Synthesis of Bis(2,4-diphenylbutyl) Phthalate and Its Application as a Plasticizer for Poly(vinyl Chloride) from Waste Polystyrene

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Synopsis

Bis(2,4-diphenylbutyl) phthalate, a plasticizer for poly(vinyl chloride) (PVC), was synthesized from 2,4-diphenyl-1-butene obtained by a thermal decomposition under reduced pressure of waste polystyrene. The heat stability of bis(2,4-diphenylbutyl) phthalate was determined by thermogravimetric analysis and compared with typical plasticizers. It was recognized that bis(2,4-diphenylbutyl) phthalate showed high heat resistant. A test sheet of plasticized PVC with bis(2,4-diphenylbutyl) phthalate and bis(2-ethylhexyl) phthalate was prepared. The test sheet was used for determination of the plasticizing performance of bis(2,4-diphenylbutyl) phthalate. Although the effect of bis(2,4-diphenylbutyl) phthalate imparting flexibility to PVC is poorer than that of bis(2-ethylhexyl) phthalate, the former phthalate is well compatible with PVC and exceedingly heat-resistant.

INTRODUCTION

The authors studied the effective reuse of waste plastics considering energy and resources conservations. A part of the study was previously reported.[1-3] On the other hand, the authors studied[4-6] the heat stability and its chemical structures on phthalic esters, which were stable plasticizers for poly(vinyl chloride) (PVC), and it had been proved that the heat stability of phthalic ester was caused mainly by the configuration of β-hydrogen atom in cis elimination reaction.[7] A suitable compound which controlled the structure on side chain are found in a thermal decomposition product of waste polystyrene.

This paper reports the synthesis of bis(2,4-diphenylbutyl) phthalate, which expects the high heat-resistant plasticizer for PVC to make the best of thermal decomposition products of waste polystyrene. From the test results of the heat stability and of plasticizing performance, it was found that the heat resistance of it is superior to those of the conventional plasticizers.

EXPERIMENTAL

Sample and Reagent. Commercial reagents of dibutyl phthalate, bis(2-ethylhexyl) phthalate and dioctyl phthalate were used for the experiment, but bis(2,4-diphenylbutyl) phthalate was synthesized according to Scheme 1.

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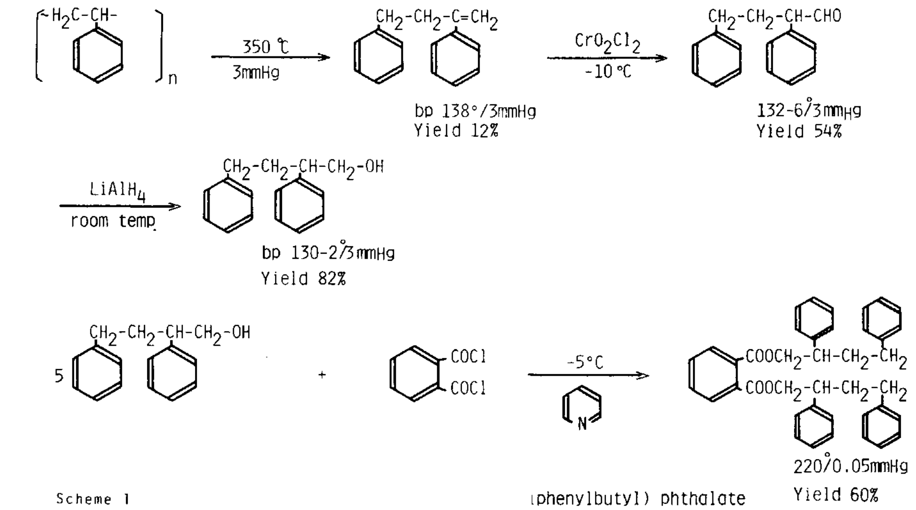

Scheme 1. Synthesis of bis(2,4-diphenylbutyl) phthalate.

Pelletized polystyrene ($\overline{M}_n = 8.32 \times 10^4$, $\overline{M}_w = 2.05 \times 10^5$, and $\overline{M}_w/\overline{M}_n = 2.47$) was used. Chromyl chloride was synthesized according to the usual procedure,[8] and the fraction of 62–64°C of the boiling point/120 mm Hg was used. Commercial products of phthaloyl dichloride and lithium aluminum hydride were used. The raw material, 2,4-diphenyl-1-butene, was obtained from polystyrene according to the method shown in Figure 1.

Analytical Apparatus. The following apparatus was used for identification of the compounds recovered from polystyrene and for qualitative analysis of the compounds on the synthesis process and of the thermal decomposition products of bis(2,4-diphenylbutyl) phthalate: NMR: Jeol FX-100 (^{1}H-NMR and ^{13}C-NMR), high-resolution-MS: Hitachi MRU-7M + Hitac 10 II, GC: Shimadzu GC-4BMF + C-R1A, HPLC: Waters 201, IR: Shimadzu

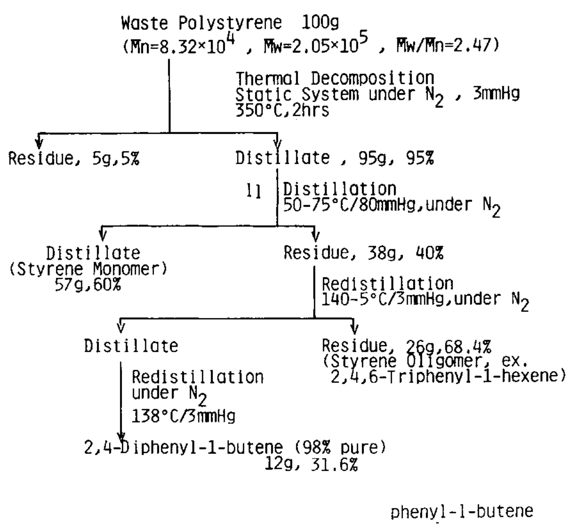

Fig. 1. A purification process of 2,4-diphenyl-1-butene from a waste polystrene.

IR-420, and thermal analyzer: Shimadzu DT20B + TG20 or EGC20 for determination of the heat stability of bis(2,4-diphenylbutyl) phthalate.

The equipment used for milling of plasticized PVC, preparing its test sheet and determining the performance[9] was the one provided by JIS or the standards conformable to it.

Analysis. The procedure of high performance liquid chromatography (HPLC) used for analyzing the thermal decomposition products of bis(2,4-diphenylbutyl) phthalate is as follows: column = 3.9 mm I.D. and 30 cm long, packed with μ Bondapak C_{18}, mobil phase = $CH_3CN:H_2O$ = 75:25 vol/vol whereto 3 vol/vol % of CH_3COOH is added, flow rate = 1 mL/min. The details of the thermal analyzer was described in the other report.[10]

Preparation of Plasticized Poly(vinyl Chloride) Sheets. The test sheets of plasticized PVC were prepared by mixing bis(2-ethylhexyl) phthalate and PVC stabilizer. The mixing method in detail was as follows: The number average degree of PVC used in the present work was 1050, and its form was powderlike. Also, AC-169 (2.5 phr), which is a one-pack type of the Ba–Zn system, bis(2-ethylhexyl) phthalate (10 or 20 phr), and bis(2,4-diphenylbutyl) phthalate (10 phr) were used as a plasticizer for mixing.

This mixture was brended at room temperature and then milled at 175°C for 5 min. Processing properties shown in Table I were measured at this time. After the plasticized PVC was preheated at 170°C for 2 min, it was pressed at 52 kg/cm^2, 170°C for 5 min.

The sheets pressed here were modified to the appropriate form and thickness for each test at the end. Their results were shown in Tables I–III and Figure 4.

RESULTS AND DISCUSSION

Synthesis of Bis(2,4-diphenylbutyl) Phthalate

The phthalic ester is synthesized from 2,4-diphenyl-1-butene recovered 12% from the waste polystyrene by thermal decomposition under reduced pressure. The reaction scheme is shown in Scheme 1. It is indispensable for the synthesis of phthalic esters to obtain the compound having a phenyl group on the β-carbon atom in the side chain since 2,4-diphenyl-1-butene was easily disconnected at the allyl position.[3] Since the disconnection of the main chain was predominant in the general oxidation process by such an oxidizing agent as potassium permanganate, 2,4-diphenyl-1-butanol shown in Scheme 1 was not produced, but the oxidation product was benzoic acid. In a low temperature (−5°C or lower), however, the selective oxidation by the electrophilic addition of chromyl chloride[11] to α-olefin gave a high yield of 2,4-diphenylbutanal, which was reduced by lithium aluminum hydride to get 2,4-diphenyl-1-butanol, and phthaloyl dichloride was made to obtain bis(2,4-diphenylbutyl) phthalate according to the usual procedure.[12]

Analysis of Thermal Decomposition Products

The thermal decomposition of bis(2,4-diphenylbutyl) phthalate was made at 400°C for 1 h under nitrogen atmosphere in a static system. The analytical result of the decomposition products by HPLC is shown in Figure 2.

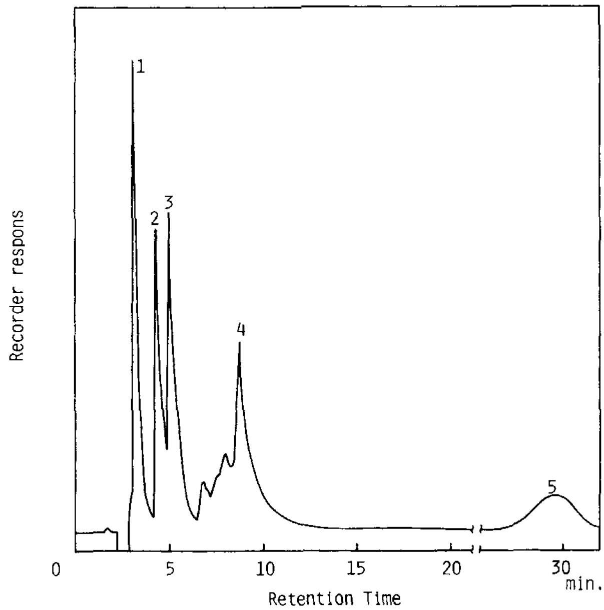

Fig. 2. HPLC chromatogram of the thermal decomposition products of bis(2,4-diphenylbutyl) phthalate apparatus, Waters 201, Column μ Bondapak C_{18}, 30 cm × 3.9 mm I.D. mobile phase, CH_3CN:H_2O = 75:25 vol/vol + 3% CH_3COOH flow rate 1.0 mL/min detector, RI peak: (1) phthalic anhydride; (2) 2,4-diphenyl-1-butanol; (3) 2,4-diphenylbutyl hydrogen phthalate; (4) 2,4-diphenyl-1-butene; (5) unreacted bis(2,4-diphenylbutyl) phthalate.

As shown in Figure 2, 2,4-diphenyl-1-butene, 2,4-diphenyl-1-butanol, phthalic anhydride, 2,4-diphenylbutyl hydrogen phthalate, and the unreacted bis(2,4-diphenylbutyl) phthalate were identified. It was understood from these decomposition products that the normal decomposition of bis(2,4-diphenylbutyl) phthalate was caused by cis elimination[7] in the same way as that of the other phthalic esters.

Heat Stability of bis(2,4-diphenylbutyl) Phthalate Alone

The heat stability of bis(2,4-diphenylbutyl) phthalate was determined by thermogravimetric analysis. The result is shown in Figure 3.

In order to compare it with those of typical phthalic esters, the determined results of dibutyl phthalate, bis(2-ethylhexyl) phthalate and dioctyl phthalate representative of phthalic esters are shown in Figure 3. Figure 3 reveals that there is a good relationship between the reaction temperature and the weight loss of each phthalic ester. A clear endothermic peak on the diagram by differential thermal analysis is observed, which is not shown in Figure 3. It was obtained from the point showing the respective percent rates (3% and 5%) of weight loss to 100% of weight loss represented by the distance between the base lines of pre- and post-test on the thermogram. Figure 3 reveals that the temperature of 3% weight loss of bis(2,4-diphenylbutyl) phthalate are 141°C higher than that of dibutyl phthalate having no branch. This shows the high heat resistance of the former, which is caused by four bulky phenyl groups introduced into butyl side chain as branches. These

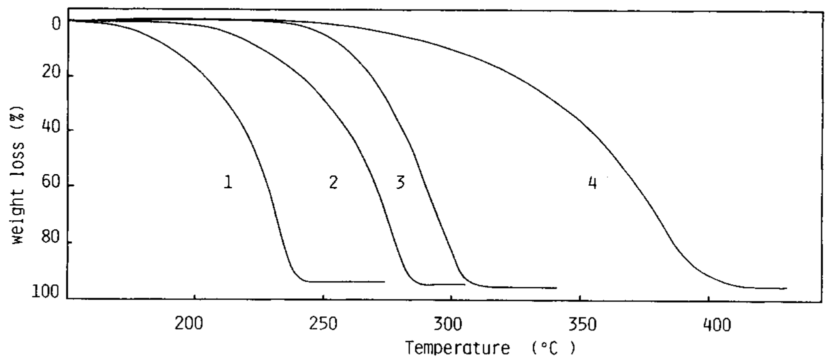

Fig. 3. Thermogravimetric analysis of phthalic esters Apparatus, Shimadzu DT 20B + TG 20, programming rate 5°C min, nitrogen flow rate 15 mL/min, chart speed 10 mm/min, sample weight 0.8 mg: (1) dibutyl phthalate; (2) bis(2-ethylhexyl) phthalate; (3) dioctyl phthalate; (4) bis(2,4-diphenylbutyl) phthalate.

phenyl groups repulse each other in the same molecule,[13] so the side chains are much more restrained from their free rotation than the general linear phthalic esters. As a result, ester bonding estimated from cis elimination[7] and the formation of six-membered-ring transition state[14] between alkyl side chains are hindered.

Test of Plasticizing Performance for Poly(vinyl Chloride)

Plasticizing performance was performed according to the method described in the experimental section.

Table I shows the compatibility determined in milling of PVC with bis(2,4-diphenylbutyl) phthalate and the bleeding property of its molding. The values listed in Table I are the relative values to the standards on the mixture of PVC and 20 phr of bis(2-ethylhexyl) phthalate of a typical plasticizer. The compatibility of bis(2,4-diphenylbutyl) phthalate was regarded as the same as that of bis(2-ethylhexyl) phthalate.

Table II lists the properties of PVC plasticized with bis(2,4-diphenylbutyl) phthalate determined using plasticized PVC sheet.

TABLE I
Compatibility for Poly(vinyl Chloride)[a]

Test items \ Added plasticizer	Bis(2,4-diphenylbutyl) phthalate 10 phr[b] + bis(2-ethylhexyl) phthalate 10 phr[b]	Bis(2-ethylhexyl) phthalate 20 phr[b]
1. Processing:		
Roll plate out	1	1
Gelation	1	1
Releasability	1	1
Odor	1	1
2. Bleeding		
(70°C, 20 days, wet)	1	1

[a] Formation: poly(vinyl chloride) (p = 1050) 100, AC-169 (as a stabilizer for PVC) 2.5 phr, plasticizer 20 phr.
[b] phr = per hundred resin.

TABLE II
Physical Properties of Plasticized PVC Sheet[a]

Test items \ Added plasticizer	Bis(2,4-diphenylbutyl) phthalate 10 phr + Bis(2-ethylhexyl) phthalate 10 phr	Bis(2-ethylhexyl) phthalate 20 phr
1. Flex temperature (T_f)	41.5°C	27.0°C
2. Electric volume resistance (VR)	$6.1 \times 10^{15}\ \Omega \cdot cm$	$2.7 \times 10^{15}\ \Omega \cdot cm$
3. Heat aging: volatile loss	−1.9%	−3.9%
4. Oil resistance extraction	+0.1%	+0.1%
5. Water resistance:		
(a) water absorption	+1.4%	+1.2%
(b) extraction	−0.2%	−0.3%

[a] Formation: poly(vinyl chloride) (p = 1050) 100, AC-169 (as a stabilizer for PVC) 2.5 phr, plasticizer 20 phr. Test method of (1) JIS K-6745, (2) JIS K-6723, (3) JIS K-6301, (4) JIS K-6723.

The test result of PVC plasticized with bis(2-ethylhexyl) phthalate is listed in Table II for comparison. Table II reveals that electric insulation properties of PVC plasticized with bis(2,4-diphenylbutyl) phthalate are higher, and its flexibility imparting effect is poorer by about 40% than the respective values of PVC plasticized with bis(2-ethylhexyl) phthalate, while loss by volatilization of the former in the heat aging test is as low as 1.9% which means little volatility.

The tensile test was made to determine the elongation of PVC plasticized

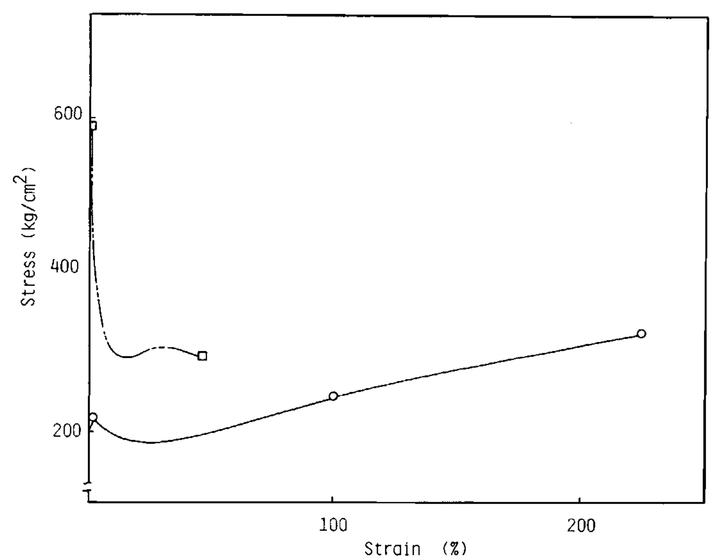

Fig. 4. Tensile test of plasticized poly(vinyl chloride) sheets, JIS K-6723 dumbbell No. 1, test temperature 30°C, tensile speed 50 mm/min: (□) with bis(2,4-diphenylbutyl) phthalate 10 per hundred resin (phr) + bis(2-ethylhexyl) phthalate 10-phr plasticized PVC sheet, tensile strength 294 kg/cm², elongation 48% yield point 592 kg/cm²; (○) with bis(2-ethylhexyl) phthalate 20-phr plasticized PVC sheet, 100% modulus 245 kg/cm², tensile strength 328 kg/cm², elongation 224 kg/cm², yield point 215 kg/cm².

TABLE III
Tensile Test of Plasticized PVC Sheets after (1) Heat Aging, (2) Oil Resistance, and (3) Water Resistance[a]

Test items \ Added plasticizers	Bis(2,4-diphenylbutyl) phthalate 10 phr + Bis(2-ethylhexyl) phthalate 10 phr	Bis(2-ethylhexyl) phthalate 20 phr
1. (a) 100% Modulus (kg/cm^2)	—	293
(b) Residual tensile strength (%)[b]	109	103
(c) Residual elongation (%)[b]	60	78
(d) Yield point (kg/cm^2)	604	374
2. (a) 100% Modulus (kg/cm^2)	313	250
(b) Residual tensile strength (%)[b]	102	103
(c) Residual elongation (%)[b]	242	102
(d) Yield point (kg/cm^2)	542	197
3. (a) 100% Modulus (kg/cm^2)	—	247
(b) Residual tensile strength (%)[b]	96	101
(c) Residual elongation (%)[b]	129	102
(d) Yield point (kg/cm^2)	532	240

[a] Formation: poly(vinyl chloride) (p = 1050) 100, AC-169 (as a stabilizer for PVC) 2.5 phr, plasticizer 20 phr. Test method of JIS K-6723 dumbbell No. 1, temperature 30°C, tensile speed 50 mm/min.

[b] Each values indicate the ratio of original values as shown in Figure 4.

with bis(2,4-diphenylbutyl) phthalate. The test results are shown in Figure 4, and the detailed data are listed in Table III.

The sign—in Table III expresses the breaking of the test piece during the test. Figure 4 and Table III reveal that the tensile strength and the elongation of PVC plasticized with bis(2,4-diphenylbutyl) phthalate are smaller than those of PVC plasticized with bis(2-ethylhexyl) phthalate.

CONCLUSIONS

Considering resources conservation, bis(2,4-diphenylbutyl) phthalate was synthesized from 2,4-diphenyl-1-butene of a thermal decomposition product of polystyrene. The heat stability of bis(2,4-diphenylbutyl) phthalate was regarded as high among phthalic esters. Test pieces of plasticized PVC were prepared to investigate the plasticizing property for PVC. From the performance test of plasticized PVC, the effect of bis(2,4-diphenylbutyl) phthalate imparting flexibility to PVC was smaller than that of bis(2-ethylhexyl) phthalate. The high heat resistance of bis(2,4-diphenylbutyl) phthalate in the presence of PVC, however, had the same trend as that of the plasticizer alone.

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