

Stereoregular polymerization of glycidyl phenyl ether catalyzed by dibutyltin oxide-tributyl phosphate condensates

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Summary

Polymerization of glycidyl phenyl ether was carried out with the dibutyltin oxide-tributyl phosphate condensate as catalyst. The product was fractionated. The yield of the acetone-insoluble fraction was in the range of 85% to 96%. The tacticity of the polymer fractions was studied using ^{13}C NMR spectroscopy. The results indicated that the microstructure of PGPE was dependent on the catalyst structure and the reaction conditions. By using the condensate of appropriate molecular weight as catalyst, the isotacticity of the acetone-insoluble fractions can reach as high as 87.4%. In some cases, however, the fractions rich in syndiotactic structure were obtained in addition to the isotactic fraction. It was suggested that more than one kind of active sites were present in the catalyst.

Introduction

Epoxy resins are typically polyglycidyl compounds. The glycidyl group is asymmetrical, yet the stereosequence in the cured resins has not been studied in detail so far. The objective of this research program is to study the stereoregular polymerization of epoxy resins and to illustrate the influence of tacticity on the properties of the materials.

While quite a number of catalyst is known to be active for the stereoregular polymerization of epoxides^[1-4], the dibutyltin oxide-tributyl phosphate condensate is preferred for the stability in air and the solubility in the polymerization medium^[5-9]. In this article, glycidyl phenyl ether (GPE) is used as model compound to demonstrate the regioselectivity and the stereoselectivity of the catalyst.

Experimental

1. Materials

Glycidyl phenyl ether was supplied by Yueyang Chemical Corporation. It was distilled under vacuum, and the fraction of 95-97 °C/2 mmHg was collected. Dibutyltin oxide was supplied by Beijing Elf Atomchem Polystab Co. Ltd. It was dried in vacuum at 80-90 °C for more than 4 hours. Tributyl phosphate was analytical reagent and used without further purification. Benzene was analytically pure and dried over sodium and distilled before use.

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2. Preparation of $Bu_2SnO-Bu_3PO_4$ condensate

The mixture of Bu_2SnO and Bu_3PO_4 (mole ratio 1:2) was heated at 220-260 °C in a three-necked glass flask equipped with a distillation head connected with a receiver through a condenser. The degree of condensation was controlled through changing the reaction temperature and the reaction time. The low molecular weight fraction was removed by extraction with acetone. The condensate was then separated into the benzene soluble fraction and the benzene insoluble fraction. They were pulverized and dried in vacuum at 140 °C for more than 2 hours before use. The condensate was designated as Sn-P catalyst. The analysis results are given in Table 1.

3. Polymerization of GPE

In a dried three-necked glass flask equipped with a stirrer and a reflux condenser, about 1wt.% of Sn-P catalyst was dissolved or dispersed in benzene, then GPE was added. After refluxing at 90-130 °C for about 1 hour the polymerization was completed. The polymer was then separated into the acetone insoluble fraction and the acetone soluble fraction. The acetone solution was further fractional precipitated with methanol.

4. Characterization

The M_n of the dibutyltin oxide-tributyl phosphate condensate was measured by vapor phase osmometer (VPO) in $CHCl_3$ at 37 °C. The elemental analyses were conducted using inductively coupled plasma spectroscopy (ICP).

The ^{13}C NMR spectra were recorded at 75.4 MHz on a DMX 300 spectrometer with proton noise decoupling. a-PGPE samples were dissolved in $CDCl_3$ (15-20 wt.%), and i-PGPEs were swollen in tetrachloroethane- d_2 (TCE- d_2). Spectra were recorded at 300 K for a-PGPE or at 350 K for i-PGPE with the number of transients 1000 and the pulse delay 3s. The central peak of $CDCl_3$ and TCE- d_2 was taken as a reference. The stereomer ratios were determined according to peak height.

The DSC thermograms were recorded on a TA Inst 2100 calorimeter at a heating rate of 10 °C/min.

Results and discussion

1. Polymerization of GPE

All the catalysts listed in Table 1 were very active for the polymerization of GPE. The conversions were practically quantitative in all the cases. In Table 2 the results of some typical experiments are given. The acetone-insoluble fraction of poly(glycidyl phenyl ether) (PGPE) is highly isotactic. It is therefore designated as i-PGPE. The acetone-soluble fraction is named a-PGPE. The yield of i-PGPE was between 85% and 96%, depending on the catalyst structure and the reaction conditions.

Table 1 Analyses of dibutyltin oxide-tributyl phosphate condensates

condensate	M _n	elemental analyses(%)			solubility	
		Sn	P	C	acetone	benzene
Sn-P1	5200	23.5	12.2	33.8	insoluble	soluble
Sn-P2	6700	23.2	11.2	31.4	insoluble	soluble
Sn-P3	8000	24.4	10.6	29.4	insoluble	soluble
Sn-P4	-	25.4	10.2	28.4	insoluble	insoluble

Table 2 Polymerization of glycidyl phenyl ether

code	composition			reaction condition		yield(%)		
	GPE(g)	catalyst(g)	benzene(ml)	°C	min	i-PGPE	a-PGPE	
PGPE-1	40.0	Sn-P1	0.400	40	95	25	87.7	8.4
PGPE-2	40.0	Sn-P3	0.381	80	105	25	85.2	14.0
PGPE-3	40.0	Sn-P4	0.351	80	125	60	95.4	3.9
PGPE-4	40.0	Sn-P2	0.385	80	110	60	96.3	3.6
PGPE-5	40.0	Sn-P3	0.380	80	115	60	86.8	12.4

2. Tacticity of PGPE

In the microstructure of PGPE both the regioregularity and the stereoregularity are considered. The assignment of ¹³C NMR signals has been studied in detail by J. C. Ronda et al.^[10]. It has been found that the main chain methylene carbon is sensitive to diad tacticity with the signal at 70.0 ppm corresponding to the isotactic diad and the signal at 69.7 ppm corresponding to the syndiotactic diad. The main chain methine carbon is sensitive to triad tacticity with the signal at 78.3 ppm corresponding to the isotactic triad and the signal at 78.0 ppm corresponding to the syndiotactic triad. The pendent CH₂ is insensitive to tacticity. The signals for the irregular chain linkage appear at 71.3 ppm and 70.9 ppm.

In Figure 1, the ¹³C NMR spectra of three typical samples are given. It is seen from the spectra of i-PGPE-1 and a-PGPE-5-0 that the signals for the irregular chain linkage do not appear. That is to say, the polymer chains have the regular head-to-tail structure. The signals for the end groups appear only in the spectrum of a-PGPE-5-4, the fraction of the lowest molecular weight. It is noticed that the chemical shift, especially for the pendent CH₂ group is changeable. The factors that cause the difference in the chemical environment are not clear yet.

Considering that T₁ and the local magnetic field of the same group are very similar for the stereomers, we calculated the content of the stereomers according to peak height. The isotacticity and syndiotacticity of different PGPE samples are summarized in Table 3.

Table 3 Stereoregularity of different PGPE samples

code	triad tacticity methine (%)			diad tacticity methylene(%)		diad isotacticity (%)	diad syndiotacticity (%)
	mm	mr	rr	m	m	r	
i-PGPE-1	87.6	-	12.4	87.6	87.2	12.8	87.4
i-PGPE-2	41.6	33.2	25.3	58.2	58.5	41.5	58.4
i-PGPE-3	83.1	-	16.9	83.1	83.6	16.4	83.4
i-PGPE-4	77.2	14.9	7.9	84.6	86.6	13.4	85.6
i-PGPE-5	66.7	8.6	24.7	71.0	72.5	27.5	71.8
a-PGPE-5-0	30.2	-	69.8	30.2	32.5	67.5	68.6
a-PGPE-5-1	22.0	31.8	46.3	37.9	35.1	64.9	63.5
a-PGPE-5-2	21.6	32.6	48.3	37.9	34.5	65.5	63.8
a-PGPE-5-3	23.1	33.2	43.7	39.7	36.6	63.4	61.8
a-PGPE-5-4	29.5	37.8	32.7	48.4	50.5	49.5	

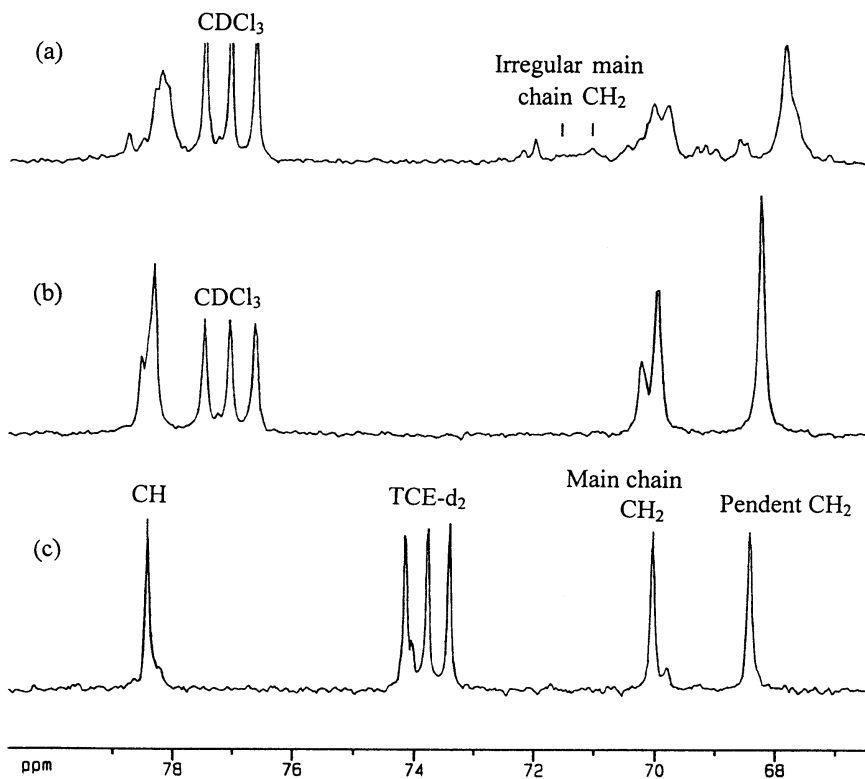


Figure 1 The ^{13}C NMR spectra of several typical PGPE samples: (a) a-PGPE-5-4 dissolved in CDCl_3 , recorded at 300K, (b) a-PGPE-5-0 dissolved in CDCl_3 , recorded at 320K, (c) i-PGPE-1 swollen in TCE-d_2 , recorded at 350K.

From Table 3, we can see that the *i*-PGPEs obtained with Sn-P1, Sn-P2 or Sn-P4 as catalyst have high isotacticity. By comparison, the highest value of diad isotacticity of the *i*-PGPE obtained with the $\text{Al}(\text{OPr}^i)_3\text{-ZnCl}_2$ catalyst was 80.4%^[10].

To study the tacticity of *a*-PGPE in detail, the polymer was dissolved in acetone and fractionally precipitated with methanol. Taking *a*-PGPE-5 as an example, *a*-PGPE-5-0 is the fraction precipitated from the acetone solution after storage at room temperature, and *a*-PGPE-5-1 through *a*-PGPE-5-4, in turn, are the fractions precipitated with methanol. It is interesting to point out that syndiotactic enchainment dominates in all the fractions except the last fraction *a*-PGPE-5-4, which is nearly atactic as shown in Table 3.

The low isotacticity of *i*-PGPE-2 and *i*-PGPE-5 can be accounted for by the presence of syndiotactic fractions. In fact, fractions rich in syndiotactic structure have been separated from these polymers. For example, by extracting *i*-PGPE-5 with the toluene/acetone solvent, a fraction of 12.6 wt.% was separated, which has a syndiotacticity of 63.7 %.

3. Thermal analysis of PGPE

i-PGPEs are crystalline polymers as demonstrated by DSC thermograms^[11, 12]. In Figure 2 the DSC thermograms for *i*-PGPE-5 and *a*-PGPE-5-0 are shown. The effect of thermal history on the crystallite structure is evident. In the thermogram for *i*-PGPE-5 annealed at 230 °C for 15 min, two endothermic peaks at 207.9 °C and 221.0 °C can be seen and the fusion enthalpy ΔH_m was 63 J/g. For the same polymer annealed at 140 °C for 2 h, three endothermic peaks at 141.5 °C, 195.5 °C and 204.5 °C were observed, and the fusion enthalpy ΔH_m was 43 J/g.

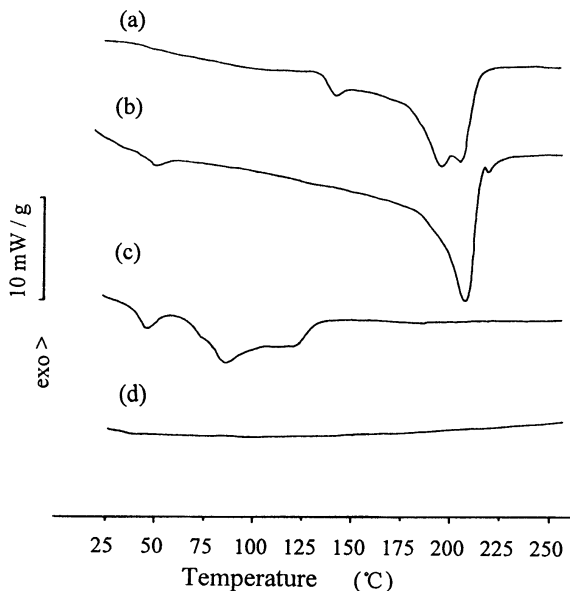


Figure 2 The DSC thermograms for PGPE: (a) *i*-PGPE-5 annealed at 140 °C for 2 hour, (b) *i*-PGPE-5 annealed at 230 °C for 15 min, (c) *a*-PGPE-5-0 and (d) *a*-PGPE-5-0 annealed at 150 °C for 6 min.

The syndiotactic-rich fraction a-PGPE-5-0 is a semicrystalline polymer too. There is a very broad endothermic peak ranging from 65 °C to 145 °C with the fusion enthalpy ΔH_m 22 J/g. The thermal induced crystallization of this polymer was very slow, as demonstrated by the disappearance of crystallites after melting at 150 °C.

4. Final remarks

All the $Bu_2SnO \cdot Bu_3PO_4$ condensates listed in Table 1 were very active for the polymerization of GPE, yet the stereoeregularity of the PGPE changed to a large extent with the catalyst and the reaction conditions. Nakata and his coworkers^[7] studied the structure of the organotin phosphate using ¹¹⁹Sn NMR spectra and found that the active species for the polymerization of epoxides was associated with the monobutyltin pyrophosphate. A mechanism for the initiation and the propagation was proposed. However, it is still not clear how the monomer coordinates on the catalyst. From the results of our recent work that the highly syndiotactic PGPE fractions were separated in addition to the isotactic fraction, it is suggested that more than one kind of active sites were present in the catalyst.

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