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New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers)

28. Glycidyl Ethers of Bisphenol- and Trisphenol-PIB and Their Curing to Epoxy Resins

Joseph P. Kennedy[1], Suhas C. Guhaniyogi[1] and Virgil Percec[2]

[1] Institute of Polymer Science, The University of Akron, Akron, OH 44325, USA

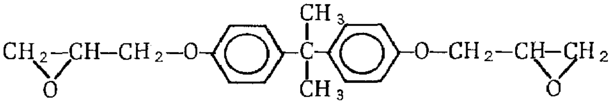
[2] Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

Summary

Glycidyl ethers of bisphenol- and trisphenol-polyisobutylenes have been prepared, characterized, and cured with amines to new flexible epoxy resins. The synthesis of these glycidyl ethers involved quantitative condensation of epichlorohydrin with phenol-capped linear or three-arm star polyisobutylenes. Proton NMR analysis of the model compound monoglycidyl ether of 2,4,4-trimethyl-2(p-hydroxyphenyl)pentane and the corresponding glycidyl ethers of phenol-capped polyisobutylenes showed the presence of epoxy end groups. According to ^{1}H NMR spectroscopy and titration data the number-average terminal epoxy functionality is close to the theory, i.e., two or three, for the linear and three-arm star products. Curing these new epoxides with triethylene tetramine resulted in transparent, non-tacky flexible films.

Introduction

Epoxy resins are versatile modern materials that find use in a host of applications, i.e., construction, engineering materials, composites, adhesives, coatings (LEE et al., 1979). These resins are conventionally prepared by curing epoxy-terminated prepolymers with multifunctional amines. The most commonly used epoxy prepolymer is the diglycidyl ether of bisphenol A (DGEBA):



Side reactions may take place during the preparation of DGEBA so that the product may also contain less well defined structures than the one shown.

Epoxy resins prepared of DGEBA and amines i.e., piperazine, triethylene tetramine, are rather brittle and due to their highly polar character quite moisture

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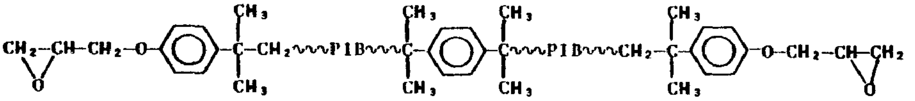
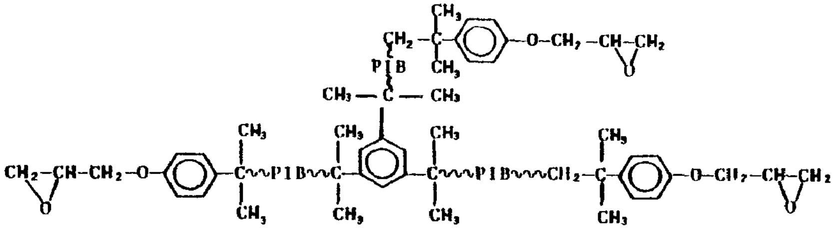
sensitive materials. Brittleness can be improved by incorporating into the resin certain rubbers, most commonly carboxy terminated butadiene-acrylonitrile copolymers (CTBN). During the curing of epoxy resins these rubbers precipitate from the initially homogeneous mix and segregate into small most likely spherical domains which greatly enhance the impact properties (toughness) of the final products (ROWE et al., 1970, SULTAN et al., 1973, MANSON et al., 1976, BUKNALL, 1977, GILLHAM et al., 1977).

In the course of our fundamental studies on telechelic polyisobutylenes PIB we have prepared linear and three-arm star phenol-capped prepolymers (bisphenol-PIB, trisphenol-PIB) (KENNEDY et al., 1982). In view of the great current interest in improved epoxy resins (Symposium on Epoxy Resins, 1982) we decided to convert bisphenol-PIB and trisphenol-PIB quantitatively to the corresponding glycidyl ethers by reaction with epichlorohydrin and to examine these inherently flexible materials as epoxy prepolymers:



Diglycidyl Ether of Bisphenol-PIB (DGE-BP-PIB)



Triglycidyl Ether of Trisphenol-PIB (TGE-TP-PIB)

These structures contain exactly two or three terminal epoxy groups and two or three "built-in" saturated hydrocarbon elastomer segments; the molecular weights of the latters can be controlled within wide limits (∿500-10,000). These di- and tri-epoxy prepolymers hold great promise to improve toughness, moisture sensitivity, and high temperature and oxidative resistance of conventional CTBN-toughened epoxy resins.

This paper describes the synthesis and characterization of DGE-BP-PIB and TGE-TP-PIB and demonstrates their curability with conventional amines.

Experimental

Materials and Instrumentation

Epichlorohydrin (Aldrich, 99+%), p-xylene (Aldrich, 99%) and benzyl trimethyl ammonium chloride (Alfa Products, 98%) were used as received. The preparation of 2,4,4-trimethyl-2(p-hydroxyphenol)pentane (TMHPP), bisphenol-polyisobutylene (BP-PIB) and trisphenol-polyisobutylene (TP-PIB) have been described in a previous publication (KENNEDY et al., 1982).

^{1}H NMR spectra were obtained by the use of a Varian T-60 spectrophotometer in CCl_4 using TMS as internal standard. Molecular weights were determined by VPO using a Knauer Vapor Pressure Osmometer at 40°C in toluene.

Preparation of Glycidyl Ethers of PB-PIB and TP-PIB.

A representative experiment was carried out as follows: To 1 mole of phenol-telechelic polyisobutylene (BP-PIB or TP-PIB) dissolved in p-xylene (b.p.: 138°C) and stirred in a three-neck flask fitted with a magnetic stirrer, reflux condenser with drying tube, Dean-Stark trap, and pressure equalizing dropping funnels, at 70-80°C were added 20 moles of epichlorohydrin. The solution was refluxed overnight and the water formed during the condensation was removed as azeotrope. Then 0.12 mole benzyl trimethyl ammonium chloride phase transfer catalyst was added and thereafter the dropwise addition of a solution of 1.2 moles of NaOH in 100 ml water was commenced. The rate of NaOH addition was regulated to be equal to that of water removal.

Excess epichlorohydrin and p-xylene were removed under reduced pressure at 90°C and the product was extracted with hexanes and washed several times with cold water to remove alkali, salt and benzyl trimethyl ammonium chloride. The solution was dried over anhydrous Na_2SO_4, filtered and the solvent was removed by rotary evaporation. Finally the glycidyl ether derivative was dried at 80-90°C in a vacuum oven for 2 days.

Determination of Epoxy Content

The epoxy content of the TMHPP model compound and/or the polymers was determined by JUNGNICKEL et al.'s method (JUNGNICKEL et al., 1953). Thus a known amount of these materials was refluxed for 2-3 hours with pyridinium chloride-chloroform reagent and titrating the excess HCl with 0.0108 N ethanolic KOH.

Curing Experiments

To 3.25 g of DGE-TP-PIB ($\overline{M}_n$= 1500, see line 4 in Table 1) dissolved in 3.26 g toluene were added 0.15 g triethylene tetramine and 0.06 g phenol. Dissolved air was removed using an aspirator and the liquid was poured in a Teflon mold. The mold was kept in a desiccator under nitrogen atmosphere at 40°C for 5 days (purging with dry nitrogen from time to time). A transparent tough rubbery sheet was obtained.

To 5.1 g of DGE-BP-PIB ($\bar{M}_n$ = 6300, see line 3 in Table 1) dissolved in 5 g benzene were added 0.48 g triethylene tetramine and 0.016 g phenol. The same procedure as above (except 4 days at 40°C and 3 days at 80°C) gave a tough rubbery transparent sheet.

Results and Discussion

The purpose of these studies was first the preparation of DGE-BP-PIB and TGE-TP-PIB of well characterized structures, in particular of well defined numbers of terminal epoxy groups, and subsequently the curing of these epoxy-capped prepolymers by amines to novel PIB-based epoxy resins. The "built-in" saturated hydrocarbon PIB elastomer segments are expected to toughen and to impart moisture resistance to these resins.

The first objective, the synthesis of the glycidyl ethers of BP-PIB and TP-PIB were achieved by contacting these phenol-capped prepolymers with a large excess of epichlorohydrin in the presence of a phase transfer catalyst (benzyl trimethyl ammonium chloride) in a relatively high boiling solvent (p-xylene). While the model compound TMHPP and DGEBA (Epon-828) are miscilbe with epichlorohydrin, BP-PIB and TP-PIB of $\bar{M}_n \sim$ 1900 and 1500, respectively, are not. However, under suitable reaction conditions, satisfactory contact between the phenol-telechelic PIB's and epichlorohydrin can be achieved and quantitative condensation occurs (see Expt.).

The products have been characterized by ^{1}H NMR spectroscopy and the epoxy end group concentration ($\bar{F}_n$) was quantitatively determined by titration.

Figure 1 shows the ^{1}H NMR spectra of the model glycidyl ether of TMHPP, the diglycidyl ether of bisphenol A (Epon 828), and the triglycidyl ether of trisphenol PIB. The key resonances (multiplets) of the model compound appear at 3.93, 3.13 and 2.60 ppm associated with the $-O-C\underline{H}_2-$, $\overbrace{CH_2-C\underline{H}}^{O}-CH_2-$ and $-CH_2-\overbrace{CH-C\underline{H}_2}^{O}$ protons respectively. The resonances in Epon-828 are shifted slightly towards lower fields (3.99, 3.23 and 2.70 ppm, respectively). The triglycidyl ether of trisphenol-PIB shows the multiplets at 3.13 and 2.66 ppm, characteristic of the methine and methylene protons of the epoxy ring. The apparent doublet characteristic of $-O-C\underline{H}_2-$ protons at 3.93 ppm is similar to that present in epichlorohydrin (3.53 ppm). That this doublet is not due to epichlorohydrin impurity in our product was established by mixing 10 wt% epichlorohydrin to TGE-TP-PIB. The spectrum of the mixture is shown in Figure 2 exhib-

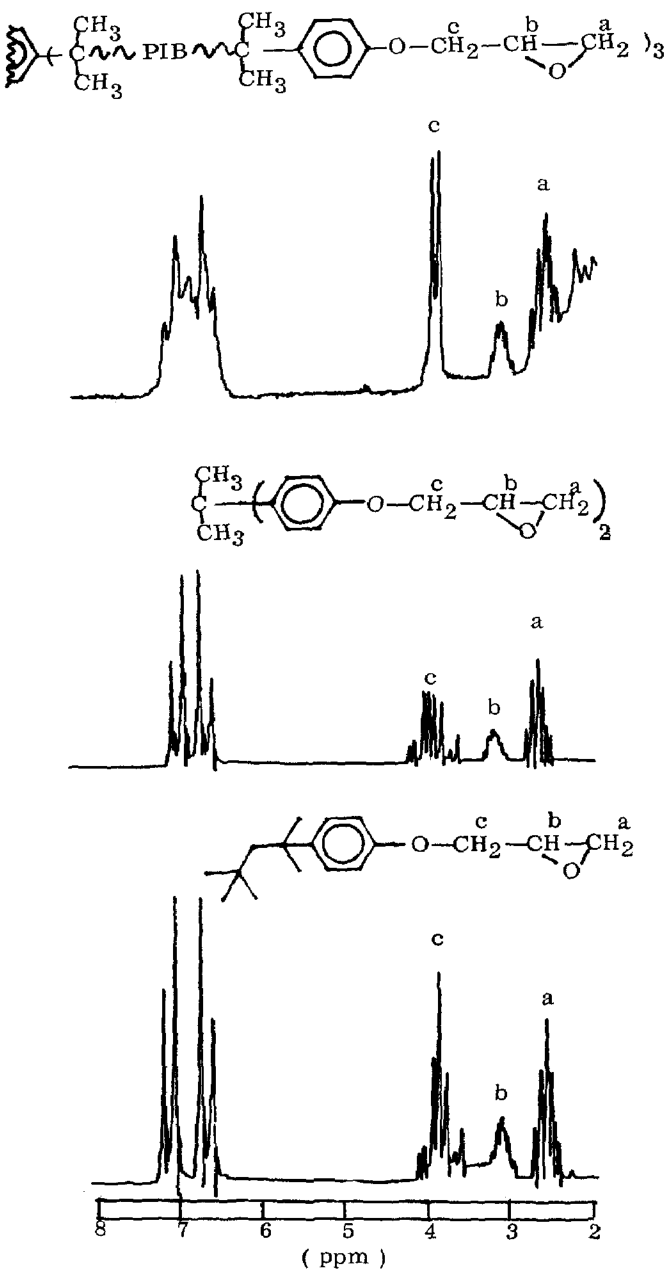


Figure 1. ^{1}H NMR Spectra of Monoglycidyl Ether of TMHPP, Epon 828, and Glycidyl Ether Derivative of Trisphenol-PIB

its all the characteristic resonances of epichlorohydrin and the triglycidyl ether derivative of PIB.

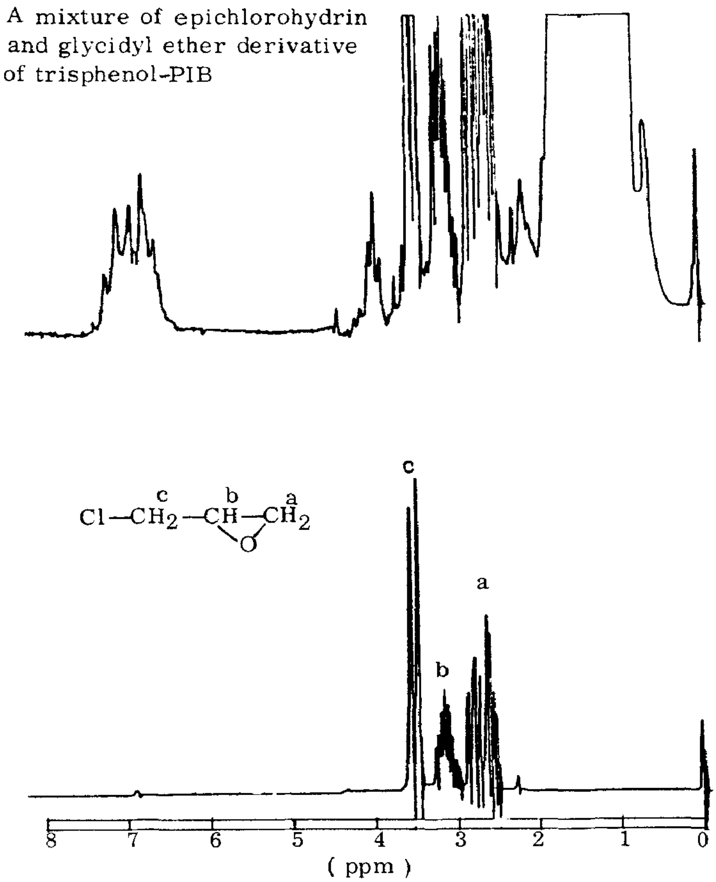


Figure 2. ^{1}H NMR Spectra of Epichlorohydrin and Glycidyl Ether Derivative of Trisphenol-PIB plus Epichlorohydrin

Table 1 shows representative results. The first line refers to results obtained with the model compound TMHPP. The phenol end group functionality ($\bar{F}_n{}^p$) was determined by UV spectroscopy (KENNEDY et al., 1982) whereas the epoxy functionality ($\bar{F}_n{}^e$) by titration. Lines 2 and 3 show results obtained with the linear prepolymer BP-PIB, and lines 3-6 those with the three-arm material TP-PIB. Details of the UV method have been described (KENNEDY et al., 1982). Titration results (last column in Table 1) reflect averages of duplicate determinations. According to these data epoxy terminal functionalities are close to theoretical.

TABLE 1

Synthesis and Characterization of Glycidyl Ethers of Bis- and Trisphenol-PIB

	Phenol-Capped PIB's		Glycidyl Ether Derivatives	
	$\overline{M}_n$	$\overline{F}_n^p$	$\overline{M}_n$	$\overline{F}_n^e$
TMHPP (model)	(206)	1.00	(262)	0.97
linear	1900	2.04	2500	1.94
linear	6300	2.12	6000	2.01
tri- star	1500	2.93	1530	2.96
tri- star	3500	2.91	3700	2.90
tri- star	6000	2.98	6400	2.92

$\overline{F}_n^p$ = phenol functionality

$\overline{F}_n^e$ = epoxy functionality

The molecular weight increase from 1900 to 2500 in line 2 of Table 1 is beyond experimental error of ∿10% (by VPO) and may be due to adventitious -OH functions in the phenol-capped prepolymer which reacted with epoxy groups. The presence of -OH in the DG-BP-PIB (line 2) has been ascertained by ^{1}H NMR spectroscopy (resonance of 3.67 ppm).

The glycidyl ether derivatives of bis- and trisphenol PIB's (lines 3 and 4) were cured with equivalent amount of triethylene tetramine TETA in the presence of ∿10 mole% phenol and tough transparent flexible materials have been obtained.

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