

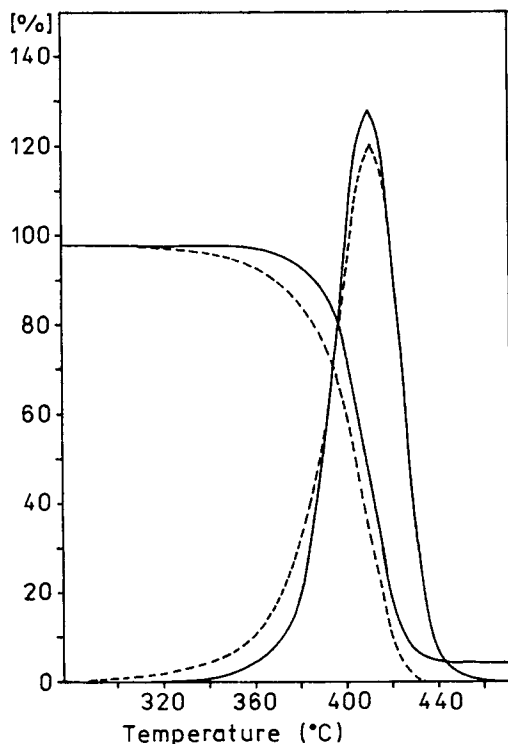
# NOTE

## Application of New Copolyimides as Phases for Gas-Liquid Chromatography

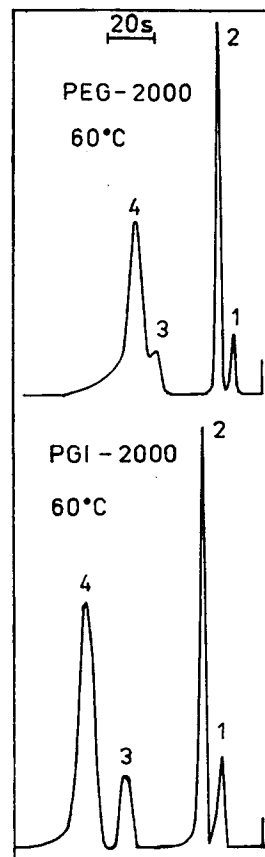
The majority of known polyimides and copolyimides are insoluble and do not melt which limits their possible applications. Recently some studies showed that copolyimides containing flexible monomer units have favorable processing properties.<sup>1,2</sup> For example, Feld with coworkers and Takeda combined a bismaleimide structure with a polyglycole chain.<sup>3,4</sup>

Polyethylene glycols (PEG) are well known as commercial phases for packing materials. Derivatives of these, such esters as adipate, terephthalate, and succinate are used for chromatography also. The presence of polar bonds in molecular structure changes the conditions of chromatographic resolution.

This paper is devoted to application of our copolyimides (PGI) for gas chromatography. The synthesis of these polymers and their physico-chemical properties were de-

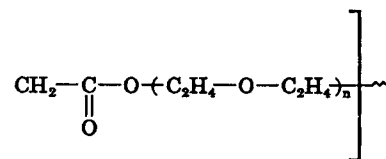
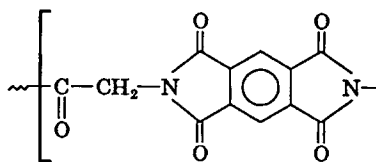


**Figure 1** TG and DTG curves of PEG-2000 [-----] and PGI-2000 [—]



**Figure 2** Chromatograms of standards mixture. 1—isooctane; 2—ethyl bromide; 3—methanol; and 4—benzene.

scribed previously.<sup>5,6</sup> The general formula of these copolymers is given below.



**Table I** The Retention Times of Copolyimide Packings (1 m long column, 60°C)

Polymer	Retention Time (s)											
	a	b	c	d	e	f	g	h	i	j	k	l
PEG-2000	62	28	34	36	14	94	28	18	8	200	10	12
PGI-6000	62	30	37	38	14	99	28	19	8	210	10	13
PGI-4000	62	32	39	41	14	109	29	22	8	221	10	16
PGI-2000	63	36	42	46	14	120	31	24	8	240	11	19

a—chloroform; b—methanol; c—ethanol; d—benzene; e—cyclohexane; f—water; g—ethyl acetate; h—acetone; i—hexane; j—pyridine; k—isooctane; and l—ethyl bromide.

Three copolyimides PGI-2000, PGI-4000, and PGI-6000 ( $n = 20, 40, 60$ ) obtained from bis(*N*-chloroformylmethyl)pyromellitimide and polyethylene glycols of different molecular weight (2000, 4000, and 6000) were chosen for investigation. Polyethylene glycol 2000 was used as a "standard" phase for comparison.

Furthermore, the thermal properties of copolyimides were studied by the TG method. The results obtained define the temperature limit for their use in the chromatographic process.

## EXPERIMENTAL

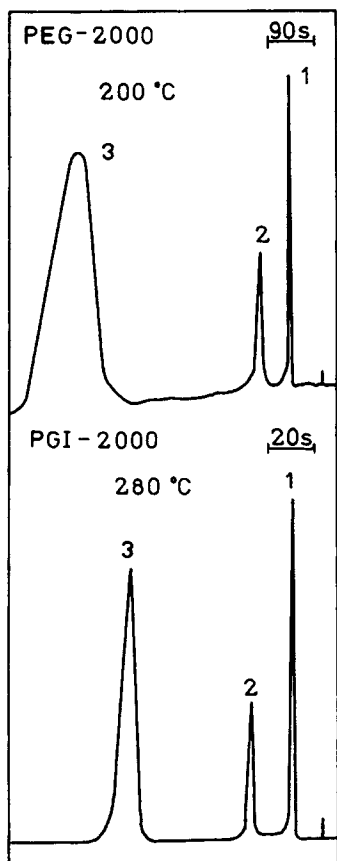
The monomer and copolymers were synthesized according to the previous description.<sup>5,6</sup> TG and DTG studies were held in a dynamic inert gas atmosphere, using TG analyzer model DuPont 1090. The heating rate was 10°C/min. Gas chromatographic analyses were carried out with nitrogen as carrier gas and with a katharometer. The investigated phases were dissolved in chloroform and spread on Chromosorb W. The concentration of phases was always 10%. The packings were placed into 1 m long steel columns.

## RESULTS AND DISCUSSION

The thermogravimetric analyses were performed for copolyimides PGI-2000, 4000, 6000, and PEG-2000 for comparison. For all copolyimides and for the polyglycol, maxima on DTG curves representing decomposition processes appear at the same temperature (408°C), however, the beginning of pyrolysis is different for these polymers. The polyglycol gradually loses weight at 300°C and decomposes totally at 430°C.<sup>7</sup> Conversely, degradation of copolyimides starts rapidly, but at a higher temperature (320°C for PGI-6000, 325°C for PGI-4000, and 330°C for PGI-2000). The greatest difference of thermal resistance appears for PGI-2000. This is clearly due to the large number of imide rings present here in the copolymer chain. For better readability, in Figure 1 TG and DTG curves are presented only for PGI-2000 and PEG-2000.

The usefulness of copolyimides as phases in packings was studied using some chromatographic standards. Polyethylene glycol 2000 was used as a reference phase. The retention times of standards tested on columns with PEG-2000 and PGI-2000 are given in Table I.

As shown for pyridine, water, alcohols, benzene, and ethyl bromide, the retention times gradually increase in accordance with the rise of percentage by weight of imide fragments in the copolymer chain. The retention times for hydrocarbons, chloroform, and others are almost identical. In Figure 2, by way of example, the analysis of a standard mixture performed under the same chromato-



**Figure 3** Chromatograms of standards mixture. 1—*p*-xylene; 2—naphthalene; and 3—*p*-chlorophenol.

graphic conditions is presented. The resolution, in case of column with PGI-2000, seems better than for PEG-2000.

Commercial polyethylene glycols usually are not recommended for work above 225°C, (for PEG-2000 up to 200°C). Thermogravimetric analyses show that copolyimides have higher thermal stability than polyglycols.

In Figure 3 the chromatogram performed in 280°C for the column with PGI-2000 is given. Good resolution of the tested mixture at this temperature is shown. Also, the base line, in this case, is straight and stabilized. In this plot the chromatogram for PEG-2000 at the highest permissible temperature for this phase (200°C) is also demonstrated. In this case, for the same standard mixture, the retentions are about five times longer than for PGI-2000. Also, the peak widths are much greater for substances developing on a column with polyethylene glycol. These facts allow for the use of PGI-2000 as a phase for gas-liquid chromatography up to 280°C.

## CONCLUSIONS

The reaction of bis(*N*-chloroformylmethyl)pyromellitimide with polyglycols of diversified molecular weight, leads to copolymers of controlled contents of imide rings in a polymer chain. This enables one to change such parameters as thermal stability or polarity. It was found that thermal resistance increased proportionally to the imide ring content.

An application of these copolyimides as phases in gas-liquid chromatography proves their usefulness as packing materials. The presence of heterocyclic structures in the polyglycol chain changes the polarity and, as consequence

of this, the time of retention in the chromatographic process. These facts, together with an extended operating temperature range up to 280°C, allow us to recommend them as new valuable supplements in the list of known phases for GLC.

## References

1. H. R. Kricheldorf and R. Pakull, *Macromolecules* **21**, 551 (1988).
2. B. A. Tagiev and R. I. Mustafar, *Wysokomol. Soj. Krat. Soob.*, **31**, 42 (1989).
3. W. A. Feld, B. Ramalingam, and F. W. Harris, *J. Polym. Sci. Chem. Ed.*, **21**, 319 (1983).
4. S. Takeda, H. Akiyama, and H. Kakichi, *J. Appl. Polym. Sci.*, **35**, 1341 (1988).
5. G. Montaudo, C. Puglisi, N. Biçak, and A. Orzeszko, *Polymer* **30**, 2237 (1989).
6. A. Orzeszko and K. Mirowski, *Makromol. Chem.*, **191**, 701 (1990).
7. A. Orzeszko and A. Kolbrecki, *J. Appl. Polym. Sci.*, **25**, 2969 (1980).

ANDRZEJ ORZESZKO  
Agricultural University  
Institute of Chemistry  
ul. Rakowiecka 26/30  
02-528 Warsaw  
Poland

Received November 27, 1989

Accepted April 23, 1990