Determination of Pendant Allyl and Monomer Content in Polydiallylphthalate

G. W. GRIFFITH, C. L. LONG, and R. E. SMITH,* *The Bendix Corporation, Kansas City Division,*† *Kansas City, Missouri 64141*

Synopsis

Methods are described for the determination of diallylphthalate monomer and pendant allyl contents in homopolymers of diallylphthalate. The monomer content was determined by gel permeation chromatography. The total allyl content was determined by FTIR and computer subtraction of solvent spectrum. The pendant allyl content can be calculated from the difference between total allyl and allyl caused by monomer. Determination of both monomer and pendant allyl content in the prepolymer is essential for accurate prediction of the physical properties of the cured polymer.

INTRODUCTION

The homopolymer of diallylphthalate has a number of uses in industry and has been the subject of investigation for years.[1-3] More recently, very informative reports on the structure and properties of this homopolymer have appeared.[4,5] Of central importance in these analyses was the determination of pendant allyl content using the IC1 titration method.[1] However, this method cannot distinguish between allyl groups caused by unreacted monomer and pendant allyl groups in the polymer. In some polymer preparations this may present no problem, since the technology does exist to remove the unreacted monomer.[6] It would be useful to have an analytical method available to determine whether there is any unreacted monomer present. A method based on gel permeation chromatography (GPC) has been recently published describing the determination of monomer content of diallylphthalate resins.[7] The infrared spectra (IR) of diallylphthalate monomer, prepolymer, and cured resins also has been reported.[8] This correspondence describes the use of GPC and Fourier transform infrared (FTIR) spectroscopy for the determination of both the unreacted monomer and pendant allyl content of diallylphthalate prepolymers.

EXPERIMENTAL

Gel Permeation Chromatography

Gel permeation chromatography (GPC) was performed on a Waters Model 200 GPC using a crosslinked polystyrene low-porosity column set. This column

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* Author to whom correspondence should be addressed.
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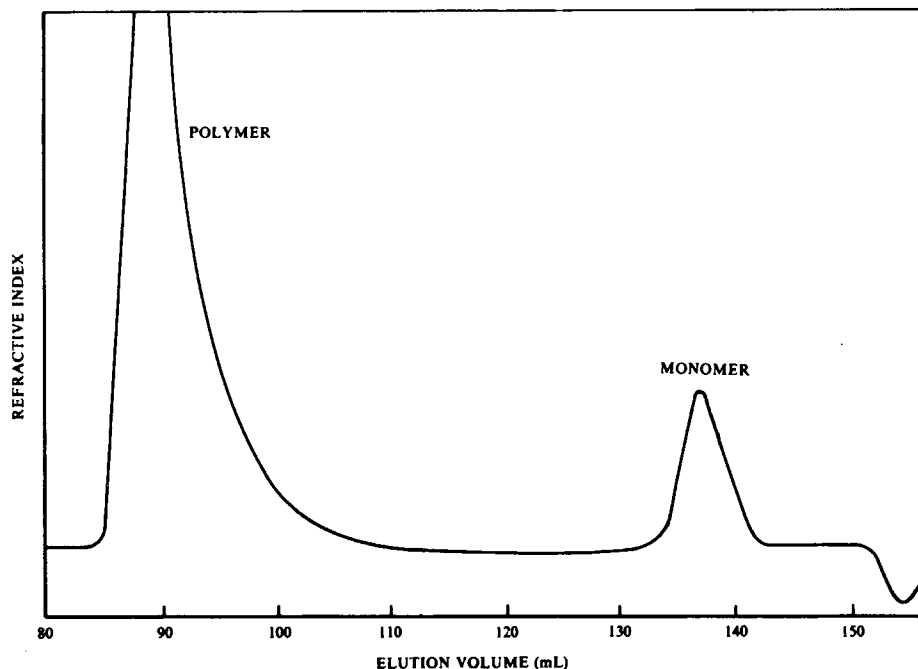
Fig. 1. GPC of prepolymer: 35 mg of a prepolymer of diallylphthalate was dissolved in 10 mL of THF and injected on the GPC.

set consisted of four tandemly linked columns with porosities arranged as follows: 250, 100, 60, and 60 Å.

Samples were dissolved in tetrahydrofuran (THF) and THF solvent flow rate of 1 mL/min was used. Peaks were detected with a differential refractometer.

FTIR

Fourier transform infrared (FTIR) spectra were measured with a Nicolet 7199 FTIR equipped with a TGS detector. All spectra were obtained using 2 cm^{-1} resolution and 300 scans. Samples were dissolved in CH_2Cl_2 and were put into a 10 mm path length liquid cell (Wilmad Glass Co., Inc., Buena, NJ).

The method used for the determination of total allyl content is as follows. Diallylphthalate standards ranging from 1 to 10 g/L in CH_2Cl_2 were prepared. The FTIR spectrum of the CH_2Cl_2 solvent was obtained and stored on magnetic disk. The spectra of the diallylphthalate standards were then recorded. The CH_2Cl_2 spectrum was then subtracted from each diallylphthalate spectrum until the band at 1552 cm^{-1} disappeared. The absorbances of the standards at 1650 cm^{-1} were plotted against the allyl concentrations to obtain a calibration curve. The spectra of the polymer or prepolymer samples were then recorded and the CH_2Cl_2 spectrum subtracted. The resulting absorbance at 1650 cm^{-1} was compared to the calibration data to obtain the total percent allyl in the polymer or prepolymer.
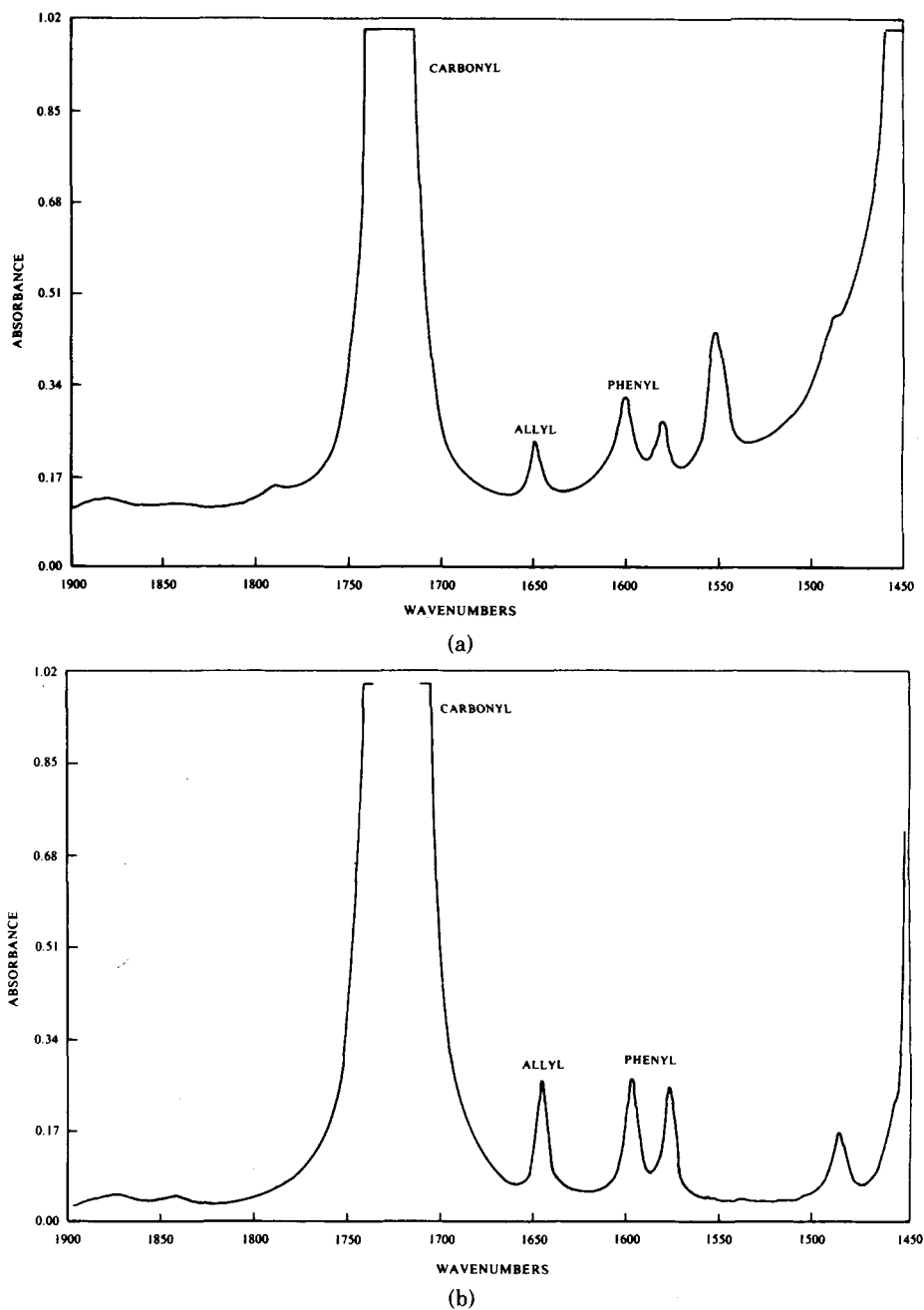
Fig. 2. FTIR of diallylphthalate: (a) original spectrum in CH_2Cl_2; (b) spectrum after subtracting the CH_2Cl_2.

RESULTS AND DISCUSSION

Samples of prepolymers analyzed were found to contain both free diallyl-phthalate monomer and pendant allyl groups. Gel permeation chromatography

TABLE I
Analysis of Prepolymer Samples

Sample no.	Monomer (w/o)[a]	Total allyl (w/o)[a]	Pendant allyl (w/o)[a]
1	5.6	9.55	7.68
2	3.1	9.69	8.66
3	12.9	13.45	9.15
4	0	8.93	8.93
5	1.0	9.19	8.86

[a] w/o = wt. %.

of one of these samples is shown in Figure 1. In addition to the large peak caused by polymer, a smaller peak eluting later was seen. This peak was identified as diallylphthalate monomer. A straight line was obtained when peak heights were plotted against diallylphthalate concentration. The concentration of diallylphthalate monomer in the prepolymers was calculated from this calibration data.

The total allyl content was then determined by FTIR. The FTIR spectra of a diallylphthalate standard in CH_2Cl_2 before and after subtracting the CH_2Cl_2 are shown in Figures 2(a) and 2(b). As seen by comparing Figures 2(a) and 2(b), the CH_2Cl_2 spectrum was subtracted until the band at 1552 cm^{-1} disappeared. This subtraction left a peak at 1650 cm^{-1} caused by the allyl group which was free from spectral interferences.

The absorbances at 1650 cm^{-1} of the diallylphthalate standards were recorded and plotted against the concentration of allyl to give a straight line. The absorbances at 1650 cm^{-1} of prepolymers were also determined and total allyl content was calculated from the calibration data. The diallylphthalate (monomer) content was determined by GPC as described previously. The amount of allyl caused by monomer was calculated by multiplying the monomer content by 82/246 (the fraction of allyl in diallylphthalate). The amount of allyl caused by monomer was subtracted from the total allyl. Results of analyses of some prepolymers are shown in Table I.

The pendant allyl content of these prepolymer samples are not constant because they were made from five different lots of monomer on five different occasions.

It is important to note that the monomer content of prepolymers analyzed has ranged from 0 to 13 wt %. Thus, it was essential that the prepolymers be analyzed for both total allyl and allyl caused by monomer. In evaluating the prepolymers a simple FTIR spectrum or IC1 titration would have given misleading data. An accurate prediction of the physical properties of the resulting polymer requires knowledge of both monomer and pendant allyl content in the prepolymer.

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