

Synthesis and Application of an Alternative Plasticizer Di(2-Ethylhexyl)-1,2-Cyclohexane Dicarboxylate

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ABSTRACT: Cyclohexane dicarboxylic acid esters are environmentally friendly and non-toxic plasticizers, and have similar performance with phthalates which have potential toxicity to human health. In this article, di(2-ethylhexyl)-1,2-cyclohexane dicarboxylate (DEHCH) was synthesized via esterification between hexahydrophthalic anhydride (HHPA) with iso-octanol by using concentrated sulfuric acid as a catalyst. The effects of reaction parameters on esterification were studied by investigating the temperature, reaction time, molar ratio of iso-octanol-to-HHPA, and catalyst content. Conversions of HHPA to esters were determined. Functional group analysis was conducted by using FTIR and $^1\text{H-NMR}$ spectroscopy. PVC compounds after addition of the synthesized plasticizer DEHCH presented similar plasticizing performance with DEHP and DINCH, as demonstrated by comparisons of the results of mechanical properties, transparency, and volatilization and migration tests obtained for plasticized PVC compounds. DEHCH can also be considered as an alternative plasticizer for DEHP. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39763.

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INTRODUCTION

A plasticizer is an additive widely used to modify polymer materials in industry, because it can lower the glass transition temperature (T_g), reduce the melt viscosity, increase the workability, make the material softer and more flexible, and increase the toughness.¹ Among these polymers, poly(vinyl chloride) (PVC) consumes the largest amount of plasticizers, and has wide application sectors such as food packaging, medical materials, children toys, and tubing systems.^{2,3}

Esters of phthalic acid are the most commonly used plasticizers worldwide for their desirable properties of a plasticizer, such as minimal interaction with resins at room temperature, produce highly elastic compounds with reasonable cold strength, satisfactory insulation for cables, and low cost. With more than 30 different phthalates on the market, di(2-ethylhexyl) phthalate (DEHP) is by far the most widely used one. In the last decade, adverse health effects of phthalates have been thoroughly investigated and discussed. These commercial plasticizers, like DEHP, can leach out from PVC into blood, certain drug solutions and fatty foods. Mankidy has discovered that DEHP at concentrations of 10 mg/L would affect the synthesis of sex steroid hormones.⁴ DEHP is moderately toxic to cells *in vitro* and in embryos of animals, and produces a spectrum of toxic effects in both developing and adult animals and in multiple organ systems, and US Food and Drug Administration (FDA) and some

European Countries have forbidden its use from food packaging, medical materials, and children toys.^{5,6} The potential toxicity to human health has caused increasing attention of manufacturers and consumers,⁷ and many researches have been driven to find non-toxic and biodegradable plasticizers to replace traditional plasticizers in recent years.

In 2002, BASF made a market introduction of di(isononyl)-1,2-cyclohexane dicarboxylate (DINCH) as an alternative plasticizer, and it has been applied to sensitive products such as medical devices, toys and food packaging.^{8,9} This plasticizer is obtained by the hydrogenation of the benzene ring that is present in *o*-phthalates, and it is biodegradable and shows no acute toxicity, no skin sensitization, no genotoxicity, and no toxicity to reproduction. On the other hand, compared to phthalates, esters of cyclohexane-1,2-dicarboxylic acid exhibit a lower density and viscosity and lead to an improvement of the flexibility at low temperatures of plastisols, and the other mechanical properties, like tensile strength, elongation at break, and hardness, have no significant differences between the two kinds of plasticizers, so they are perfectly exchangeable.^{10–12}

BASF's DINCH is obtained by hydrogenating the diisononyl phthalate under high temperature and high pressure, and it is a little expensive. In this study, di(2-ethylhexyl)-1,2-cyclohexane dicarboxylate (DEHCH), which has a similar chemical structure

with DEHP and DINCH, was synthesized by esterification between iso-octanol and *cis*-cyclohexane-1,2-dicarboxylic anhydride, also called hexahydrophthalic anhydride (HHPA). Concentrated sulfuric acid was used as the catalyst because of its wide use in producing DEHP. The synthesis of DEHCH is as the same as the production of DEHP. And the production conditions and the raw materials except anhydride are also similar with those of DEHP. So, in the industry, it does not need to purchase new production equipments and the cost is much cheaper, especially in China, where the DEHP is still the most widely used plasticizer. This study includes optimization of esterification conditions for the ester synthesized, characterization of the ester, and comparisons of the properties of PVC resin respectively plasticized by synthesized DEHCH, DEHP, and DINCH.

EXPERIMENTAL

Materials

Cis-cyclohexane-1,2-dicarboxylic anhydride (HHPA, purity > 98%) was obtained from Alfa Aesar (Beijing, China). Iso-octanol and concentrated sulfuric acid were analytical grade from Beijing Chemical Works (Beijing, China). DEHP was obtained from Beijing Huaying Chemicals Co. (Beijing, China), while DINCH was obtained from BASF (Beijing, China). Poly(vinyl chloride) resin S-65 ($K=65$) in powder form was obtained from Formosa Plastics Industry Co. (Ningbo, China).

Synthesis of DEHCH

Weighed amounts of HHPA and iso-octanol were firstly added to a flask with a reflux condenser, a water segregator, a nitrogen catheter, and an electric stirring apparatus. The mixture was heated to a certain temperature and concentrated sulfuric acid was added. The reaction was then carried out for a certain time. The solution obtained was placed into a separator funnel and then neutralized with 2% sodium hydroxide solution until acid number (mg KOH/g) was lower than 0.1. Then the organic solution was washed by 80°C water for twice. Finally the organic solution was separated from water phase and then it was added with sodium sulfate to draw water residue and was evaporated. Conversion of HHPA was determined by the following simplified expression:

$$C = \left(1 - \frac{A_m}{A}\right) \times 100\%$$

where C was the conversion of HHPA, A was the acid number of the mixture of HHPA and iso-octanol, and A_m was the acid numbers of the crude reaction mixture.

Characterization of DEHCH

The obtained ester was characterized by analyzing their functional groups using Fourier transform infrared spectroscopy (FTIR, Tensor27) from Bruker (Beijing, China), and their proton peaks using $^1\text{H-NMR}$ (AV600 Spectrometer) from Bruker (Beijing, China) in CDCl_3 .

Plasticization of PVC Resin

The synthesized plasticizer DEHCH was incorporated into PVC compounds in order to evaluate its plasticizing performance compared with DEHP and DINCH.

Preparation

PVC compounds were prepared using a high-speed mixer according to procedure described by Wadey.¹¹ The 100 phr

(per hundred resin) PVC resin was added to the mix and heated to 50°C at 1500 rpm. The speed was reduced to 750 rpm and 50 phr plasticizer was added. The rotar speed was again increased to 1500 rpm and the mixture dried. Then 2 phr Ca/Zn stabilizer was added and the mixer speed was increased to 2500 rpm until the temperature reached 120°C. The dry blend was then cooled in the cooling mixer and bagged at 30°C. The dry blends were milled on a two-roll mill 5 min past banding at 165°C. The milled sheets were pressed to a thickness of 2 mm for 3 min at 180°C to ensure the ultimate physical properties would be developed.

Mechanical Properties

Tensile strength, percentage tensile elongation at break (ultimate elongation), and the modulus at 100% elongation were determined at 25°C using a universal testing machine (LR30K, Ametek Co., England) according to Chinese standard GB/T1040–2008. And the tensile speed was 50 mm/min. Hardness was also determined at 25°C using a shore durometer (XY-1, Shanghai Chemical Machinery Factory, China) according to Chinese standard GB/T531–1999. Impact strength was determined at –40°C using a resiliometer (Ceast Co., Italy) according to Chinese standard GB/T1843–2008.

Transparency

Transmittances of PVC compounds were measured by using a photometer (WGT-S, Shanghai Precision & Scientific Instrument Co., China) according to Chinese standard GB/T2410–2008. The samples had substantially plane-parallel surfaces free of dust and internal voids with 1 mm thickness.

Volatility Tests

The volatilization loss of the plasticizer from PVC compounds was determined according to ISO176–2005. Samples (in triplicate) were weighed and hanged in metal containers at 100°C in which laid some activated carbon. After 24 h the samples were taken out and cooled to room temperature. The weights of cooled samples were measured and average percentage weight losses were determined.

Migration Stability Tests

Migration of the plasticizer from PVC compound samples was carried out in three different solvents (water, ethanol, and petroleum ether) at 25°C.¹³ Samples (in triplicate) were weighed and kept in 150 mL of each solvent for 48 h, and then dried in a drying oven at 40°C for 48 h. The weights of the dried samples were measured and average percentage weight losses were determined.

RESULTS AND DISCUSSION

Characterization of the Ester Synthesized

The functional groups of the obtained plasticizer can be analyzed by FTIR spectra and $^1\text{H-NMR}$ spectra to determine that the esterification has happened. FTIR data showed that there was shifting of C=O absorption band from 1709 to 1730 cm^{-1} as shown in Figure 1, which indicated that C=O of anhydride had been transformed into that of ester. The absorption peak at 1180 cm^{-1} was attributed to C–O–C, and the alkane angular deformation (CH_2) was mainly at 2930 and 2860 cm^{-1} . The absorption band regarding OH angular deformation at

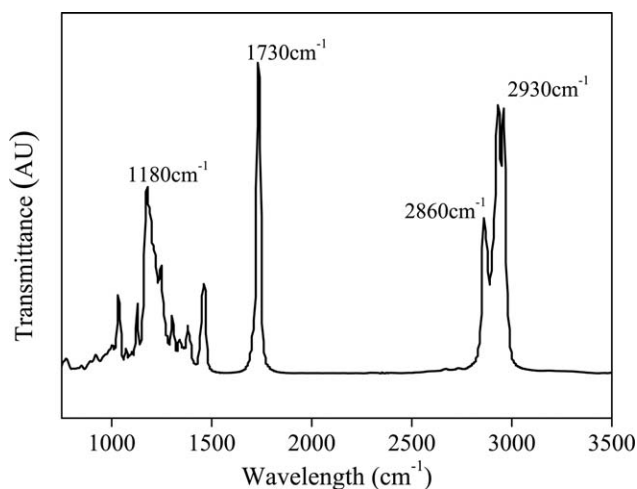


Figure 1. FTIR spectrum of DEHCH.

3445 cm^{-1} was disappeared. As shown in Figure 2, the obtained $^1\text{H-NMR}$ spectra presented the characteristic appearance of $\text{R-COOCH}_2\text{-R}'$ at 3.98 ppm and disappearance of $\text{HO-CH}_2\text{-R}'$ at 3.50 ppm. All the above indicated that the product had been successfully synthesized.

Optimization of Ester Synthesis

Di(2-ethylhexyl)-1,2-cyclohexane dicarboxylate (DEHCH) was synthesized via esterification between hexahydrophthalic anhydride (HHPA) and iso-octanol by using concentrated sulfuric acid as a catalyst. Like esterification of phthalic anhydride with alcohol,¹⁴ this reaction also takes place in two stages as shown in Scheme 1. The first stage is so rapid that it can be carried out in the absence of catalyst. However, esterification of the second carboxylic group is very slow and needs to be facilitated by acid catalyst and the resulting water must be removed from the reaction mixture. So the reaction equilibrium and conversion of HHPA could be changed by controlling variables such as reaction temperature, time, catalyst content, and feed molar ratio.

Effects of Reaction Temperature and Time on the Conversions of HHPA

In esterification reaction, the investigation on the effect of temperature is very important, because the reaction temperature has a direct effect on the activity of catalyst. With an increase in reaction temperature, the initial reaction rate can increase substantially, which yields greater conversion of HHPA at a fixed contact time.¹⁵ The conversion of HHPA also increases with the

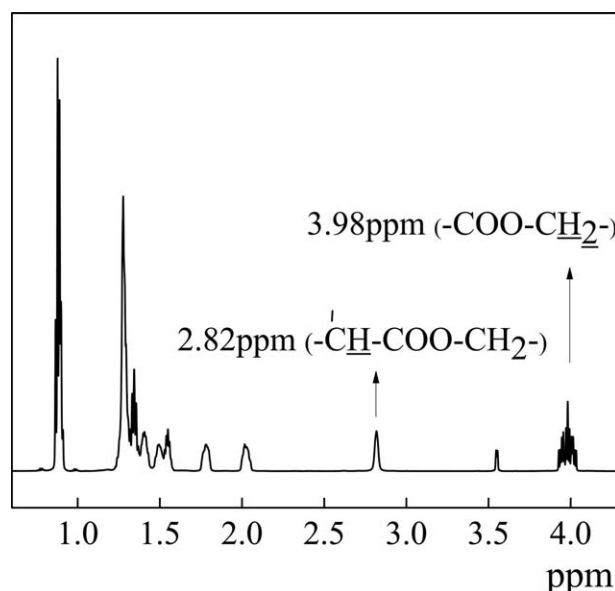
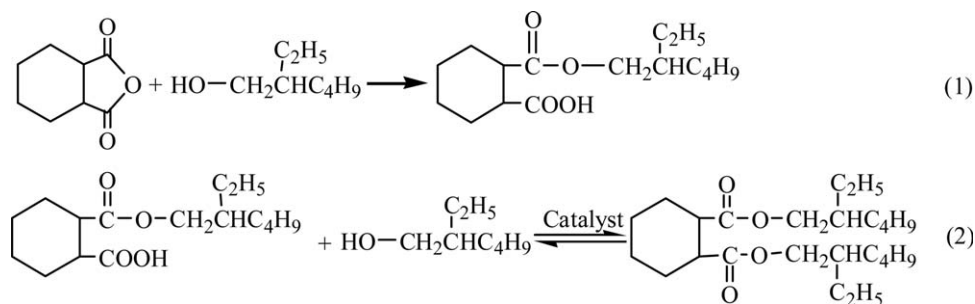


Figure 2. $^1\text{H-NMR}$ spectrum of DEHCH.

increasing of reaction time. But too high temperature or too long time both will lead to oxidation, decreasing the conversion of HHPA and the color of product getting deeper. Figure 3 shows the changes of the conversions of HHPA with reaction temperature and time, while keeping the molar ratio of iso-octanol-to-HHPA at 2.4 : 1 and the catalyst content at 0.1% of HHPA weight. The conversions of HHPA increased with the temperature increasing, but when reaction time exceeded 1.5 h, the conversions of HHPA at 180°C were lower than those at 170°C and the color at 180°C was also deeper. These were owing to concentrated sulfuric acid catalyzing iso-octanol to oxidize at a too high temperature. When reaction temperature was at 170°C , the conversions of HHPA increased slowly and almost reached the reaction equilibrium and the color got deeper after 2 h. So the best reaction condition was at 170°C and not beyond 2 h.

Effect of Catalyst Content on the Conversion of HHPA

The catalyst content does not have any effect on the equilibrium conversion, but has an effect on the time required to reach the reaction equilibrium.¹⁵ The time required to reach the reaction equilibrium reduces owing to the increase of catalyst content. Table I shows the effect of catalyst content on the conversions of HHPA, while keeping the molar ratio of iso-octanol-to-HHPA at



Scheme 1. Esterification between HHPA and iso-octanol.

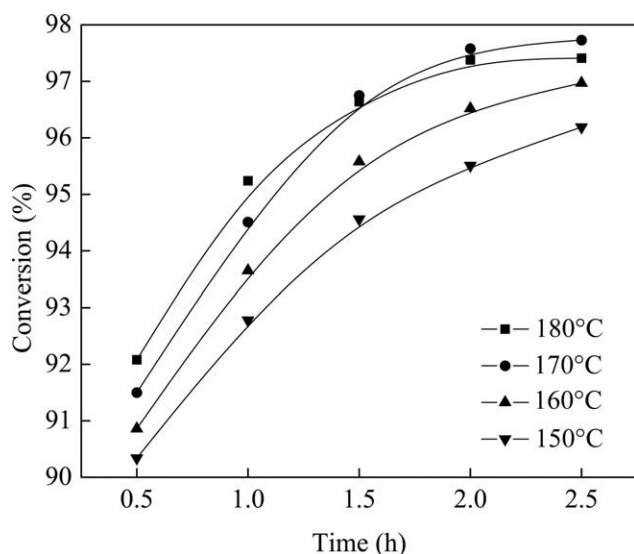


Figure 3. Effects of reaction temperature and time on conversions of HHPA.

2.4 : 1 and the temperature at 170°C. The reaction conducted using 0.2% catalyst gave higher conversion of HHPA than those of 0.1 and 0.4%. When the catalyst content was 0.2% of HHPA weight, the reaction reached equilibrium after 1.5 h, while the reaction using 0.1% catalyst did not. And when the catalyst content was 0.4%, the color of the reaction mixture became yellow and even brown after 1 h. Addition of excess amount of concentrated sulfuric acid catalyst may oxidize the alcohol and product and decrease the conversion yield.¹⁶

Effect of the Molar Ratio Between Iso-Octanol and HHPA on the Conversion of HHPA

In esterification reaction, excess of alcohol is usually employed to improve the conversion of acid, and alcohol and water can form a azeotrope to take the water generated from esterification out of the reaction mixture, which also can improve the conversion of acid.¹⁷ Study on the effect of the molar ratio of iso-octanol-to-HHPA on the conversion of HHPA was conducted at 170°C and 0.2% catalyst, and the conversions of HHPA after 1.5 h were shown in Figure 4. When the ratio was 2.4 : 1, the conversion of HHPA reached the highest value 98.41%. And too much iso-octanol would lead to decrease of the conversion of HHPA as the result of reducing the concentration of HHPA.

Reproducible Experiments at the Optimal Condition

Considering all the above, the optimal condition of synthesizing DEHCH via esterification was as followed: the molar ratio of

Table I. Effect of Catalyst Content on the Conversions of HHPA

Time (h)	Conversion (%)		
	Catalyst 0.1%	Catalyst 0.2%	Catalyst 0.4%
0.5	91.50	94.73	95.25
1.0	94.51	97.64	98.13
1.5	96.75	98.41	98.06
2.0	97.58	98.49	-

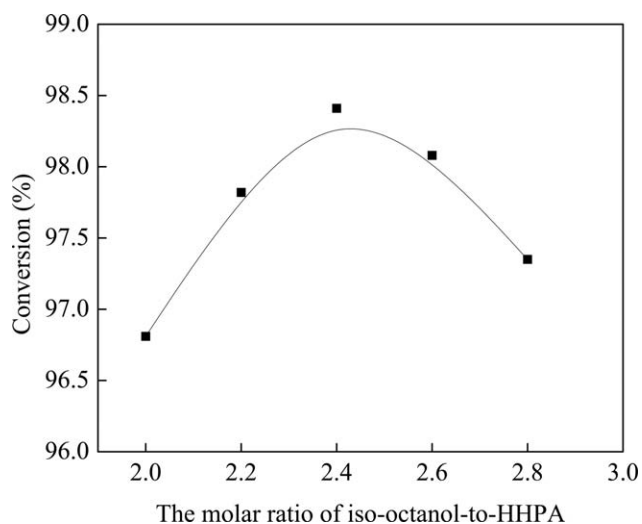


Figure 4. Effect of the molar ratio of iso-octanol-to-HHPA on the conversion of HHPA.

iso-octanol-to-HHPA was 2.4 : 1; concentrated sulfuric acid content was 0.2% of HHPA weight; and reaction temperature and time were respectively 170°C and 1.5 h. Then five times of synthesis experiments were conducted at the optimal condition to check its reproducibility. There was not big difference between the conversions of HHPA of each time. The average conversion was 98.39%, and the standard deviation was 0.11%, which indicated that the optimal condition was reliable.

Properties of PVC Resin Plasticized by DEHCH

To evaluate the plasticizing performance of synthesized DEHCH, properties of PVC compound respectively plasticized by DEHP, DEHCH, and DINCH were compared by analyzing mechanical properties, transparency, volatility, and migration stability.

Mechanical Properties

The mechanical properties of PVC compound are shown in Table II, The contents of the three plasticizers are all 50 phr and 10 samples were measured on every test. The synthesized DEHCH showed similar plasticizing performance with DEHP

Table II. Mechanical Properties of Plasticized PVC Resin

Projects	DEHP	DEHCH	DINCH
Shore A	83	86	85
Tensile strength (MPa)	21.5	22.4	21.6
Elongation at break (%)	281	272	284
Modulus at 100% elongation (MPa)	11.0	12.3	11.7
Impact strength (-40°C, kJ/m ²)	18.9	22.7	21.8

Table III. The Light Transmittance of PVC Compounds

	DEHP	DEHCH	DINCH
Transmittance (%)	84.6	83.8	84.3

Table IV. The Mass Loss of PVC Compounds at a High Temperature

	DEHP	DEHCH	DINCH
Mass loss (%)	0.6	1.2	0.4

Table V. Migration of Plasticizers from PVC Compounds into Different Solvents

Solvents	Mass loss (%)		
	DEHP	DEHCH	DINCH
Water	1.4	1.6	1.3
Ethanol	10.2	9.5	9.8
Petroleum ether	16.1	14.8	15.6

and DINCH. The PVC resin plasticized by DEHCH presented better strength and modulus but a little worse flexibility.

Transparency

Since PVC is a transparent polymer, a study of transparency is a necessary method for investigating the plasticizing performance of plasticizers. The transparency of the PVC compounds is shown in Table III. The PVC compound plasticized by DEHCH showed high light transmittance as well as DEHP and DINCH.

Volatility Tests

Table IV shows the volatility tests results. At high temperature plasticizers will migrate from PVC resin to the surface. An increased plasticizer volatility will cause a lower stability of mechanical properties of PVC resin.¹⁸ PVC compounds plasticized by DEHCH presented more mass loss during the experimental period (24 h, 100°C). So it is better to not be used in wires and cables.

Migration Stability Tests

If a polymeric material comes into contact with liquids (water, solvents) the probability of plasticizer extraction increase.¹³ In Table V, the three plasticizers all showed lower migration rates into water compared with weakly polar and nonpolar solvents, which is in agreement with the hydrophobic character of these plasticizers. The DEHCH plasticized PVC compound showed the best migration stability in solvents.

CONCLUSIONS

Di(2-ethylhexyl)-1,2-cyclohexane dicarboxylate (DEHCH) could be synthesized via esterification between hexahydrophthalic anhydride (HHPA) and iso-octanol using concentrated sulfuric acid as a catalyst. It presented similar plasticizing performance with DEHP and DINCH in mechanical properties, transparency,

and volatilization and migration stability. It could be an alternative plasticizer to DEHP. However, further toxicological, ecotoxicological, and mechanical assessments must be done in order to consider DEHCH as a non-toxic plasticizer in sensitive application sectors such as food packaging, medical materials, and children toys.

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