

# Synthesis and Properties of Segmented Polyurethane Using Phenolphthalein\* as Chain Extenders

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## SYNOPSIS

Three series of novel polyurethane elastomers containing phenolphthalein as chain extenders were synthesized. The structure of the polyurethane was analyzed using IR and wide-angle X-ray diffraction studies. Tensile strength and percentage of elongation of all the series of polymers were studied. Thermal decomposition was studied using differential scanning calorimetry. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polyurethane film is comparatively a newcomer, although polyurethanes are well known in other forms including foam, elastomer, and surface coating.<sup>1,2</sup> As a film, it is soft but very tough. It can be made by extrusion, casting or by calendering. It has very high tear strength and high abrasion resistance to oils and greases. It is used for specialized packaging in industries and military fields. Because of this versatility, several patents were acquired in this area. There are three major ingredients in polyurethane film: a long-chain polyol, either polyester or polyether, an aliphatic or aromatic diisocyanate, and a chain extender to yield an isocyanate-terminated prepolymer. Chain-extended polyurethanes are known to impart good mechanical properties.

Phenolphthalein-containing polymer possesses excellent properties. The glass transition temperature of copolymers of aromatic polyether-polysulfone containing phenolphthalein increases with increased phenolphthalein content.<sup>3</sup> Several patents were obtained using phenolphthalein as one of the constituents of the polymer. Polyurethanes made of phenolphthalein, isophoronedisocyanate, diethylene glycol dimethylether, and naphthaquinone-(1,2)diazodo-(2)-5-sulfonyl chloride show high sensitivity and storage stability and are suitable for

preparing lithographic plates.<sup>4</sup> Improved fire resistance occurs for phenolphthalein-based polycarbonates and polyesters compared to bisphenols.<sup>5,6</sup> Polycarbonates, polyamides, and polyesters of phenolphthalein were prepared and their flammabilities evaluated with regard to their oxygen index and char formation.<sup>7</sup> Aromatic polyester carbonates prepared from terephthaloyl chloride and/or isophthaloyl chloride, phosgene, bisphenols, halogenated diphenols, and, optionally, phenolphthalein were prepared that had a heat distortion temperature of 229°C.<sup>8</sup> Polycondensation of 4,4'-diphenyl methane diisocyanate with various glycols and oligoesters from terephthaloyl chloride, ethylene glycol, and phenolphthalein form poly(acrylate urethane) coatings.<sup>9</sup> Dyes such as  $\alpha$ -naphtholphthalein, thymol blue, and sulfonated phenolphthalein were used to prepare inks.<sup>10</sup>

In this paper, novel polyurethanes using phenolphthalein as chain extenders are prepared and characterized for their physicomechanical properties.

## EXPERIMENTAL

### Materials

Castor oil was obtained from a commercial source. It was dried and degassed overnight at 90°C at 3 mmHg. Hydrogenated castor oil (supplied by Bombay Oil Industries Private Ltd) was dried and used. Hexamethylene diisocyanate (HMDI), 4,4'-diphenyl methane diisocyanate (MDI), toluene diiso-

\* Systematic name: 1(3H)-Isobenzofuranone,3,3-bis(4-hydroxyphenyl).

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**Table I** IR Absorption Frequency and Vibrational Assignment for Polyurethane

Vibration Assignments	Absorption Frequency cm <sup>-1</sup>
N—H stretching	3320
C=C stretching	1695
—O—C—O— stretching of phenolphthalein	1741
CH—CO stretching	1599
—CO—NH— <i>trans</i> -stretching	1534
C—O—C stretching	1059

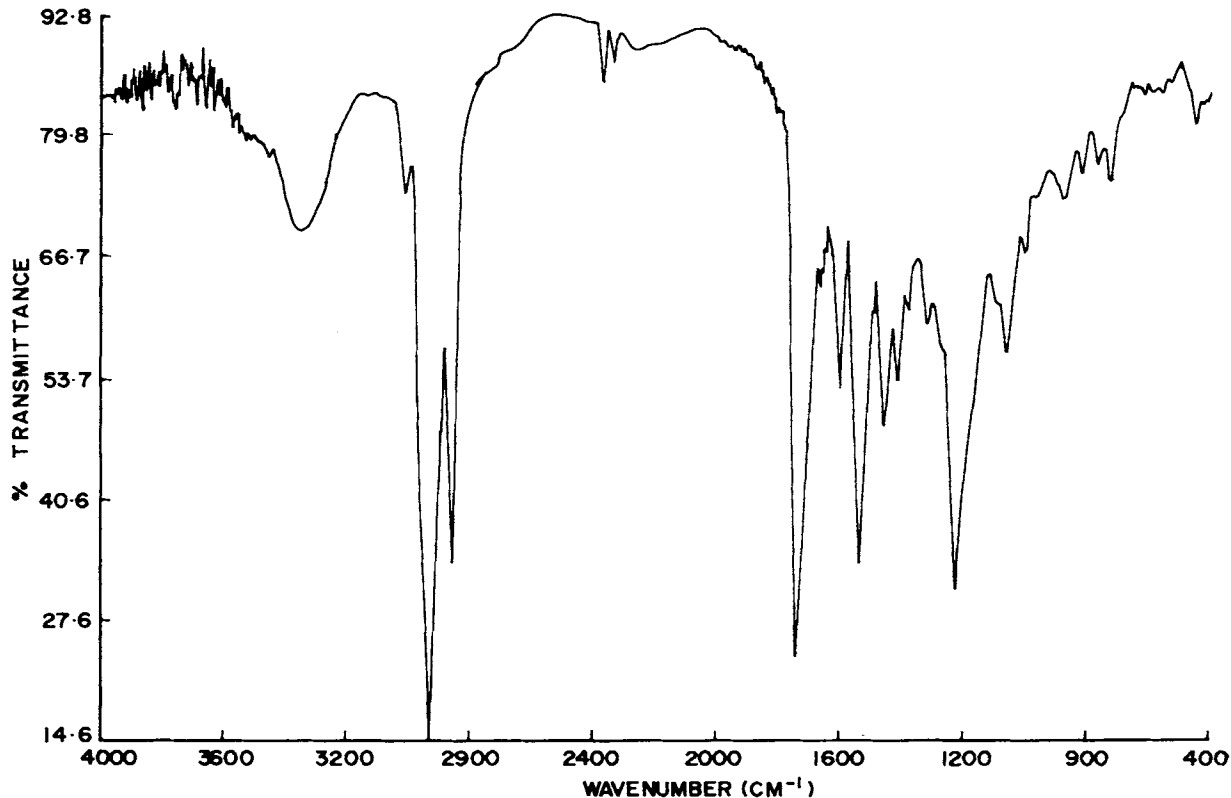
cyanate (TDI), and dibutyltin dilaurate (catalyst) all supplied by Fluka were used as received. Methyl ethyl ketone (MEK) (purex) was used after distillation.<sup>11</sup> Phenolphthalein solid (BDH Chemicals) was used as received.

### Preparation of Polyurethane

Castor oil, 9.37 g (0.01 mol), was initially dissolved in 50 mL of MEK and placed in a three-necked flask.

HMDI, 2.37 mL (0.01485 mol), was added followed by 2 to 3 drops of catalyst and the contents of the flask were stirred mechanically for about 10 h under nitrogen at 60–70°C. Phenolphthalein, 0.04297 g (0.0027 mol), was weighed accurately and was completely dissolved in 10 mL MEK. This was then transferred to the prepolymer and stirred again for 10 more h under nitrogen purge at 60–70°C. The solution was degassed under vacuum and poured over a mercury bed. The solution was left for evaporation overnight and the resulting clear film was carefully removed. The above procedure was repeated by varying the NCO/OH ratio and the following polymers were prepared: Castor oil/TDI/phenolphthalein, with NCO/OH of 1.1 (the remaining free —NCO groups were saturated with phenolphthalein) 1.2 and 1.3; castor oil/HMDI/phenolphthalein, with NCO/OH of 1.1, 1.2, and 1.3; castor oil/MDI/phenolphthalein, with NCO/OH of 1.1, 1.2, and 1.3 were prepared.

In the case of hydrogenated castor oil, it was first dissolved in MEK by gently warming it. After the complete dissolution of the hydrogenated castor oil, isocyanate was added and the solution was warmed to 60–70°C and purged with nitrogen. The same combinations of isocyanate/castor oil/phenol-



**Figure 1** FTIR spectrum of castor oil/TDI/phenolphthalein copolymer.

phthalein for castor oil were repeated for hydrogenated castor oil.

## MEASUREMENTS

The IR spectrum of the polymer film was recorded on a Nicolet 20-DX 3 FT IR spectrometer. Mechanical properties of the films were measured using an Instron Universal testing model 1112 by ASTM D1708-79.<sup>12</sup> Four samples from each film were taken for analysis. Tensile strength and percent elongation were calculated. The X-ray pattern was obtained using a Philip's wide-range X-ray diffractometer PW 1720, using Ni-filtered CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Differential scanning calorimetric studies were carried out with a Perkin-Elmer DSC-IB instrument with the samples in sealed aluminum pans under

nitrogen atmosphere at a heating rate of 10°C per min.

## RESULTS AND DISCUSSION

For the IR spectrum of the polymer, a thin film of the copolymer of TDI/castor oil/phenolphthalein with a NCO/OH ratio of 1.1 was prepared and washed many times with NaOH and water until no pink color was formed with NaOH, to remove any trace of unreacted phenolphthalein. The film was then dried in vacuum and the IR spectrum was taken. Table I shows the IR absorption frequency and vibrational assignments of the polyurethane. The IR spectrum of castor oil/TDI/phenolphthalein of NCO/OH = 1.1 is shown in Figure 1.

As the IR spectrum shows, the stretching fre-

**Table II Tensile Strength and Percent Elongation**

Polymer with Various NCO/OH Ratios	Tensile Strength (kg/cm <sup>2</sup> )	% Elongation
Castor oil/HMDI/phenolphthalein copolymer		
1.1	8.8	159
1.2	11.3	136
1.3	16.0	120
Castor oil/TDI/phenolphthalein copolymer		
1.1	18.0	108
1.2	25.8	91
1.3	31.4	71
Castor oil/MDI/phenolphthalein copolymer		
1.1	22.7	76
1.2	31.0	61
1.3	35.9	50
Hydrogenated castor oil/HMDI/ phenolphthalein copolymer		
1.1	17.4	111
1.2	19.7	98
1.3	33.8	83
Hydrogenated castor oil/TDI/phenolphthalein copolymer		
1.1	35.1	71
1.2	45.7	55
1.3	50.4	43
Hydrogenated castor oil/MDI/ phenolphthalein copolymer		
1.1	49.2	39
1.2	60.1	28
1.3	74.8	21
Copolymer of TDI and castor oil without phenolphthalein	5.5	210
Copolymer of TDI and hydrogenated castor oil without phenolphthalein	10.5	137

quencies of  $—O—CO—O—$  and  $C—O—C$ <sup>13</sup> clearly indicate that phenolphthalein is incorporated into polyurethane. Table II shows the tensile strength and elongation of various phenolphthalein-containing polyurethanes.

In the case of the copolymer of castor oil, HMDI, and phenolphthalein, as the NCO/OH ratio increases from 1 (containing no phenolphthalein) to 1.1 (where the remaining free NCO/OH groups are saturated with phenolphthalein), there is a significant increase in tensile strength. This is due to the presence of rigid aromatic rings in phenolphthalein that increase the tensile strength. In other words, there is an introduction of more symmetry into the ring that tends to increase tensile strength. As the content of phenolphthalein increases, the tensile strength also increases.

As one goes from the HMDI to the TDI series, tensile strength increases because of the rigid benzene ring in TDI. Likewise, when we descend the series in the TDI/castor oil/phenolphthalein copolymer series, the tensile strength increases because of the increase in the amount of phenolphthalein. The copolymer of MDI castor oil and phenolphthalein also shows the same trend of increasing tensile strength because the MDI contains two aromatic rings, but TDI has only one. The tensile strength increases when the system goes from TDI to MDI and when the phenolphthalein content increases.

While comparing the tensile strength of the copolymer of castor oil/TDI and hydrogenated castor oil/TDI, where there is no phenolphthalein in these two copolymers, the tensile strength is high for the

hydrogenated castor oil/TDI copolymer because of saturation of all the double bonds in castor oil, which induces rigidity into the system. Likewise, as phenolphthalein content increases in the case of hydrogenated castor oil, tensile strength also increases and it is greater than the tensile strength of the castor oil system of a particular NCO/OH ratio.

In regard to percent of elongation, as expected, it is indirectly proportional to the NCO/OH ratio, i.e., as NCO/OH increases with increase in phenolphthalein content, the percent of elongation decreases.

The X-ray diffraction spectrum<sup>14</sup> of polyurethane film of hydrogenated castor oil/MDI/phenolphthalein (NCO/OH = 1.1) was run and the  $d$  values for the corresponding  $2\theta$  values are shown in Table III.

From the X-ray diffraction pattern of MDI/castor oil/phenolphthalein (NCO/OH = 1.1), a broad peak at  $2\theta = 21.6$  with 100% intensity was observed. Petrovic and Fajnik<sup>15</sup> observed two peaks at  $2\theta$ -20 and  $2\theta$ -8 for MDI/castor oil polyurethane. The appearance of these peaks are caused by the existence of short-range ordering corresponding to the first and second spheres of coordination.<sup>15,16</sup> No melting was observed in the DSC in the case of MDI/castor oil polyurethanes by Petrovic and Fajnik.<sup>15</sup> Hence, it is concluded that MDI/TDI polyurethane is completely amorphous. Metal-containing polyurethanes of the type  $Zn[\text{mono}(\text{hydroxyethyl})\text{phthalate}]_2/\text{MDI}$  is found to be semicrystalline as revealed by the X-ray pattern.<sup>17</sup>

The DSC study of castor oil/MDI/phenolphthalein copolymer with NCO/OH = 1.1 shows a sharp change in  $\Delta H$  at 295°C and, thereafter, the base line levels off. The DSC was run from 37 to 425°C at a scan rate of 10°C per min. After 295°C, the polymer undergoes decomposition.

Since the X-ray diffraction pattern of MDI/hydrogenated castor oil/phenolphthalein shows broad peaks and DSC shows a sudden change in  $\Delta H$ , the polymer is semicrystalline.

**Table III** X-ray Diffraction Pattern Data for the Copolymer Hydrogenated Castor Oil/MDI/Phenolphthalein (NCO/OH = 1.1)

$2\theta^a$	$I/I^b$	$d^c$	Description of Peaks
21.6	100.0	4.11	Very broad
44.4	7.1	2.04	Aluminum 2.02 <sup>d</sup>
65.0	9.0	1.43	Aluminum 1.43 <sup>d</sup>
78.3	6.5	1.22	Aluminum 1.22 <sup>d</sup>

<sup>a</sup> Angle of diffraction.

<sup>b</sup> Ratio of intensity of diffraction to intensity of strongest line in percent.

<sup>c</sup> Spacings between parallel planes.

<sup>d</sup> The  $d$  spacing values for aluminum obtained from the Joint Committee for Powder Diffraction USA (1950).

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