Biobased Plasticizers from Tartaric Acid: Synthesis and Effect of Alkyl Chain Length on the Properties of Poly(vinyl chloride)

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ABSTRACT: A series of tartaric acid (TA) esters with different side chain lengths [dibutyl TA esters (DBTAE)-Cn], as plasticizers for poly(vinyl chloride) (PVC), is herein reported. Their structures have been fully characterized using proton nuclear magnetic resonance and Fourier-transform infrared spectroscopy. Their compatibility and plasticizing effect for soft PVC were evaluated using thermogravimetric analysis, dynamic mechanical analysis, tensile testing, and migration testing. The results showed that all these TA esters exhibit good plasticizing performance. At a concentration of 30 phr in PVC, the best results for the plasticizing effect, in terms of glass transition temperature reduction and elongation at break, were achieved when the ester DBTAE-C4 was used. However, the longer side chains of these esters improved the thermal stability of soft PVC blends yet exacerbated the migration behavior of these esters from PVC films in n-hexane. The properties of the plasticized PVC blends depended on the structural features of DBTAE-Cn. The plasticizing performances of the esters DBTAE-C1 and DBTAE-C4 rivaled that of dioctyl phthalate (DOP), suggesting that they have the potential to replace DOP in soft PVC materials.

1. INTRODUCTION

Poly(vinyl chloride) (PVC) is a thermoplastic polymer and is widely used in packaging materials, children’s toys, electrical cables, medical devices, and so forth.1−4 However, PVC is a rigid and brittle material due to the strong polar interactions between the chains. Therefore, plasticizers that can disrupt these interactions are essential for improving the flexibility and processability of PVC.5 Plasticizers are often resins or liquids with low molecular weight that can insert between PVC chains and reduce PVC−PVC chain interactions, thereby improving the flexibility and workability of the polymeric materials.6 An ideal plasticizer should contain two molecular features: one is a polar group and the other is a nonpolar portion. The former ensures that the plasticizer is miscible with PVC, while the nonpolar moiety is conducive to plasticizer insertion between polymer chains and helps to separate PVC chains.7,8

Phthalate esters play a significant role among commercial plasticizers, owing to their outstanding plasticizing performance and relatively low price.9−11 Phthalate esters possess one aromatic ring, two ester groups, and two alkyl chains, a combination of polar and nonpolar groups that ensure their outstanding plasticizing properties for PVC. However, there are many controversies about using phthalate plasticizers because of their potential toxicity to humans and easy migration from the polymeric matrix.12,13 Phthalate plasticizers currently may not be used in toys or child-care products in some countries.14−16 Moreover, phthalates are mostly petroleum-based products, which are unsustainable.17,18 Thus, it is necessary to develop alternatives to phthalates.

Recently, there has been great interest in designing plasticizers from nontoxic, renewable, and biobased sources as an alternative to phthalates.19−23 Although some biobased plasticizers are already on the market, their performance is rarely comparable to petro-based phthalates. Thus, the synthesis and investigation of new compounds remain an important challenge to develop better plasticizers. As we mentioned above, an ideal plasticizer contains two different types of functional groups, suggesting that their performance can be optimized by modifying their molecular structure. As noted, the plasticizing efficiency of a plasticizer can be optimized by modifying its structural features.24−30 For example, the plasticizing performance of a plasticizer has been improved by the incorporation of different numbers of ethyoxyl units into the structure.31 Furthermore, new alkyl
terminal hyperbranched polyglycerol (alkyl-HPG) plasticizers with different polar group contents have been prepared by changing the molar ratios of glycidol and trimethylolpropane. It was found that the alkyl portion of alkyl-HPG was the crucial factor for improving the plasticizing efficiency regardless of the ether group content. Introducing a rotating substituent into the molecule was suggested as a means to increase the steric hindrance of the plasticizer, which can obviously improve the plasticizing performance of the plasticizer.

Tartaric acid (TA) is a green product found in many fruits. TA derivatives are biodegradable and have been widely applied in the food industry, effervescent antacids, and drug synthesis. TA is a tetrafunctional molecule and can be easily modified. Previous works with TA-based plasticizers have mainly been focused on the introduction of different alkyl chains to the TA carboxyl group or benzene ring to the hydroxyl group of TA esters. Less work has been focused on introducing side chains at the hydroxyl group of TA esters to obtain branched molecules. Accordingly, an integrated effort to develop a new class of plasticizers derived from TA is herein reported, and four biobased plasticizers with branched molecules have been prepared by introducing different alkyl chains (Scheme 1). The adjustment of the alkyl chain length can alter the ratio of polar and nonpolar groups in the molecule as well as the steric size of the plasticizer. This synthetic flexibility allows the easy adjustment of the molecular structure, thereby improving the plasticizing efficiency. Their use in PVC has been assessed, and a comparison with the performance of dioctyl phthalate (DOP) as a plasticizer has been made. Through structural characterization and evaluation of the plasticizing efficiency of these esters, the relationship

Scheme 1. Schematic Synthetic Route of Dibutyl TA Esters (DBTAE)-Cₙ

Figure 1. $^1$H NMR spectra of DBTAE and DBTAE-Cₙ.
between the plasticizer structure and PVC properties can be further studied.

2. RESULTS AND DISCUSSION

2.1. Synthesis of TA-Based Plasticizers. To confirm the structures of these four plasticizers, proton nuclear magnetic resonance (\(^1\)H NMR) was used, as shown in Figure 1. In Figure 1a, the double peaks at 4.54 ppm were assigned to the proton of methylene connected to the hydroxyl group of dibutyl TA esters (DBTAE). The multiplet at 3.40 ppm originated from the proton of the hydroxyl group. The other peaks at 4.26, 1.67, 1.39, and 0.95 ppm were assigned to the protons of the methylene and methyl groups. Figure 1b displays the \(^1\)H NMR spectrum of DBTAE-C1. In comparison with the precursor DBTAE, the proton of the hydroxyl group at 3.40 ppm disappeared, and a new single peak appeared at 2.17 ppm. The new singlet could be assigned to the proton of the methyl group connected to the ester group of DBTAE-C1. Furthermore, the doublet from the methyne group at 4.54 ppm turned into a single peak and shifted to 5.70 ppm due to its proximity to the strong electron-withdrawing ester group, which further supported the fact that the ester group was successfully formed. In Figure 1c–e, the peaks at 2.42 ppm belonged to the methylene group that was linked to the ester group. The peaks at 1.35 ppm can be assigned to the methylene proton on alkyl chains, and the integral number increased with the increasing length of the side alkyl chain.

The chemical structures of DBTAE and DBTAE-C\(_n\) were further confirmed by Fourier-transform infrared (FTIR) spectroscopy (Figure 2). After the esterification of TA, the broad absorption band at 2300–3900 cm\(^{-1}\) disappeared, and the stretching vibration band from the carbonyl group also shifted from 1730 to 1740 cm\(^{-1}\) due to the formation of ester groups at the carbonyl groups. Meanwhile, new peaks were observed at 2870–2960 cm\(^{-1}\), representing the typical bands of –CH\(_3\) and –CH\(_2\). These results indicated that DBTAE was obtained. Compared with DBTAE, the broad OH group absorption band at 3443 cm\(^{-1}\) disappeared in the spectra of DBTAE-C\(_n\), supporting that the esterification reaction between the hydroxyl group on DBTAE and alkyl chloride was successful. In combination with the \(^1\)H NMR data, FTIR showed that the desired plasticizers were successfully synthesized.

2.2. Thermal Stability of the TA-Based Plasticizers and Soft PVC Samples. The thermal stability of the plasticizers and the blends with PVC blends is a vital parameter for their practical applications. Here, the effect of the side alkyl chains on the resulting thermal stabilities of the newly synthesized TA esters and the plasticized PVC films was studied with thermogravimetric analysis (TGA). As shown in Figure 3a and Table 1, the weight of the TA esters and DOP rapidly decreased between 170 and 300 °C. The trend in the onset temperature (\(T_{\text{onset}}\)) was DBTAE-C1 (168.74 °C) < DBTAE-C4 (191.12 °C) < DOP (203.63 °C) < DBTAE-C7 (204.61 °C) < DBTAE-C11 (223.82 °C), indicating that the synthesized TA esters had better or comparable thermal stability than DOP. Moreover, it can be clearly seen that the \(T_{\text{onset}}\) temperature increased with the alkyl chain length in the TA esters, suggesting that the thermal stability also increased. Besides, the thermal degradation of these TA-based esters mainly occurred over the temperature range of 150–360 °C.

As shown in Figure 3b, all the PVC films underwent two thermal degradation processes. The first degradation process began at 200 °C and continued to 350 °C, which could mainly be attributed to the decomposition of the plasticizer and the dehydrochlorination of PVC.\(^{39,40}\) The second degradation process occurred over the temperature range of 450 to 550 °C, which could be attributed to the cross-linking reaction of C═C bonds to form aromatic compounds.\(^{41,42}\) The thermal degradation data of PVC samples including the \(T_{\text{onset}}\) weight loss of 10% (\(T_{\text{10\%}}\)), and the weight loss of 50% (\(T_{\text{50\%}}\)) are also summarized in Table 1. Compared to the pure PVC film, the PVC samples plasticized with DBTAE-C\(_n\) had higher values of \(T_{\text{onset}}\), \(T_{\text{10\%}}\), and \(T_{\text{50\%}}\) except for PVC-C1, which could be due to the lower thermal stability of DBTAE-C1 compared to the other plasticizers. Also, this suggested that the addition of these TA-based plasticizers (except for DBTAE-C1) could improve the thermal stability of PVC. Interestingly,
it was also found that the \( T_{\text{onset}} \), \( T_{10\%} \), and \( T_{50\%} \) increased gradually by increasing the alkyl chain length of DBTAE-C\(_n\). It can be concluded that the longer alkyl chains in DBTAE-C\(_n\) could improve the thermal stability of both the plasticizer and the plasticized PVC films. It can be explained that the TA ester with a longer alkyl chain had higher molecular weight and showed higher thermal stability of the plasticizer, which can suppress the evaporation of the plasticizer in PVC materials, thereby improving the thermal stability of PVC samples. Moreover, the \( T_{\text{onset}} \), \( T_{10\%} \), and \( T_{50\%} \) values of PVC-C\(_1\), PVC-C\(_4\), PVC-C\(_7\), and PVC-C\(_{11}\) films were higher than those of PVC-D, which might be due to the higher molecular weight of the esters with longer side chains.

The discoloration tests at 180 °C were also performed to further study the thermal performance of PVC samples. As shown in Figure 4, the pure PVC film turned brown after 20 min and was even darker after 40 min, suggesting its poor thermal stability. Meanwhile, the other five samples transitioned from colorless to yellow to black after 50 or 60 min, indicating that the plasticizers had a positive effect on the thermal stability of PVC films. Comparing the four samples plasticized with the TA-based compounds studied herein, PVC-C\(_{11}\) remained colorless for the longest time and only turned slightly yellow after 30 min of heat treatment. In addition, the color of the PVC samples after 30 min darkened with decreasing side alkyl chain length of the plasticizer, suggesting that the films were less thermally stable samples. These results from the discoloration tests also agreed with TGA tests.

2.3. DMA Measurements. It is well known that the glass transition temperature (\( T_g \)) is a crucial factor for evaluating the plasticizing efficiency of an additive, with a lower \( T_g \) representing a better plasticizer.\(^{33,34}\) The \( T_g \) values of PVC blends were compared by using dynamic mechanical analysis (DMA) to investigate the influence of the molecular structure of DBTAE-C\(_n\) on its miscibility and the plasticizing efficiency with PVC. As shown in Figure 5, the DMA trace for each PVC blend exhibited one symmetrical peak, indicating that the DBTAE-C\(_n\) plasticizers were highly miscible in the PVC matrix. The \( T_g \) values of the films PVC-C\(_1\), PVC-C\(_4\), PVC-C\(_7\), and PVC-C\(_{11}\) were 52.43, 51.91, 65.32, and 83.91 °C, respectively. Obviously, a decrease in the \( T_g \) value was observed for all the plasticized PVC samples compared to the pure PVC film (\( T_g = 89.16 \) °C). These results indicated that the TA esters were excellent plasticizers for PVC.

Interestingly, it was easy to find that the \( T_g \) value of PVC samples increased as PVC-C\(_4\) < PVC-C\(_1\) < PVC-C\(_7\) < PVC-C\(_{11}\), indicating that DBTAE-C\(_4\) showed the best performance as a plasticizer. To explain this trend, we should note two aspects. As the alkyl chain length in the TA ester increased, the relative content of polar groups in the molecule decreased; meanwhile, the molecular volume of the TA esters increased.

| Table 1. TGA Data of Plasticizers and PVC Samples |
|-------------------------------------------------|
| **samples** | PVC-C\(_1\) | PVC-C\(_4\) | PVC-C\(_7\) | PVC-C\(_{11}\) | PVC-D | PVC |
| \( T_{\text{onset}}/°C \) | 173.55 | 199.27 | 241.57 | 258.07 | 234.68 | 174.21 |
| \( T_{10\%}/°C \) | 209.37 | 239.26 | 264.44 | 275.99 | 253.61 | 238.55 |
| \( T_{50\%}/°C \) | 283.16 | 305.60 | 306.96 | 310.96 | 293.41 | 305.38 |
| **samples** | DBTAE-C\(_1\) | DBTAE-C\(_4\) | DBTAE-C\(_7\) | DBTAE-C\(_{11}\) | DOP |
| \( T_{\text{onset}}/°C \) | 168.74 | 191.12 | 204.61 | 223.82 | 203.63 |
| \( T_{10\%}/°C \) | 182.93 | 209.38 | 243.29 | 270.90 | 217.32 |
| \( T_{50\%}/°C \) | 216.46 | 253.97 | 327.89 | 329.49 | 258.16 |

Figure 4. Discoloration results of PVC samples at 180 °C.

Figure 5. DMA curves of PVC samples.
Therefore, the molecular volume of the plasticizer is another critical factor for effective plasticization. However, as proposed by the free volume theory, a plasticizer reduces dipolar interactions between the polymeric chains by increasing the free volume between the polymeric chains and thereby leading to the reduction of $T_g$. Therefore, the molecular volume of the plasticizer is another vital factor for decreasing the $T_g$ of the polymer matrix.

For the TA esters, the short alkyl chains in the plasticizer were not granted a large enough molecular volume of the plasticizer to effectively isolate the PVC chains, while the long alkyl chains did not have enough polar groups to interact with the polymeric chains. When the alkyl chains were too long, there were also strong intermolecular nonpolar interactions between plasticizer molecules, which also led to lower plasticizing efficiency compared with the pure PVC sample, the plasticized PVC samples were studied (Figure 8a). The weight loss in volatilization decreased according to PVC-C1 (1.55%) > PVC-C7 (0.88%) > PVC-C11 (0.40%).

These results indicated that the weight loss of PVC samples plasticized by DBTAE-Cn decreased gradually with the increase of the side alkyl chain length. Accordingly, the volatility and migration of the plasticizer may depend on its molecular weight, solubility, and structural features. Thus, the volatility and migration behaviors of the plasticized PVC samples were studied (Figure 8a). The weight loss in volatilization decreased according to PVC-C1 (1.55%) > PVC-C4 (1.38%) > PVC-C7 (0.88%) > PVC-C11 (0.40%).

### 2.4. Morphological Analysis

The miscibility of the synthesized plasticizers with PVC can also be observed by the microstructure of PVC materials. The microstructure of the fractured surfaces of the PVC blends was studied by scanning electron microscopy (SEM), and the images are shown in Figure 6. As shown in Figure 6a, the surface of PVC exhibited many agglomerates and showed a rough and irregular microstructure, which resulted from the strong intertwining of PVC chains.

With the plasticizer addition into PVC blends, the rough microstructure and agglomerates disappeared. PVC plasticized by DOP and DBTAE-Cn showed homogeneous and smooth surface microstructures, with no irregular holes and aggregates. This observation indicated the good compatibility between the plasticizer and the PVC matrix.

### 2.5. Mechanical Properties of PVC Samples

The plasticizing effects of DBTAE-Cn on PVC films were further evaluated with the tensile test. As shown in Figure 7 and Table 2, all the plasticized PVC samples displayed typical stress–strain curves characteristic of flexible PVC. As expected, compared with the pure PVC sample, the plasticized PVC samples had better elongation at break but lower tensile modulus, which indicated that DBTAE-Cn and DOP had an excellent plasticizing effect on PVC. The improved elongation at break can be attributed to the decreasing entanglements between the PVC chains after the addition of a plasticizer. The stiffness of PVC decreased with the addition of a plasticizer because the additive separated the long PVC chains.

At the same weight ratio of the plasticizer (30 phr), the elongation at break of PVC samples plasticized with DBTAE-Cn increased in the order PVC-C11 < PVC-C7 ≈ PVC-D < PVC-C1 < PVC-C4, which was similar to the trends in the DMA data. As mentioned above, DBTAE-C4 not only has more polar groups to ensure strong interaction with PVC chains but also has a large enough molecular volume to effectively isolate the PVC chains and reduce their entanglements. Thus, PVC-C4 was more flexible and stretchable.

### Table 2. Tensile Properties of PVC Samples

| samples | tensile strength (MPa) | tensile modulus (MPa) | elongation at break (%) |
|---------|-----------------------|-----------------------|------------------------|
| PVC     | 35.2 ± 0.9            | 1427.8 ± 34.0         | 25.0 ± 15.6            |
| PVC-D   | 30.1 ± 0.8            | 396.7 ± 16.5          | 272.2 ± 8.6            |
| PVC-C1  | 31.9 ± 0.6            | 402.6 ± 9.8           | 355.3 ± 7.8            |
| PVC-C4  | 36.4 ± 0.9            | 390.91 ± 20.4         | 358.2 ± 5.4            |
| PVC-C7  | 32.0 ± 0.7            | 635.0 ± 11.3          | 272.3 ± 8.9            |
| PVC-C11 | 33.7 ± 1.3            | 687.2 ± 14.6          | 263.2 ± 2.6            |

Figure 6. SEM images of fractured surfaces of PVC samples with different plasticizers.

Figure 7. Stress–strain curves of the pure and plasticized PVC films.
molecules themselves, which also led to a lower plasticizing intermolecular nonpolar interactions between plasticizer chains and instead favored the formation of strong groups to form interactions with the polar groups on the PVC chains resulted in a plasticizer that did not have enough polar.

The migration behavior of DBTAE-Cn and DOP was measured by the leaching test in distilled water and n-hexane, and the results are shown in Figure 8b. As expected, all of the plasticizers displayed higher weight losses in n-hexane than that in water, which could be attributed to these plasticizers being organic chemicals. It was worth noting that the weight loss in n-hexane increased gradually with the increase of the alkyl chain length in TA esters, which was opposite to the trend seen in the volatilization tests. This result could be explained by the fact that the nonpolar content of the plasticizer increased with the increasing alkyl chain length and decreased the overall polarity of the molecule. According to the principle of similitude, less polar molecules are more soluble in the nonpolar solvent, and therefore the solubility of the DBTAE-Cn esters in n-hexane increased with the increasing alkyl chain length. In addition, the weight losses of PVC-C1 (1.86%) and PVC-C4 (3.75%) in n-hexane were lower than that of PVC-D (8.45%), indicating that the esters DBTAE-C1 and DBTAE-C4 migrated less than DOP. Thus, DBTAE-C1 and DBTAE-C4 might be more suitable than DOP for use in PVC products that come into contact with the nonpolar solvents.

3. CONCLUSIONS
In summary, four TA esters (DBTAE-Cn) with different side alkyl chains were synthesized. The effect of varying side chain lengths in the molecule on the properties of their blends with PVC was investigated systematically. The results showed that there was a clear correlation between the structural features of the DBTAE-Cn esters and the properties of their blends with PVC. DMA and tensile results indicated that DBTAE-C4 showed the best plasticizing effect on soft PVC. However, the thermal stability of PVC samples improved and the volatility of plasticizers decreased, as the side chain length increased, which was related to the growing molecular weight. Finally, the leaching tests indicated that increasing the alkyl chain length in the esters was not conducive to improving the migration resistance of the plasticizer. Overall, the plasticizing performances of the newly synthesized DBTAE-C1 and DBTAE-C4 rivaled that of DOP, suggesting that they have the potential to replace DOP in soft PVC materials.

4. EXPERIMENTAL SECTION
4.1. Materials. TA, p-toluenesulfonic acid (p-TSA), DOP (AR), dichloromethane, triethylamine, tetrahydrofuran (THF), and butyl alcohol were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. and were used as received. Acetyl chloride (CH₃ COCl), valeryl chloride (CH₃ CH₂ CH₂ CH₂ COCl), n-capryl chloride [CH₃(CH₂)₉COCl], and lauroyl chloride [CH₃(CH₂)₁₁ COCl] were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. PVC (K value = 72−71, Mₗ = 83,000, and Mₘ = 210,000 g/mol) was acquired from Shanghai Aladdin Co., Ltd., China. All chemicals were used as received without further purification.

4.2. Synthesis of Dibutyl TA Esters (DBTAE). DBTAE was prepared using a similar method and the solvent was replaced with cyclohexane. In a three-neck round-bottomed flask equipped with a water-collecting Dean−Stark trap connected to a reflux condenser, TA (1 equiv) and butyl alcohol (5 equiv) were dissolved in cyclohexane under stirring, and p-TSA (0.1 equiv) was added. The reaction mixture was heated to 100 °C, and the reaction was monitored by thin-layer chromatography. After 6 h, the reaction was quenched with an aqueous solution of sodium bicarbonate, 100 mL of ethyl acetate (EA) was added, and the organic phase was washed with saturated NaCl aqueous (3 times) and then dried over anhydrous sodium sulfate. Finally, the solvent was removed under reduced pressure. The product was used without further purification. DBTAE was obtained in 91.0% yield as a clear colorless oil.

3H NMR (CDCl₃, 400 MHz): δ 0.95 (t, 6H, CH₃), 1.36−1.45 (m, 4H, CH₂), 1.64−1.71 (m, 4H, CH₂), 3.37−3.43 (m, 2H, OH), 4.21−4.31 (m, 4H, CH₂), and 4.54 (d, 2H, CH).

4.3. Plasticizer Synthesis. As shown in Scheme 1, the TA esters were prepared by a similar method.
4.3.1. DBTAE with the C1 Chain. In a 100 mL three-neck round-bottomed flask, DBTAE (1 equiv) was dissolved in 30 mL of CH₂Cl₂, and then, triethylamine (3 equiv) was added,
and the mixture was stirred for 20 min at 0 °C with an atmosphere of nitrogen. To the solution, the mixture of acetyl chloride (2.5 equiv) and CH₂Cl₂ (30 mL) was dropped using a syringe for 20 min. The reaction was further stirred for 3.5 h. The mixture was diluted by CH₂Cl₂ (100 mL) and washed with aqueous sodium hydroxide solution and brine. After being dried by anhydrous sodium sulfate, the solvent was removed with aqueous sodium hydroxide solution and brine. After being washed with distilled water and hexane at 30 °C for 60 min. One sample was tested three times, and the results were averaged.

The microstructure of PVC samples and compatibility of the PVC plasticizer were observed on fractured surfaces of PVC blends using a Regulus 8230 (Hitachi, Japan) SEM instrument. The fractured surfaces were obtained by freezing with liquid nitrogen and gold sputtering before observation.

Tensile tests were performed on the PVC samples according to GB/T 1040.1-2006 (China) on an Instron 5967 universal testing machine (USA). The cross-head speed was 100 mm/min. Each sample was tested three times, and the results were averaged.

The volatility of the synthesized TA esters and DOP was measured by putting plasticized PVC samples (20 mm × 20 mm × 0.5 mm) in an oven at 70 °C for 24 h and then cooling the films in a desiccator for 1 h. The volatility rate was calculated by weighing the sample before and after heating according to eq 1

\[
\text{volatility rate (\%) =} \frac{W_0 - W_f}{W_0} \times 100\% \quad (1)
\]

where \(W_0\) is the weight of the PVC sample before heating, and \(W_f\) is the weight of the PVC sample after heating.

The migration resistance of the plasticizers was studied by immersing PVC samples (20 mm × 20 mm × 0.5 mm) in distilled water and n-hexane at 30 °C. After 24 h, the PVC samples were wiped and then dried in an oven (30 °C) for 24 h. The weight was recorded before and after the migration test. The weight loss of each PVC sample was calculated according to eq 1, and then, the data were normalized by the pure PVC weight loss to obtain the migration degree of the plasticizer.

Table 3. Formulation of PVC Samples*  

| PVC films | PVC (phr) | DBTAE-C1 (phr) | DBTAE-C4 (phr) | DBTAE-C7 (phr) | DBTAE-C11 (phr) | DOP (phr) |
|-----------|-----------|----------------|----------------|----------------|----------------|-----------|
| PVC-C1    | 100       | 30             | /              | /              | /              | /         |
| PVC-C4    | 100       | /              | 30             | /              | /              | /         |
| PVC-C7    | 100       | /              | /              | 30             | /              | /         |
| PVC-C11   | 100       | /              | /              | /              | 30             | /         |
| PVC-D     | 100       | /              | /              | /              | /              | 30        |
| PVC       | 100       | /              | /              | /              | /              | /         |

*/* means none.

[1] 4.3.3. DBTAE with the C7 Chain (DBTAE-C7). Yield: 96.3%, ¹H NMR (CDCl₃, 400 MHz): δ 0.86–0.93 (m, 12H, CH₂), 1.25–1.37 (m, 20H, CH₂), 1.55–1.65 (m, 8H, CH₂), 2.32–2.46 (m, 4H, CH₂), 4.09–4.19 (m, 4H, CH₂), and 5.68 (s, 2H, CH).

[2] 4.4. Preparation of Soft PVC Films. As we know, PVC materials can be classified as hard PVC (0–30 phr), soft PVC (30–70 phr), and paste PVC (>80 phr) according to the amount of the plasticizer. Among them, soft PVC was the most widely used. To investigate the plasticizing effect of synthesized esters in soft PVC, PVC and the plasticizer were dissolved in THF to obtain a homogenous solution (100 mg/mL) and then poured into a glass Petri dish (10 cm). As shown in Table 3, plasticizers were added to the solution such that there were 30 parts of the plasticizer per one hundred parts of the resin (phr). The solvent evaporated at room temperature for 48 h, and then, the film was dried at 50 °C for 24 h to remove any residual THF.

[3] 4.5. Characterization. The chemical structures of the compounds were characterized using ¹H NMR spectroscopy and FTIR spectroscopy. The ¹H NMR spectra were recorded on a Bruker Avance spectrometer (400 MHz) using CDCl₃ as the solvent. The FTIR spectra were collected by using a Vertex 80 FT-IR. Data were collected using 32 scans from 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹.

TGA was conducted on a TGA-5500 instrument to investigate the effects of the side alkyl chain on the thermal stability of DBTAE-Cn and PVC samples plasticized by DBTAE-Cn. Each sample was measured from 35 to 800 °C with a heating rate of 10 °C/min in the N₂ atmosphere. The thermal stability of the PVC samples was also measured by a discoloration test in an oven at 180 °C for 60 min. One sample was taken out every 10 min.

DMA measurements of the soft PVC samples were carried out on a DMA Q800 (TA Instruments, US) at a fixed frequency of 1 Hz in tension mode to evaluate the plasticizing effect of the TA esters. The soft PVC samples (30 × 6 × 0.5 mm) were scanned from −50 to 150 °C with a heating rate of 5 °C/min.

The microstructure of PVC samples and compatibility of the PVC plasticizer were observed on fractured surfaces of PVC blends using a Regulus 8230 (Hitachi, Japan) SEM instrument. The fractured surfaces were obtained by freezing with liquid nitrogen and gold sputtering before observation.
Author Contributions
The manuscript was written with the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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