Anomalous Melt Condensation Behavior of Pure Isomers of Protocatechuic Acid Derivatives

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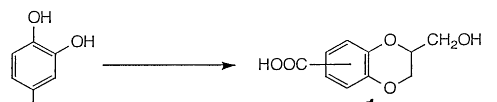
Separation of a mixture of regio isomers of 6- and 7-carboxy-2-hydroxymethyl-1,4-benzodioxane (**1**) was successfully carried out by the fractional crystallization of their acetyl derivatives. Pure **1a** (or **1b**) gave an infusible product upon heating at 280 °C for 90 (or 30) min under reduced pressure, while a mixture of the regio isomers **1a** and **1b** polymerized to yield a high-molecular-weight spinnable polyester under the same conditions.

In previous papers, it has been reported that the reaction of protocatechuic acid with epichlorohydrin in a basic medium afforded a mixture of regio-isomer 6- and 7-carboxy-2-hydroxymethyl-1,4-benzodioxane (**1a** and **1b**) [1,2] and that the regio isomer mixture was converted into a high-molecular-weight spinnable polyester by thermal polycondensation. Properties of the polyester thus obtained should be influenced by the regio isomer ratio in the monomer (**1a**/**1b**), which is greatly dependent on preparation conditions of **1**. However, complete separation and characterization of the two isomers has not been still achieved so far. Present study was undertaken to separate a regio isomer mixture into 6- and 7-carboxy derivatives **1a** and **1b**, and then to make clear the condensation behavior of each of the pure isomers.



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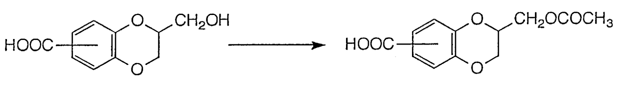

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Protocatechuic acid derivative **1** was conveniently prepared by the reaction of protocatechuic acid or its ester with epichlorohydrin. Distillation under reduced pressure of the ester was needed in order to obtain rather pure regio isomer mixture of **1a** and **1b**. Separation of the mixture into each of pure **1a** and pure **1b** was successfully carried out by fractional crystallization of their acetyl derivatives **2a** and **2b**. An acetylated mixture was prepared by refluxing a mixture of **1a** and **1b** (10.47 g, 0.05 mol) in large excess acetic anhydride for 4 h. The product was dissolved in toluene and separated into three fractions by fractional crystallization. The isomer ratio was greatly dependent on the starting reactants and the reaction conditions. For example, a typical mixture yield of the first fraction was 3.57 g (mp 166-168 °C), the second, 4.93 g (mp 155-160 °C) and the last, 4.06 g (mp 120.5-122 °C). The crystal structure of the first fraction was analyzed by X-ray analysis.[3] The structural determination revealed that the crystal is 6-carboxy isomer **2a** (Figure 1.). The first and last fractions of completely separated isomers were saponified with a boiling aqueous sodium hydroxide solution and recrystallized from water to give pure **1a** (200-201 °C)and **1b** (182-185 °C), respectively.[4]

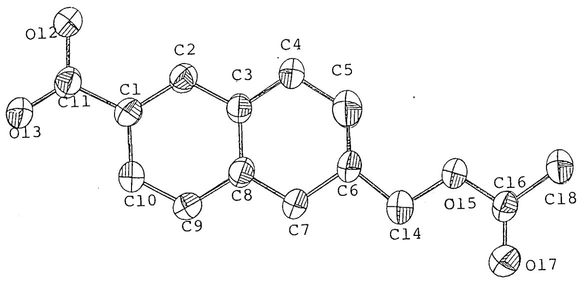


Figure 1. Crystal structure of **2a**.

Thermal condensation at 280 °C under reduced pressure gave any polymer neither from pure **1a** nor pure **1b**, but gave infusible crystalline product (**3a** and **3b**), having a very high melting point (>350 °C), from **1a** and **1b**, respectively, within a short period (30-90 min). IR spectra of products **3a** and **3b** were very similar to each other and to that of the expected condensation polymer, in which a strong new absorption of a ester group (**3a**:1719 cm^{-1} and **3b**:1713 cm^{-1}) was observed whereas two absorptions of hydroxy and carboxy groups (**1a**:3328 and 1685 cm^{-1}, and **1b**:3345 and 1685 cm^{-1}) completely disappeared . In contrast to the formation of an amorphous linear polymer from a regio isomer mixture, condensation products **3a** and **3b** were highly crystalline, showing several sharp X-ray diffraction peaks. The results suggest that the products are not of high polymers but of low-molecular-weight compounds.

In order to estimate the molecular weight of the infusible crystalline products, LI mass spectroscopic analyses were performed; these spectra definitely indicated that each of **3a** and **3b** mainly consisted of a cyclic dimer (MW=384), with a small amount of cyclic oligomers and a much smaller amount of acyclic oligomers, as is illustrated for the products from **1a** in Figure 2A. Since appreciable reaction did not proceed by thermal condensation below their melting point of each of **1a** and **1b**, their topochemical processes to **3a** and **3b** are not plausible. Although any reasonable explanation can not be proposed, such a highly selective dimer formation in the melting state is particularly interesting .

Thermal polycondensation of each of the two isomers of acetyl derivatives **2a** and **2b** was also carried out (280 °C, 8-9 h, under reduced pressure). The IR spectrum of the product from **2a** or **2b** showed that it was a condensation product. In contrast to the cases of **1a** and **1b**, thermal treatment of **2a** and **2b** did not

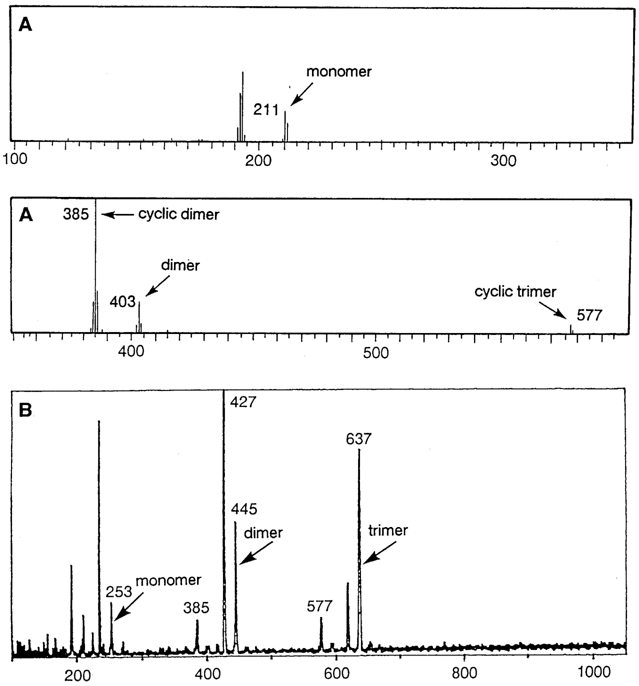
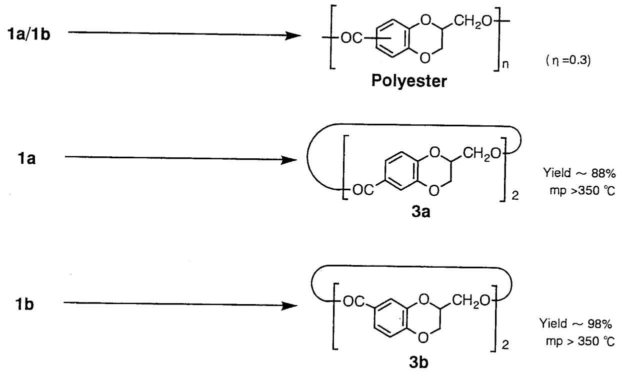


Figure 2. LI mass spectra of **3a** (**A**) and **4a** (**B**).



afford high melting crystalline solid masses, but gave linear polyesters **4a** and **4b**, respectively.

The results of X-ray diffraction analysis and LI mass spectroscopy revealed that each of the products from **2a** and **2b** at the early stage of the reaction (reaction time 20 min) again consisted of acyclic oligomers with a small amount of cyclic dimer and cyclic oligomers, as is exemplified for the product from **2a** in Figure 2B. Of further interest is that total amount of cyclic oligomers in the cases of **2a** and **2b**, is considerably less than that of the oligomers in the cases of **1a** and **1b**, reflecting their difference of chemical structure and/or reactivity. This result suggest that the polycondensation process of **2a** and **2b** consists of step-growth cyclization followed with ring-opening polyaddition of lactone derivatives.

Further work is in progress in order to explain the characteristic features of the reaction behavior of **1a** and **1b**, and their acetyl derivatives.

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References and Notes

1 L.H.Bock and J.K.Anderson, *J.Polym.Sci.*, **28**, 121 (1958).
2 M.Hasegawa, *Iho Seni-Kogyo Shikenjo*, **46**,1(1958).
3 Crystal Data for **2a**:$C_{12}H_{12}O_6$, $P2_1/n$, a=15.233(7), b= 5.631(2), c= 13.730(5) Å, b=103.24(4) deg, V=1146.3(8) Å^3, Z=4, D_{cal}=1.45 g/cm^3, CuKα(1.54178) Å, R=0.071, R_w=0.096. Supplementary Material Available. Listings of table of data collection and structure refinement parameters; table of bond distances; table of bond angles ; table of thermal parameters (5 pages).
4 6-carboxy-2-hydroxymethyl-1,4-benzodioxane **1a** : mp 200-201°C; IR (KBr) 3288, 2949, 2647, 1685, 1588, 1444, 1298, 1205, 1042, 892, 768, 756 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60MHz) δ 3.72-3.78 (m, 2H, C$\underline{H}_2$-OH), 4.03-4.50 (m, 3H, >C$\underline{H}$-C$\underline{H}_2$-), 6.93 (d, 1H, Ar-$\underline{H}$, *J*=9Hz), 7.52 (d,d, 2H, Ar-$\underline{H}$, *J*=7 and 7Hz). 7-carboxy-2-hydroxymethyl-1,4-benzodioxane **1b** : mp 182-185°C; IR (KBr) 3345, 2938, 2650, 1680, 1587, 1448, 1279, 1205, 870, 833, 771 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60MHz) δ 3.67-3.75 (m, 2H, C$\underline{H}_2$-OH), 4.03-4.53 (m, 3H, >C$\underline{H}$-C$\underline{H}_2$-), 6.93 (d, 1H, Ar-$\underline{H}$, *J*=9Hz), 7.52 and 7.55 (d,d, 2H, Ar-$\underline{H}$, *J*=6 and 6Hz). 6-carboxy-2-acetoxymethyl-1,4-benzodioxane **2a** : mp 166-168°C; IR (KBr) 3083, 2883, 2647, 1746, 1678, 1587, 1442, 1309, 1236, 1123, 1047, 902, 837 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 90MHz) δ 2.07 (s, 3H, -C$\underline{H}_3$), 4.04-4.47 (m, 5H, -C$\underline{H}_2$>C$\underline{H}$-C$\underline{H}_2$-), 6.89-6.99 (m, 1H, Ar-$\underline{H}$), 7.43-7.54 (m, 2H, Ar-$\underline{H}$). 7-carboxy-2-acetoxymethyl-1,4-benzodioxane **2b** : mp 120.5-122°C; IR (KBr) 2981, 2883, 2647, 1747, 1685, 1585, 1446, 1272, 1236, 1121, 1031, 895, 838 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 90MHz) δ 2.06 (s, 3H, -C$\underline{H}_3$), 4.08-4.48 (m, 5H, -C$\underline{H}_2$>C$\underline{H}$-C$\underline{H}_2$-), 6.95 (d, 1H, Ar-$\underline{H}$, *J*=8.7Hz), 7.41-7.52 (m, 2H, Ar-$\underline{H}$).