

# Polyurethane Anionomers Using Phenolphthalins. II

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## SYNOPSIS

Polyurethane anionomers based on phenolphthalins have been characterized by differential scanning calorimetry, swelling, and mechanical studies. DSC study shows that introduction of ionic groups into the polymer chain lowers the  $T_g$  of the polyurethane. Swelling studies reveal that water uptake is high for ionomers. From the tensile data we observe that  $Zn^{+2}$  neutralized ionomers showed enhanced properties. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polymers based on aromatic units are of interest due to their superior thermal stability and improved mechanical properties like good strength and toughness. Incorporation of aromatic units as chain extenders have been of interest to prepare cast, functionalized, and liquid crystalline polyurethanes.<sup>1-3</sup> Morgan's detailed work in preparing polyesters using phenolphthalein and substituted phenolphthaleins<sup>4</sup> threw a new light on the use of these compounds for polymer synthesis. Subsequently, phenolphthalein and its derivatives have been used to prepare a variety of polymers.<sup>5-7</sup>

Phenolphthalins, due to their ionic functionality and triphenyl methane units, yield polymers with superior properties. They have been used to prepare heat-resistant polyethers,<sup>8</sup> fire-resistant thermosets, and thermoplastics for aircraft and aerospace applications.<sup>9,10</sup> Recently, phenolphthalins and their derivatives have been used to prepare fluorescent poly(arylene ether)s,<sup>11</sup> poly(imidoaryl ether ketone)s, and poly(imidoaryl ether sulfone)s.<sup>12,13</sup>

Polyurethane ionomers are versatile materials that offer an interesting combination of properties to the needs of end user by the incorporation of different ionic groups into the polyurethane chain.<sup>14-26</sup> In this work we have used these compounds for the synthesis of polyurethane ionomers and studied their properties.

## EXPERIMENTAL

Polyurethanes were prepared by chain extending the prepolymer based on PTMG and TDI with the phthalins in different mole ratios. They were then converted into sodium and zinc anionomers. The detailed synthetic procedure is given in our earlier publication.<sup>27</sup> The polymer and ionomer codes are given in Table I.

### Physicochemical Characterization Techniques

Differential scanning calorimetric study was performed using a Du Pont 910 instrument equipped with a standard cell at a heating rate of 10°C/min under nitrogen atmosphere. The scanning temperature range was from -100 to +120°C. The samples were quenched on the cell using liquid nitrogen to attain low temperatures. The amount of samples taken for each run was 5 ± 0.2 mg.

Swelling studies were performed for the samples in water. Samples of size 2 × 2 cm were cut and immersed in water at 30°C. The samples were taken out at stipulated times, wiped with a tissue paper, and allowed to stand for a minute in air and then weighed accurately.

Mechanical properties of the polymers were evaluated using an Instron universal testing machine model 4501 at a crosshead speed of 50 mm/min. The specimens were cut into a dumbbell shape of length 2.1 cm and breadth 0.4 cm. An average of four specimens for a sample was considered.

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**Table I** Glass Transition Temperatures and Mechanical Properties of the Polyurethanes and their Anionomers

Polymer Compositions	Polymer Codes	$T_g$ (°C)	Tensile Strength at Break (MPa)	% Elongation at Break	
PTMG <sub>1000</sub> /2TDI/Phenolphthalin	PH	-55.0	2.50	1293	
	PH-Na	-61.0	4.70	2869	
	PH-Zn	-58.0	12.10	2004	
PTMG <sub>1000</sub> /2TDI/Phenolphthalein	PH <sub>R</sub>	-59.5	0.53	502	
	PTMG <sub>1000</sub> /2TDI/Thymolphthalin	TH	-46.0	0.39	2020
		TH-Na	-52.5	0.62	2505
PTMG <sub>1000</sub> /2TDI/Tetrabromo phenolphthalin	TH-Zn	-50.0	1.33	1208	
	BrPH	-50.5	0.17	189	
	BrPH-Na	-54.5	0.34	467	
PTMG <sub>1000</sub> /2TDI/Phenolphthalin + 1,4-butane diol	BrPH-Zn	-53.0	0.98	296	
	PHB	-50.0	0.38	763	
	PHB-Na	-55.5	0.53	1347	
	PHB-Zn	-53.5	1.05	986	

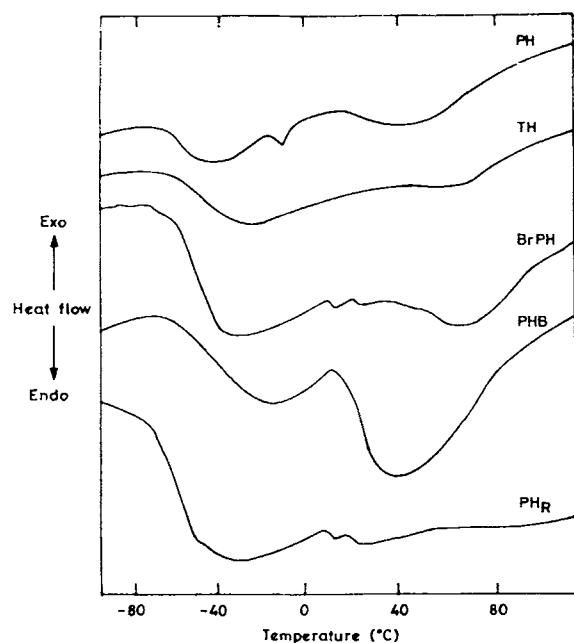
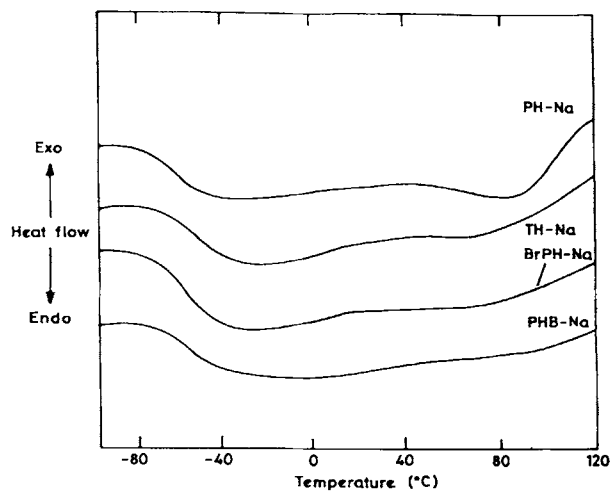
## RESULTS AND DISCUSSION

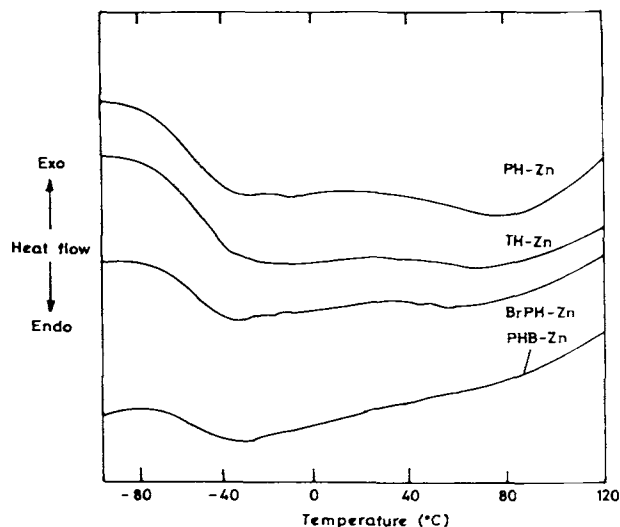
### DSC Study

The DSC curves of polyurethanes and that of ionomers are given in Figures 1-3. The midpoint of the transition is given as the glass transition temperature and the values are mentioned in Table I. For all the polyurethanes the  $T_g$  was well below the room temperature, which is characteristic of PTMG<sub>1000</sub>-based polymers. For these chain extended

systems the transitions of the hard segments were not clearly observable. This is consistent with the work by Cooper et al., based on the work on the polyurethane anionomers using dimethylol propionic acid.<sup>16</sup> For the PHB polymer, a broad endotherm observed at 41°C is due to a short range ordering of hard domains. This is due to the introduction of butanediol units along with phenolphthalin in the chain extension stage.

When we compare the  $T_g$  of the ionomer to those with carboxylic acid groups, we observe a shift in  $T_g$  towards lower values. This is due to phase separation caused by the realignment of hydrogen bonding between the hard and soft segments by the ionic groups

**Figure 1** DSC curves of polyurethanes.**Figure 2** DSC curves of polyurethane ionomers with Na<sup>+</sup> counterions.



**Figure 3** DSC curves of polyurethane ionomers with  $Zn^{2+}$  counterions.

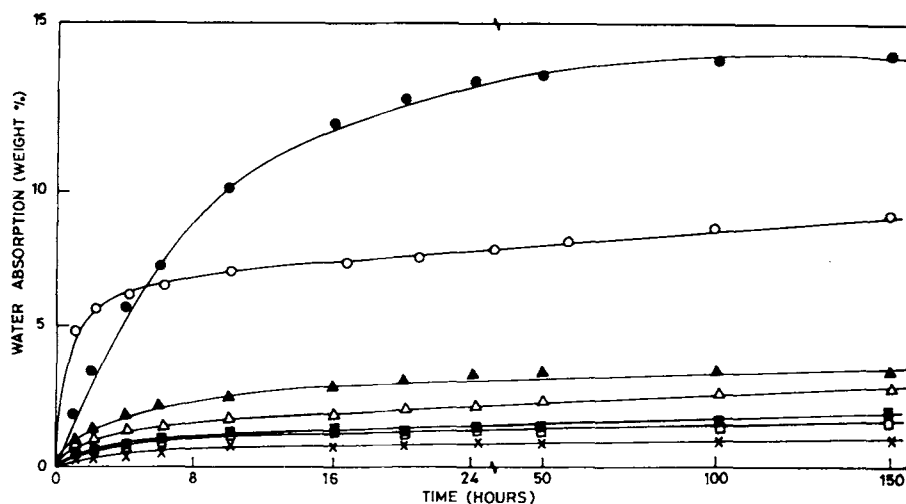
leading to more phase purity of soft segments. Thus, the  $T_g$  shifts towards that of the basic polyol unit. When we compare the  $T_g$  values of polyurethanes with Na and Zn as counterions, no appreciable shift is observed, which is also consistent with the results observed by Cooper et al.<sup>16</sup> But the magnitude of phase separation observed here for the ionomers is less than those of carboxylate systems based on aliphatic groups. This may be due to the rigidity of these aromatic systems, which hinder significant phase separation of the hard segments, which are dispersed well in the soft segments.

### Swelling Studies

The water absorption studies of polyurethanes and ionomers are shown in Figures 4 and 5. Generally, ionomers showed increased water absorption than their nonionic counterpart. The water uptake value of PH and  $PH_R$  were low when compared to PH-Na and PH-Zn. Once the carboxyl groups were converted into the sodium salt, water uptake increases. When we compare the ionomers containing sodium as a counterion with that of zinc as a counterion, water uptake is more for the former. This is due to chemical crosslinking by the divalent metal ion zinc, which is also proved by mechanical properties study.

### Mechanical Properties

The uniaxial stress-strain graphs of the polyurethane and ionomers are given in Figures 6 and 7. The ultimate tensile strength and percentage of elongation at break are given in Table I. Polyurethanes containing  $-COOH$  groups had enhanced properties compared to the reference sample  $PH_R$  without the  $-COOH$  groups. All the ionomers showed an increase in tensile strength more than their base polymer. As the ionic groups are introduced into the polymer chain the aggregated hard segments act as strong physical networks, leading to an increase in tensile strength. Among the polyurethane ionomers, those with zinc as counterions showed enhanced tensile strength. This is due to the chemical crosslinking of  $Zn^{+2}$  ions across two carboxyl groups apart from the columbic forces. This ionic crosslinking imparts more chain stiffness to



**Figure 4** Water absorption behavior of (×)  $PH_R$ , (■) PH, (●) PH-Na, (▲) PH-Zn, (□) TH, (○) Th-Na, and (△) TH-Zn.

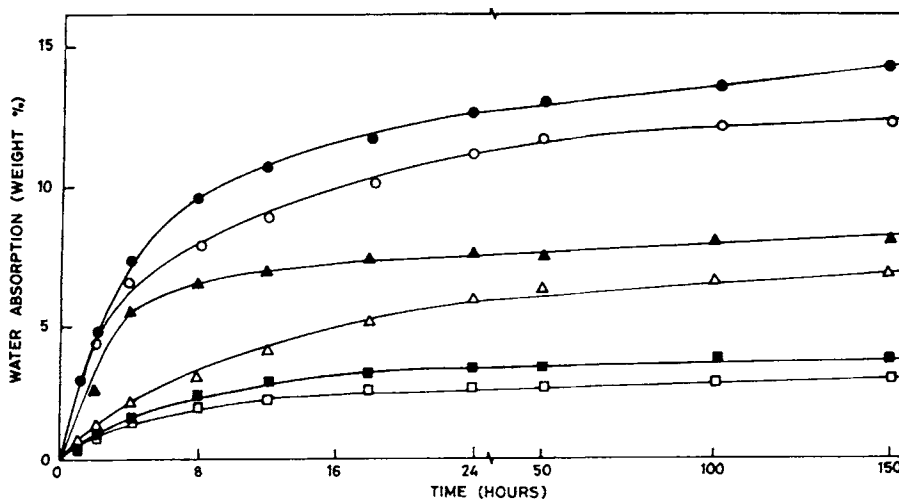


Figure 5 Water absorption behavior of (□) BrPH, (○) BrPH-Na, (Δ) BrPH-Zn, (■) PHB, (●) PHB-Na, and (▲) PHB-Zn.

the polyurethane chain and, thus, elongation is less than that of Na<sup>+</sup> as a counterion.

The overall excellent elongation observed for these polymers is due to the stress-induced crystallization of the soft segment, which stops early failure

of the sample. Ionization of the —COOH groups drives the system towards more phase separation, which in turn, enhances the ability of the soft segment to crystallize under further strain. When we

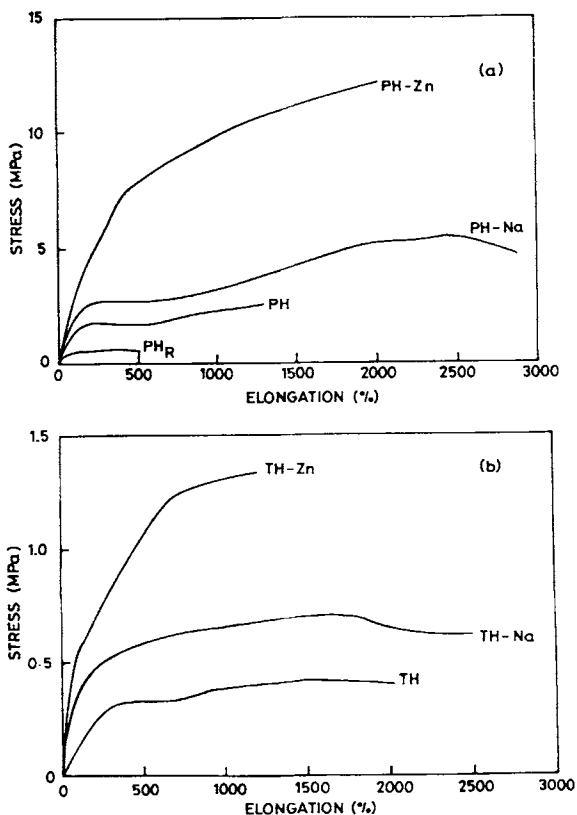


Figure 6 Stress-strain curves of (a) PH systems and (b) TH systems.

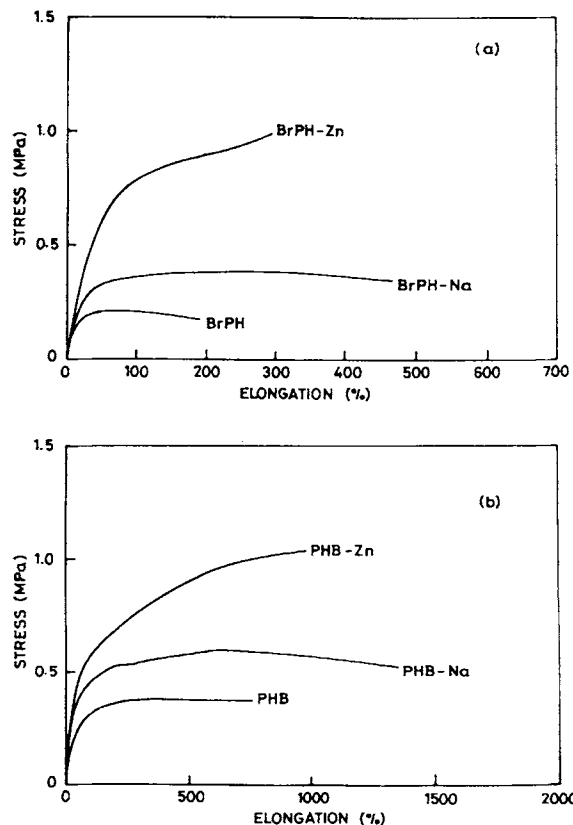


Figure 7 Stress-strain curves of (a) BrPH systems and (b) PHB systems.

compare the polyurethanes using different phthalin chain extenders, the one prepared from phenolphthalin (PH) showed superior properties than tetrabromo phenolphthalin or thymolphthalin (TH and BrPH). One reason may be due to the reasonably higher molecular weight of the former.<sup>27</sup> Apart from this, phenolphthalin moieties introduce rigid aromatic hard segments imparting good mechanical strength. In the case of substituted phenolphthalins as chain extenders, efficient packing of the phthalin units in the chain is hindered due to the alkyl and halogen groups on the phenyl rings. In the case of the PHB polymer using a mixed chain extender (phenolphthalin and butanediol) ordered arrangement is hindered due to a difference in the size and shape of the extenders. Thus, PH possess more superior properties than PHB. Chain extended polyurethanes synthesized using phenolphthalins, and the prepolymer based on PTMG units have been found to be of extensive application in the area of coatings onto leather, paper, and textiles.

## CONCLUSIONS

Differential scanning calorimetric study shows that the phase separation occurs in ionomers, leading to more soft segment purity. Swelling studies reveal that water uptake is higher for ionomers than their nonionic counterpart. Tensile strength data indicate that polyurethanes containing Zn<sup>+2</sup> ions possess enhanced mechanical properties.

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