

CHARACTERIZATION OF COMPOSITIONAL HETEROGENEITY OF SEGMENTED COPOLYMERS BY GPC TECHNIQUE*

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ABSTRACT

The GPC technique with two detectors has been used to study the heterogeneity in composition (hard segment content) of a series of polyethylene terephthalate/polycaprolactone segmented copolymers. Improvement in data treatment has been made to avoid the difficulty resulted from the lack of low molecular weight hard segment homopolymers. Results show that for each sample the molecules of larger coil size in CHCl_3 usually have higher hard segment content. A parameter, the average deviation of hard segment content, has been proposed to characterize the heterogeneity in composition of the samples. It is found that the heterogeneity of the samples increases with increasing their average hard segment content.

INTRODUCTION

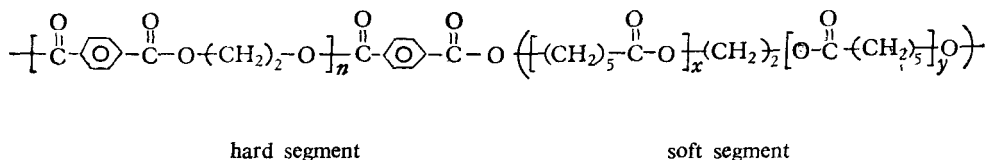
The macromolecules of segmented copolymers are usually considered to be statistically identical in chemical composition and average hard segment length. The microphase separation of hard and soft segments is postulated to explain the morphological features and properties of these copolymers. It has been found recently that in the case of segmented polyester-polyether copolymer^[1] and polyurethanes^[2] because of the heterogeneity of the reaction system their molecules can be quite different in their chemical composition and average hard segment length, and both microphase separation of segments and macrophase separation of macromolecules with different hard segment content and average length should be considered. As this phenomenon is supposed to be common for segmented copolymers, it becomes necessary to have methods convenient to characterizing the compositional heterogeneity of these molecules. The methods used in the previous papers^[1,2], the thin layer chromatography and solvent extraction, can give a crude estimation of the heterogeneity and are more feasible for very heterogeneous samples. The gel permeation chromatography is a powerful technique for determining the molecular weight distribution of polymer samples due to its ability in separating macromolecules according to their size in the elution solvent. Much effort has been made in extending the GPC technique to the characterization of compositional heterogeneity of copolymers. Usually a GPC furnished with a dual detector system consisting of differential refractometer and IR or UV spectrometer is used for this purpose, and the composition at each elution volume (the so-called point by point composition) can be deduced from the measure-

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ment. In some cases the combination of GPC and thin layer chromatography and/or pyrolysis gas chromatography has been adopted^[3,4]. Samples studied include statistical copolymers like poly(vinyl chloride-co-vinyl stearate)^[5], poly(styrene-co-methyl acrylate)^[6], poly(styrene-co-methyl methacrylate)^[7], poly(α -methyl styrene-co-butadiene)^[8] and poly(styrene- ω -butadiene)^[9]. Besides, di- or tri-block copolymers of polystyrene with polymethyl methacrylate or polybutadiene^[10,12] and graft copolymers^[13] have also been studied. In this work the GPC technique with two detectors is used successfully in characterizing the compositional heterogeneity of a series of polyethylene terephthalate (PET)/polycaprolactone (PCL) segmented copolymers.

EXPERIMENTAL

Segmented PET/PCL copolymers with PET content from 40%—80% by weight were synthesized by a two step method involving ester exchange and polycondensation reactions^[14]. Polycaprolactone diols of molecular weight 2000, 5000 and 8000 were used. The molecules are composed of hard and soft segments as shown below:



The intrinsic viscosity of the samples in phenol was measured at 30°C. The samples have been separated by extraction with different solvents, and no detectible difference in composition has been found for soluble and insoluble fractions of each sample.

The chromatograph used was a Waters Model LC/GPC 244 with a differential refractometer and a UV detector connected in series. The ultraviolet spectrophotometer was set at 280 m μ for monitoring the concentration of PET segment. At this wavelength PCL is transparent. Two Waters columns containing μ -Styragel with the size designations of 10⁴Å and 500Å respectively were used. The flow rate was 1 ml/min.

RESULTS AND DISCUSSION

In our GPC measurements the UV detector is set to measure the hard segment, while RI detector measures both hard and soft segments. Consequently

$$r' = k'_h f G_c \quad (1)$$

$$r = k_h f G_c + k_s (1-f) G_c \quad (2)$$

where r' and r are the output of the UV and RI detectors respectively, k'_h , k_h and k_s are the proportionality constants and G_c is the amount of the copolymer with hard segment content f . If constants k'_h , k_h and k_s have been obtained from calibration measurements of soft and hard segment homopolymers, then the dependence of hard segment content on elution volume can be deduced from experimental GPC curves r' and r according to equations 1 and 2. The

difficulty for segmented copolymers is that usually no hard segment homopolymer of proper molecular weight is available, and constant k_h is molecular weight dependent. In order to avoid this trouble equation 3 was derived from equations 1 and 2.

$$1/f_i - 1/f_{i+1} = (R_i - R_{i+1})k'_h/k_s \quad (3)$$

$$\Sigma[(r'_i/\Sigma r'_i)/f_i] = 1/\bar{f} \quad (4)$$

Here $R_i = r_i/r'_i$, and indices i and $i+1$ indicate the elution volume position. Combining eq. 3 and the law of mass conservation (eq. 4), one can determine the hard segment content f at any GPC count from experimental curves. $\bar{f}$ in eq. 4 is the average hard segment content of the sample and can be determined by NMR or UV measurements. A model compound dimethyl terephthalate (DMT) was used for UV detector calibration. The curves for determining k'_h and k_s are given in Fig. 1.

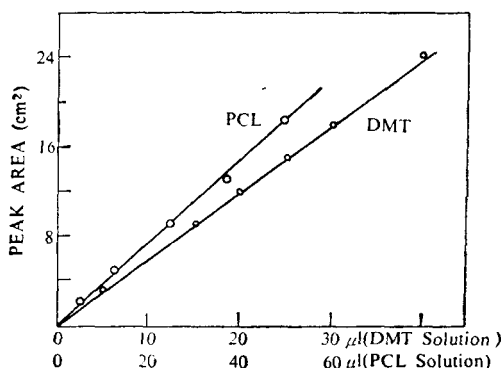


Fig. 1 The calibration curves for UV and RI detectors. The concentrations of PCL and DMT solutions in CHCl_3 are $9.322 \times 10^{-2} \text{ mg}/\mu\text{l}$ and $4.035 \times 10^{-4} \text{ mg}/\mu\text{l}$ respectively

Some of the results are given in Figs. 2—4, which show the distribution of the amount of copolymers $W_i = G_i/\Sigma G_i$ and the hard segment content f_i as functions of elution volume. The compositional heterogeneity of the samples is obvious and usually molecules of larger coil size in CHCl_3 have higher hard segment content. A parameter H , the average deviation of f with respect of $\bar{f}$, is proposed to quantitatively characterize the degree of heterogeneity and is

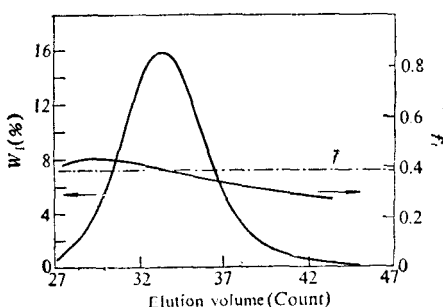


Fig. 2 Dependence of W_i and f_i on the elution volume for sample E20-2

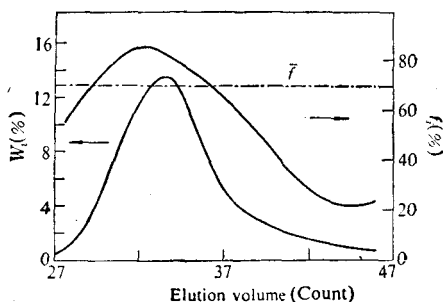


Fig. 3 Dependence of W_i and f_i on the elution volume for sample E55-2

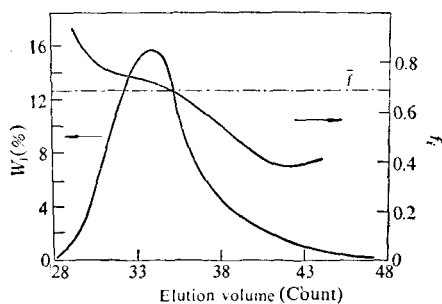


Fig. 4 Dependence of W_i and f_i on the elution volume for sample E55-8.

defined as:

$$H = \sum |f_i - \bar{f}| W_i \quad (5)$$

The H values of the samples are listed in Table 1. Comparison of the results of different samples (Fig. 5) indicates that the heterogeneity of these copolymers in composition increases with increasing their average hard segment content $\bar{f}$, especially when $\bar{f}$ is higher than about 65%. The influence of the molecular weight of polycaprolactone diols on the degree of heterogeneity in composition is not regular.

Table 1 Data of PET/PCL segmented copolymers

Sample	E20-2	E40-2	E55-2	E70-2	E55-5	E55-8
$[\eta](\text{dl/g})$	1.03	0.96	0.88	0.60	0.73	0.71
M of PCL diol	2000	2000	2000	2000	5000	8000
$\bar{f}, (\%)$	39.5	59.6	69.3	81.1	64.0	68.6
H	0.036	0.045	0.120	0.097	0.040	0.083

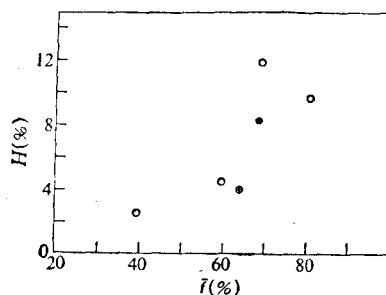


Fig. 5 Dependence of heterogeneity H on the average hard segment content of the samples

In GPC measurements the macromolecules are separated according to their coil size in the elution solvent. It is difficult to discriminate the influence of molecular weight and the composition of the macromolecules on their coil size. So the composition distribution can only be obtained from GPC measurements by assuming that the macromolecules at any GPC count are homogeneous in their composition. Typical results of our samples are given in Figs. 6 and

7. It can be seen that the compositional distribution is not very wide, and the distribution curves are not symmetric with respect to their peak position.

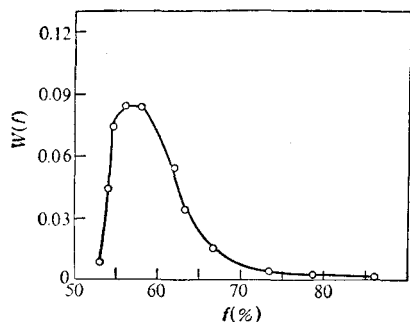


Fig. 6 Compositional distribution curve of sample E40-2

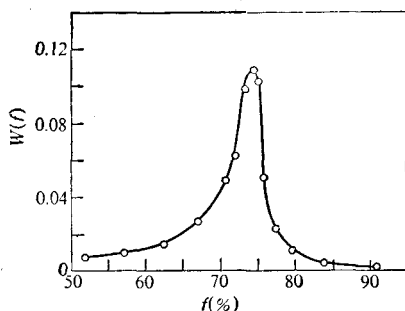


Fig. 7 Compositional distribution curve of sample E55-8

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