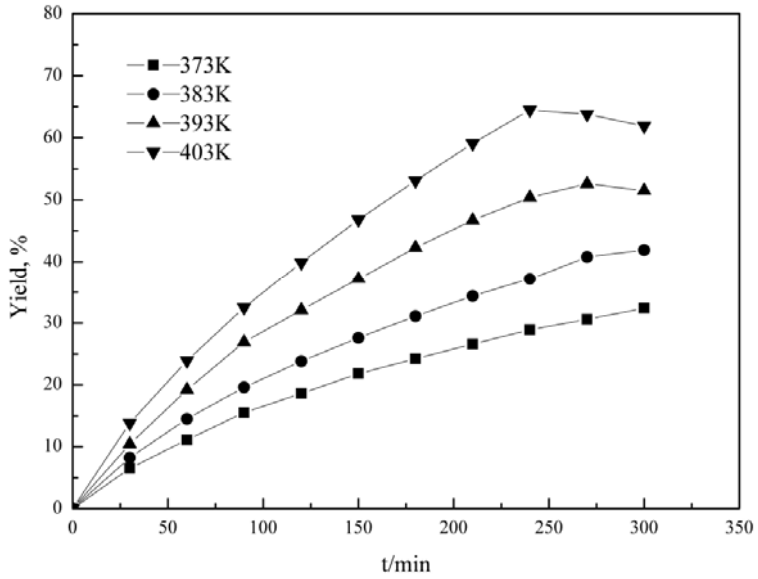

Fig.7. The effect of reaction temperature and reaction time on the yield of PEDA (N_{AA}/N_{PER}=2.7, t=240 min, w_{eat} =2.0 wt%)

5. Conclusions

In this work, pentaerythritol diacrylate (PEDA) is synthesized by reacting pentaerythritol (PER) with acrylic acid (AA) using PTSA-Silica as catalyst and toluene as solvent. The product of PEDA is purified by chromatography, and the purified product is qualitatively analyzed by Fourier transform infrared spectrometer (FT-IR) and nuclear magnetic resonance carbon (^{13}C-NMR)infrared spectroscopy. The results show that there are two alcoholic hydroxyls in the formula of the product, indicating it is the target product PEDA. The effects of various operating conditions such as the catalyst concentration(w_{cat} 0.5~2.5wt%), the reaction temperature (T, 373~403 K), the reaction time (t, 50~300 min), and the reactants mole ratios ($N_{AA}/N_{PER,}$ 2.1~2.9) on the yield of PEDA are investigated. The results show that the yield of PEDA increases with increasing in w_{cat} up to 2.0 wt%, and then tends to be gentle, and the highest yield of PEDA reaches to 64.5% when the operation conditions are as follows: N_{AA}/N_{PER} =2.7, T=403 K, t =240 min and w_{cat}=2.0 wt%.

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