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The synthesis and the structural analysis of advanced PVC plasticizer, 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate

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Abstract **:** New PVC plasticizer, 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate was synthesized via simple esterification with butyric acid and Texanol(a trademark of Eastman Chemicals), the mixture of 2,2,4-trimethyl-1,3-pentanediol-3-isobutyrate and 2,2,4-trimethyl-1,3-pentanediol-1-isobutyrate. The analysis of ^{1}H-1D, ^{13}C-1D NMR and HMBC spectra identified internal-ester-transfer of 2,2,4-trimethyl-1,3-pentanediol-1-isobutyrate during the reaction. 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate gave better properties in PVC than 2,2,4-trimethyl-1,3-pentanediol diisobutyrate(TXIB, a trademark of Eastman Chemicals) such as lower viscosity, higher tensile strength and better elongation. In particular, remarkably reduced migration compared with TXIB suggested a reduced emission of VOC(volatile organic compound) from PVC.
Keyword : PVC plasticizer, NMR, HMBC, VOC(volatile organic compound)

INTRODUCTION

Polyvinyl chloride is used in a variety of application. Examples of the major uses of plasticised polyvinyl chloride include wire and cable coating, other electrical applications such as plugs, film, foil and sheeting, flooring, wall covering, roofing and membranes.[1] 2,2,4-trimethyl-1,3,-pentanediol diisobutyrate(TXIB, a trademark of Eastman Chemicals) is marketed as a primary or secondary plasticiser used in manufacturing toys, sheet vinyl flooring, and other high-quality vinyl products.[2]

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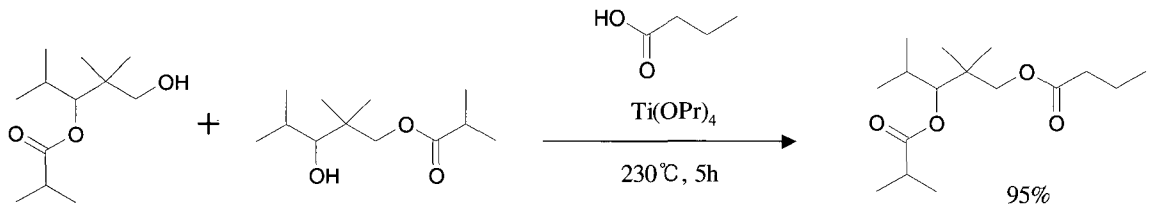
As a large amount of TXIB is used in many PVC products, it is also detected in the water or from the air. For example, TXIB was observed in the water of the Delaware River, USA[3] and the Lipper River, Germany[4]. TXIB was also emitted from a carpet manufactured by Vorwerk & Co. (Hameln, Germany), PVC flooring manufactured by Sommer SA (Wiltz, Luxembourg) and an acrylic latex paint manufactured by Tikkurila OY (Vanta, Finland).[5] In 1997, Wieslander et al. reported that the prevalence of asthma was significantly elevated among subjects living in newly painted dwellings and 57-60% of volatile organic compounds in the dwellings was TXIB.[6] Therefore, it is important to reduce the migration of plasticiser from PVC as well as to improve the properties.

Herein, we describe the synthesis of the modified plasticiser, 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate and its structural analysis using ^{1}H-1D, ^{13}C-1D NMR and HMBC spectra. We also present the improved properties of 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate as a plasticiser.

RESULTS AND DISCUSSION

Synthesis of 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate

The mixture of butyric acid and 2,2,4-trimethyl-1,3-pentanediol isobutyrate (Texanol., a trademark of Eastman Chemicals) with $Ti(OiPr)_4$ was stirred for 5 hours at 230℃, as depicted in Scheme 1. H_2O, by-product was continuously extracted through the distillation column during the reaction.

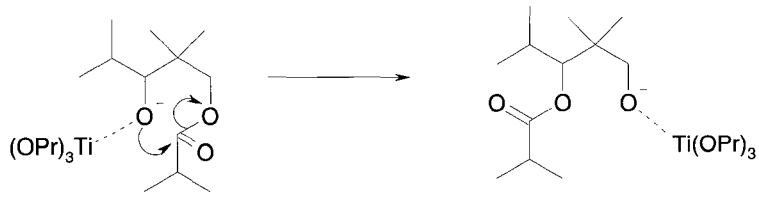


1a (45%) **1b** (55%) **2**

SCHEME 1. Synthesis of 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate

According to ^{1}H NMR and HMBC spectra, Eastman Texanol, the reagent, was not a single compound but the mixture of 2,2,4-trimethyl-1,3-pentanediol-3-isobutyrate(45%), **1a** and 2,2,4-trimethyl-1,3-pentanediol-1-isobutyrate(55%), **1b**. It was also confirmed with GC and GC-MS. However, **1b** was transferred to **1a** during esterification and final product was 95% of 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate, **2**.

The reactivity of alcohols and carboxylic acids toward esterification primarily depends on the steric hindrance of both the alcohol and the carboxylic acid. Thus, esterification with the primary alcohol is faster than the secondary alcohol.[7] According to the structure of **1b**, the stabilized O^- by Titanium can easily attack carboxylic carbon to transfer isobutyrate from 1 to 3 position of 2,2,4-trimethyl-1,3-pentanediol.



Structural analysis of compound 2

The structure of **2** was identified by ^{1}H-1D, ^{13}C-1D NMR and HMBC using Varian AS500 spectrometer. ^{1}H NMR of **2** showed that butyrate and isobutyrate was 1:1. ^{13}C NMR and HMBC experiment were performed to obtain the information of connectivity between 2,2,4-trimethyl-1,3-pentanediol and each of butyrates. ^{13}C NMR of TXIB and 2,2,4-trimethyl-1,3-pentanediol-dibutyrate was compared with ^{13}C NMR of **2** to confirm the frequencies of 2 different carboxylic carbon, which were 173ppm from butyrate and 176ppm from isobutyrate. The result was shown in Figure 1. HMBC clearly showed that isobutyrate was connected on 3 position and butyrate was connected on 1 position of 2,2,4-trimethyl-1,3-pentanediol through long-range C-H coupling as described in Figure 2. Based on those information, Figure 3 gave complete assignment of ^{1}H NMR spectrum of **2**.

The improved properties of compound 2 as a plasticiser

Four different PVC samples were produced to compare the performance of

plasticisers. The plasticisers of PVC samples were composed of 80 phr(parts per hundred resin) of DOP and 20 phr of the mixture with 4 different composition of TXIB, **2**, and 2,2,4-

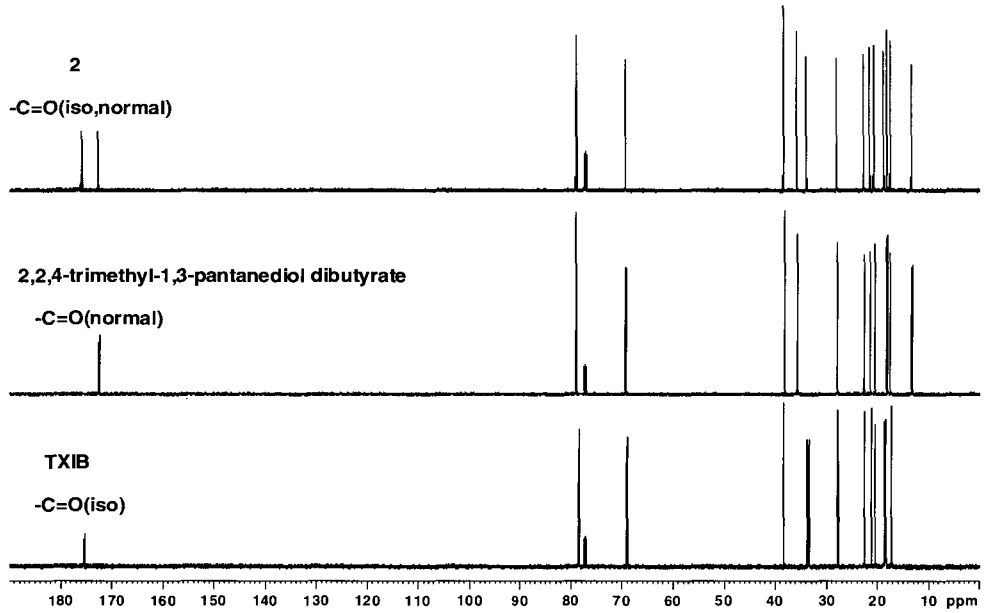


Fig. 1. ^{13}C spectrum of compound 2, 2,2,4-trimethyl-1,3-pentanediol-dibutyrate and TXIB

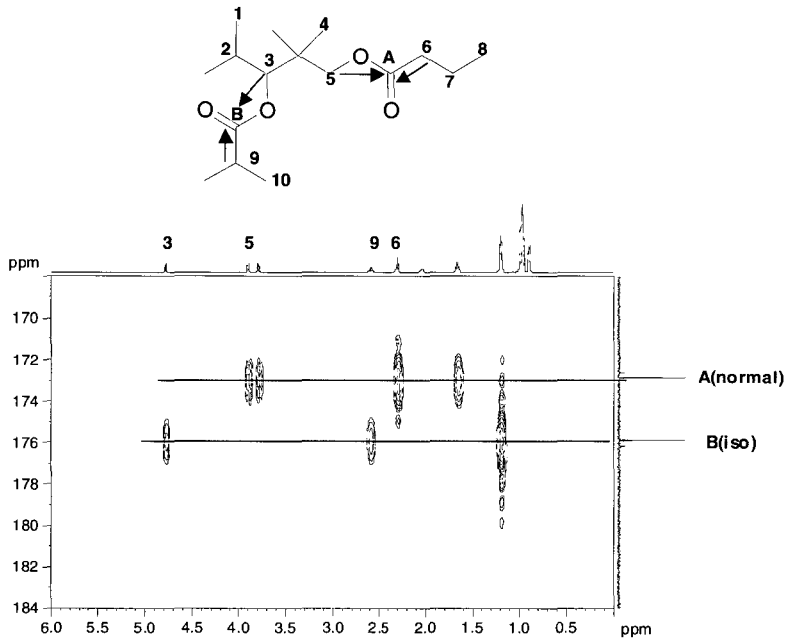


Fig. 2. HMBC spectrum of compound 2.

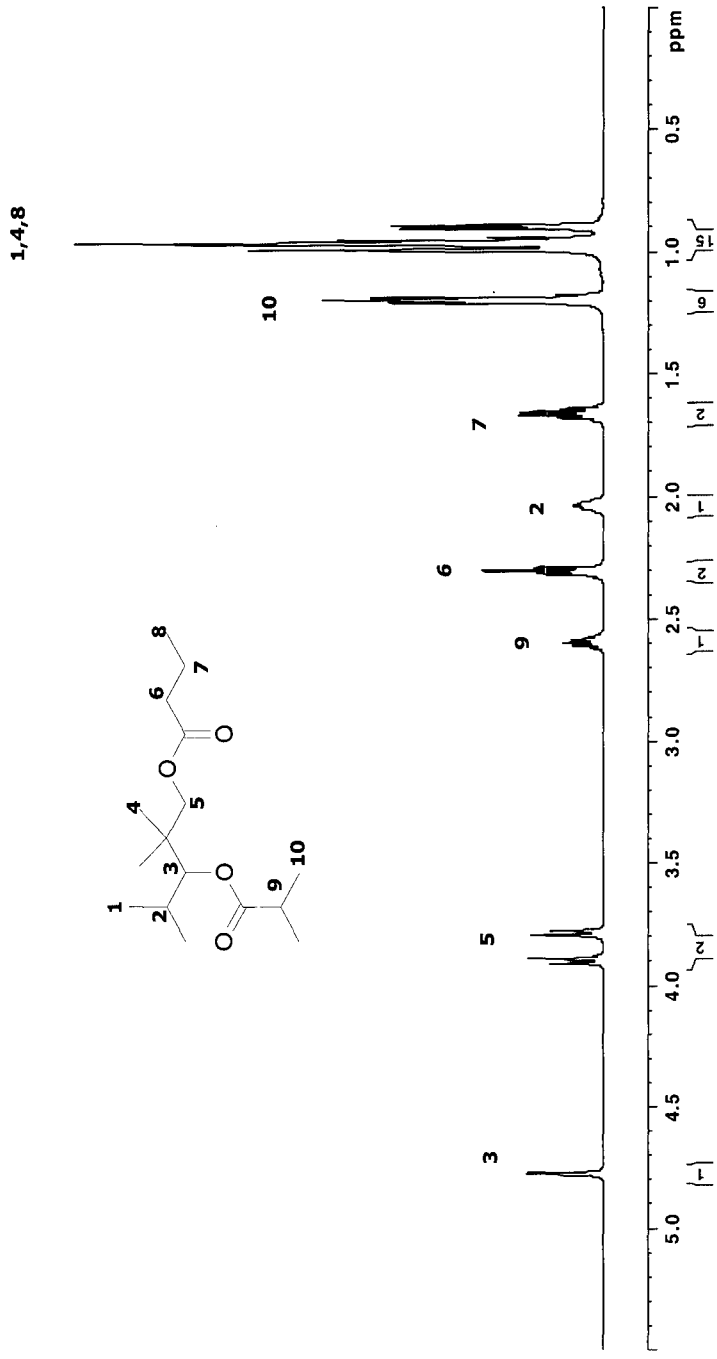


Fig. 3. Complete assignment of ^{1}H spectrum for compound 2.

trimethyl-1,3-pentanediol-dibutyrate. The test results were listed in Table 1.

Adding the mixture of TXIB, **2**, and 2,2,4-trimethyl-1,3-pentanediol-dibutyrate to PVC, sample A and C, gave equal or lower viscosity than only TXIB, sample D, which improves handling characteristics, making pumping and pouring easier. Sample B and C also had higher tensile strength and better elongation than sample D. Especially, the migration of plasticisers in sample A, B and C was decreased to 65-80% compared with Sample D, which was expected to reduce the emission of VOC from PVC products.

Table 1. Performance of plasticiser blends in PVC plastisols.

Formulation		Sample A	Sample B	Sample C	Sample D
PVC[a], phr		100	100	100	100
DOP[b], phr		80	80	80	80
2[c], phr		18	17	17	-
TXIB[d], phr		-	2	1	20
TXNNB[e], phr		2	1	2	-
stabilizer[f], phr		2	2	2	2
ESO[g], phr		1.5	1.5	1.5	1.5
*Tensile strength, kg/cm^2		115	126	123	119
*Ultimate elongation, %		434	470	464	432
**Viscosity(55℃), Poises	1 day	54	71	49	54
after aging :	3 days	106	126	88	104
***Migration %		0.401	0.501	0.482	0.617

* Tensile strength and ultimate elongation were measured according to ASTM D412 procedure

** Viscosity was measured by Brookfield viscometer with 5 shear rate(γ)

*** Migration test – Sample films(3×3cm) of 0.3mm dry thickness were inserted in between polystyrene sheets and baked for 48 hours at 70℃

[a] Polyvinylchloride available as LP170G from LG Chem, Ltd.

[b] Di-20ethylhexylphthalate available as Lgflex DOP from LG Chem, Ltd.

[c] 2,2,4-trimethyl-1,3-pantanediol-1-butyrate-3-isobutyrate

[d] 2,2,4-trimethyl-1,3-pantanediol diisobutyrate

[e] 2,2,4-trimethyl-1,3-pantanediol dibutyrate

[f] calcium/zinc stabilizer available as CZ-200 from Songwon Corporation

[g] Epoxidized soybean oil available as DSO from Songwon Corporation

CONCLUSIONS

We synthesized new PVC plasticizer, 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate via simple esterification with butyric acid and the mixture of 2,2,4-trimethyl-1,3-pentanediol-3-isobutyrate(45%), and 2,2,4-trimethyl-1,3-pentanediol-1-isobutyrate(55%). The internal-ester-transfer of 2,2,4-trimethyl-1,3-pentanediol-1-isobutyrate during the reaction produced 95% yield of the final compound, which was thoroughly analyzed by ^{1}H-1D, ^{13}C-1D NMR and HMBC spectra. We confirmed that 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate gave better properties in PVC such as lower viscosity, higher tensile strength and better elongation than TXIB. Especially, the migration of 2,2,4-trimethyl-1,3-pentanediol-1-butyrate-3-isobutyrate in PVC was decreased to 65-80% compared with TXIB.

REFERENCES

1. Ko D, Park K, Lee S, Moon J, Eom S, Rew D, KR-10-2005-0063752
2. Eastman TXIB Plasticizer, Eastman Chemicals Publication no. L-151k (1998).
3. Sheldon L, Hites R, *Environ, Sci. Technol.* **13**: 574 (1979).
4. Dsilowitzky L, Schwarzbauer J, Kronimus A, Littke R, *Chemosphere*, **10**, 1275 (2004).
5. De Bortoli M, Kephalopoulos S, Kirchner S, Schauenburg H, Vissers H, *Indoor air*, **9**, 103 (1999).
6. Wieslander G, Norback D, Bjornsson E, Janson C, Boman G, *Int. Arch. Occup. Environ. Health* , **69,** 115 (1997).
7. Hoydonckx H, De Vos D, Chavan S, Jacobs P, *Topics in Catalysis,* **27**,83 (2004).