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SYNTHESIS AND THERMAL ANALYSIS OF POLYESTERS HAVING SPIRO-DIOXANE RINGS AND GUAIACYL UNITS

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1. INTRODUCTION

Vanillin, 4-hydroxy-3-methoxybenzaldehyde, industrially obtained by oxidative degradation of lignin, has two reactive functional groups, and is easily converted to various derivatives. Therefore, the use of vanillin as a raw material for synthetic polymers has been attempted by several researchers^{1,2)} since the 1950's when Bock et al.^{3,4)} developed polyesters.

In recent years, we have studied synthetic polymers obtained from lignin related phenol derivatives with respect to the relationship between the chemical structure and physical properties. Studies on poly(4-hydroxy-3-methoxystyrene)⁵⁻⁹⁾ and poly(oxy-2-methoxy-1,4-phenylenecarbonylmethylene)¹⁰⁾ have been reported in detail elsewhere.

Recently, 3,9-bis(4-hydroxy-3-methoxyphenyl)-2,4,8,10-tetraoxa-spiro[5.5]undecane, designated bisphenol (I), which contains a spiro-dioxane ring, was synthesized, and polyesters were obtained through reactions with terephthaloyl or sebacoyl chloride. In the present paper, synthesis and some thermal properties of these polyesters are discussed in relation to their chemical structure.

2. EXPERIMENTAL

2.1 Materials

Vanillin and pentaerythritol, reagent grade, were obtained commercially and used as received. Commercially obtained terephthaloyl chloride and sebacoyl chloride were purified by recrystallization from benzene and distillation under reduced

pressure, respectively.

Dichloromethane was purified and dried by distillation over phosphorous pentoxide.

2.2 Synthesis

2.2.1 Synthesis of 3,9-bis(4-hydroxy-3-methoxyphenyl)-2,4,8,10-tetraoxa-spiro[5.5]undecane (I)

Vanillin (7.5g), pentaerythritol (3.4g) and *p*-toluenesulfonic acid monohydrate (0.60g) were dissolved in benzene (150ml) and refluxed for 4 hr. Water formed during the reaction was removed by a Dean-Stark trap. After cooling to room temperature, the reaction mixture was washed with aqueous alkaline solution of sodium carbonate (0.34g)/water (100ml) and then with water. After drying with sodium sulfate, the reaction mixture was concentrated under reduced pressure. A precipitate was obtained by addition of ethyl ether to the above reaction mixture. The precipitate was then collected and recrystallized from toluene. Yield was 4.50g (50%), mp 169–171°C (colorless needles). IR (KBr), cm^{-1} : 3325 (–OH), 1610, 1520 (phenyl, C–H). NMR (CDCl_3 , TMS), δ ppm: 3.54–4.07 (6H, m, $-\text{CH}_2-$, $-\text{CH}(\text{H})-$), 4.00 (6H, s, Ar–OCH₃), 4.37–5.10 (2H, d, $-\text{CH}(\text{H})-$), 5.47 (2H, s, Ar–OH), 5.77 (2H, s, Ar–CH), 6.97–7.45 (6H, m, Ar).

Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_8$: C, 62.37; H, 5.98. Found: C, 62.4; H, 6.0.

2.2.2 Synthesis of polyesters

Polymerization was carried out as follows. A dichloromethane solution (5ml) of terephthaloyl chloride (0.305g) was added to dichloromethane (10ml) containing bisphenol (I) (0.607g) and

triethylamine (0.45ml). This mixture was mechanically stirred for 24 hr at room temperature. The reaction mixture obtained was added to methanol (400ml). The precipitate formed was collected and washed with methanol. Purification of the polymer was carried out by reprecipitation using *m*-cresol and methanol. Yield was 0.743g (92.7%). IR (KBr). cm^{-1} : 1740 (ester, C=O).

Anal. Calcd for $C_{29}H_{26}O_{10}$: C, 65.16; H, 4.90.
Found: C, 65.0; H, 4.9.

Polysebacate was also obtained through a similar procedure using sebacoyl chloride instead of terephthaloyl chloride. Yield was 93.7%. IR (KBr), cm^{-1} : 1760 (ester, C=O).

Anal. Calcd for $C_{31}H_{38}O_{10}$: C, 65.25; H, 6.71. Found; C, 65.1; H, 6.7.

2.3 Measurements

Infrared spectra were obtained with a JEOL A-3 spectrometer. A NMR spectrum was measured with a Varian EM-360 spectrometer. Heat capacities were determined using a Perkin-Elmer differential scanning calorimeter (DSC) model DSC-II equipped with a Textronix 31 calculator. A sensitivity of 2 mcal/sec and heating rate of 10K/min was used. Thermogravimetric measurement was carried out using a Shimadzu TGA-30M thermogravimeter. X-ray diffractograms were obtained with a Rigaku Denki model 2171 X-ray diffractometer.

3. RESULTS AND DISCUSSION

3.1 Synthesis

Conrad et al.¹¹⁾ reported the synthesis of mono-

and bis-acetals and ketals by the reactions of pentaerythritol with aldehydes and ketones in benzene with a catalytic amount of p-toluenesulfonic acid. Therefore, in the present study, bisphenol (I) was synthesized by a method similar to that reported.

As illustrated in scheme 1, bisphenol (I) was synthesized from vanillin and pentaerythritol in benzene with the addition of a catalytic amount of *p*-toluenesulfonic acid, using a Dean-Stark trap to remove water.

Polyesters were obtained by the reaction of bisphenol (I) with terephthaloyl chloride or sebacoyl chloride in chloroform using triethylamine as an acid acceptor. The yields and the inherent viscosities of polyesters are shown in Table 1. As seen here, polyesters having high η_{inh} 's could be obtained. These polyesters dissolved in *m*-cresol

Scheme 1

Table 1. Properties of obtained polymers.

Polyester	Yield %	$\eta_{\text{inh}}^{\text{a)}$ dl/g	Heating Rate K/min	T_g K	$T_d^{\text{c)}$ K
Polysebacate	93.7	0.89	0 ^{b)}	358	527
			2.5	359	
			5	361	
			10	363	
			20	366	
			40	369	
Polyterephthalate	92.7	1.30	20	not found	568

a) Measured at a concentration of 0.125g/dl in *m*-cresol at 30°C

^b) T_g obtained by extrapolation of heating rate to zero

c) Measured in nitrogen

and *o*-chlorophenol. However, they did not dissolve in *N,N*-dimethylformamide, dimethyl sulfoxide or chloroform.

3.2 Thermal Analysis

The thermal stability of the obtained polyesters, polyterephthalate (PTS) and polysebacate (PSS) having spiro-dioxane rings, was analyzed by thermogravimetry (TG). Fig. 1 shows TG curves of the polyesters measured in an atmosphere of purified nitrogen. PTS started to decompose at 568K and PSS at 527K. This shows that the former is thermally more stable than the latter.

DSC studies of the above polymers were carried out in an atmosphere of nitrogen at the heating rate 10K/min from room temperature to a temperature, a few Kelvins below the thermal decomposition temperature (T_d) determined by TG (see Table 1). Although no transition was detected in the DSC curve of PTS, a glass transition at 363K was seen in that of PSS. T_g 's of PSS measured at various heating rates are shown in Table 1.

The X-ray diffractogram of PTS showed a crystalline pattern while that of PSS showed an amorphous halo pattern.

One of the purpose of the present study is to investigate the relationship between the properties and structure of these polymers. Generally speaking, as T_g value of a polymer depends on its rigidity, it should be possible to estimate the rigidity of the spiro-dioxane rings in PSS by comparing the T_g with those of polysebacates from other bisphenolic compounds.

Among the polyesters from bisphenolic compounds, the thermal properties of polyesters from

di-substituted bis(4-hydroxyphenyl)methane have been studied in detail. Therefore, we attempted to compare the T_g of PSS with those of a series of polyesters obtained from di-substituted bis(4-hydroxyphenyl)methane¹²⁾, which have three-dimensional connecting units such as

or (B), and their thermal properties have

been studied in detail, respectively. The reported T_g 's of polysebacates (A) and (B) are 424, and 417K. Therefore, the difference between the chemical structures of PSS and (A) or (B) is that PSS has a spiro-dioxane ring and methoxyl groups at the 3-position of each aromatic ring while (A) and (B) lack these structural features. The η_{inh} of PSS is 0.89 and those of (A) and (B) are reported as 0.73 and 1.03¹²⁾, respectively. Therefore, we may consider the molecular weights of the above polymers to be not very much different. As reported previously⁷⁾, the presence of a methoxyl group on the aromatic ring increases molecular mobility. As is clearly seen, the T_g of PSS is almost 60K lower than those of (A) and (B). On the other hand, the T_g of polysebacate from 2,2-bis(4-hydroxyphenyl)propane¹³⁾ was reported to be 280K which is significantly lower than that of PSS. Therefore, if we consider the effect of the methoxyl groups, which bring about a decrease in the T_g of the polymers, it may be reasonable to assume that the rigidity of the spiro-dioxane ring is almost similar to those of (A) and (B), even though the T_g of PSS is almost 60K lower than those of (A) and (B).

As mentioned above, no transition was detected in the polyester PTS by DSC measurements. Therefore, for the purpose of comparing the thermal stability of PTS and PSS, we measured the heat capacity (C_p) of both polymers in the temperature range 352K to 386K. As seen from Table 2 and Fig. 2, the C_p of PTS is lower than that of PSS. This indicates that the thermal stability of PTS is greater than that of PSS. This fact also agrees well with the results shown that the T_d of PTS is higher than that of PSS.

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Fig. 1 TG curves of polyterephthalate (PTS) and polysebacate (PSS).
—: PTS, - - - - -: PSS.

Table 2. Heat capacities of polyterephthalate (PTS) and polysebacate (PSS) polymers.

Temp. K	C_p , J/deg g		Temp. K	C_p , J/deg g	
	PTS	PSS		PTS	PSS
352	1.271	1.515	370	1.350	1.761
354	1.285	1.534	372	1.357	1.858
356	1.294	1.546	374	1.366	1.859
358	1.304	1.563	376	1.374	1.848
360	1.310	1.580	378	1.380	1.853
362	1.316	1.600	380	1.385	1.860
364	1.327	1.627	382	1.390	1.862
366	1.333	1.665	384	1.394	1.870
368	1.344	1.720	386	1.403	1.881

Fig. 2 Heat capacities of polyterephthalate (PTS) and polysebacate (PSS).

—: PTS, - - - - -: PSS.

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スピロジオキサン環とグアヤシル基を有する
ポリエステル合成およびその熱的性質

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バニリンとペンタエリスリトールを原料として、スピロジオキサン環を有する 3,9-ビス(4-ヒドロキシ-3-メトキシフェニル)-2,4,8,10-テトラオキサスピロ[5.5]ウンデカン(I)を合成した。さらに、ビスフェノール(I)

からポリテフタレート(PTS)及びポリセバケート(PSS)を合成した。

X線回折測定によりPTSは結晶性であり、PSSは無定形であることがわかった。さらに、熱重量分析の結果、

PTSおよびPSSの熱分解温度は、それぞれ、568 Kおよび527 Kであり、PTSの方が熱的に安定であった。

また、示差走査熱量計による分析では、PTSは昇温測定により相転移は認められなかったが、PSSは363 Kにガラス転移(T_g)が認められた。PSSの T_g と、すでに知られている9,9-ビス(4-ヒドロキシフェニル)フ

ルオレンあるいは9,9-ビス(4-ヒドロキシフェニル)-9,10-ジヒドロアントラセンのポリセバケートの T_g と比較を行い、スピロジオキサン環の剛直性を推定した。

さらに、PTSとPSSの熱容量(C_p)の352 Kから386 Kの温度範囲で測定し、PTSの C_p が低いことから、その熱的安定性のよいことを明らかにした。