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GPC Study of Ethylene-Propylene Copolymers Combined with Viscometry and IR Spectroscopy

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SUMMARY

By combining GPC fractionation with IR spectroscopy of ethylene-propylene copolymer (EP) samples, it has been shown that copolymer composition of EP's used in this study does not depend on molecular weight. Thus, contrary to earlier investigations by others, molecular weight distributions (MWD) and averages of EP's have been determined by using only experimental data such as GPC traces, universal calibration curve of GPC, and intrinsic viscosities. A comparative study has been carried out by using the MV method (called median value method) and the method of Ogawa and Inaba (OI method) for determination of MWD's and molecular weight averages of EP's. Application of the MV method results in lower molecular weight averages than the use of the equations proposed by Ogawa and Inaba for calculation of Mark-Houwing constants of EP's. However, polydispersities were found to be the same in both methods. The MV method also yields composition depending reliable pairs of Mark-Houwink constants, a and K, for EP's in 1,2,4-trichloro-benzene at 135 ^oC.

INTRODUCTION

Nowadays gel permeation chromatography (GPC) is the most frequent method used for determination of molecular weight distribution (MWD) and molecular weight averages of polymers. However, most of the papers concern only with homopolymer's GPC and MWD, and much less studies are known dealing with GPC of copolymers. Since GPC has proved to be a fruitful method in studying a wide variety of phenomana, e.g., synthesis and degradation, in polymer research for homopolymers, it is obvious that polymer scientists wish also to obtain quantitative data by GPC for processes of copolymers. However, GPC separates macromolecules according to their hydrodynamic volumes, thus, if the copolymer composition depend on molecular weight, quantitative treatment of GPC curves desires more information than those provided by the universal calibration curve (SAMAY 1977, OGAWA and INABA 1977).

During our continuing investigations on thermooxidative degradation of polyolefins we became interested in studying scission of the polymer chain and changes of MWD during degradation of ethylene-propylene (EP) copolymers (LÁSZLÓ-HEDVIG et al., 1981). In the past few years Ogawa and coworkers (OGAWA et al., 1973, 1974a, 1974b, 1977) have extensively studied fractionation and determination of MWD of EP's by GPC. Ogawa and

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coworkers attempted to simulate MWD of EP's using a bivariant distribution function. They have also proposed simple relationships between chemical composition of EP's, intrinsic viscosity and Mark-Houwink constants (OGAWA and INABA, 1974a).

This paper concerns study of GPC combined with viscometry and infrared spectroscopy of EP copolymers.

EXPERIMENTAL

A. Materials

Commercial EP copolymers (Profax type) of various polyethylene (PE) content (see Table I), a low density polyethylene (LPDE; FA 2210) and an isotactic polypropylene (IPP; Moplen S30 G) were used. Samples were purified by dissolution and precipitation as described in a previous paper (BODOR et al.,1977).

B. Techniques

IR spectroscopy

Films (~60 μm) were pressed in Ar atmosphere at 190-195 °C from the purified polymer powders. In the case of polyethylene and polypropylene mixtures before making films for IR spectroscopy, samples were homogenized by a rolling mill. The hot films were immediately cooled in ice-water mixture for 30 sec. IR spectra of these films were taken with an UR-10 (Zeiss, Jena) spectrophotometer.

GPC

A Waters GPC instrument (Model 200) was used with four Styragel columns (10^6, 10^5, 10^4, 10^3 Å). Distilled 1,2,4-trichlorobenzene (TCB) containing 0.2% antioxidant was used as solvent; flow rate: 1 ml/min, operating temperature: 135 °C. Calibration was made with polystyrene (Waters) and polypropylene (National Physical Laboratory) standards. The concept of universal calibration (GRUBISIC et al., 1967) was used and chromatograms were corrected according to Pierce and Armonas (PIERCE and ARMONAS, 1968). Fractions of EP copolymers were collected at four elution volume ranges (see Figure 3). Copolymer fractions of all the three EP's (EP-1, EP-2, and EP-3) were purified by precipitation into excess of cold methanol. Then the fractionated samples were dried in vacuum at 40 °C. Finally, for IR measurements films were pressed as described in the previous section.

Viscometry

The solvent and conditions were the same as for GPC measurements, i.e., the viscosity of polymer samples was determined in TCB at 135 °C according to ASTM D1601-61. The capillary was of lower diameter to achieve reasonable efflux time for the pure solvent.

RESULTS AND DISCUSSION

A. Chemical Composition of EP Copolymers Determined by IR Spectroscopy

The composition of EP copolymers was determined by IR spectroscopy using a modification of the method of DRUSCHEL and IDDINGS (1963). These authors synthesized EP copolymers from propylene and C^{14}-labelled ethylene. Composition of EP's were determined by comparing characteristic IR intensity ratios to that of obtained by liquid scintillation counting. In this work, the $A_{720+734}/A_{1170}$ integral absorption ratios has been used for calculating compositions of our EP copolymers. The corresponding band areas are illustrated in Figure 1 which shows the IR spectrum of EP-2 copolymers. The IR calibration curve, shown in Figure 2, was obtained by using film samples of polyethylene (PE) and polypropylene (PP) mixtures containing various ratios of PE/PP. According to the data in Table I, our investigated copolymer samples, EP-1, EP-2, and EP-3 contain 8,18, and 29 % PE, respectively

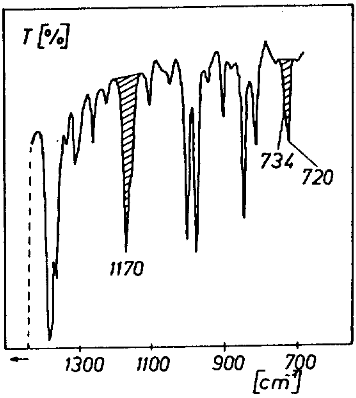

Figure 1.
The IR spectrum of EP-2 copolymer film.
(T = transmittance)

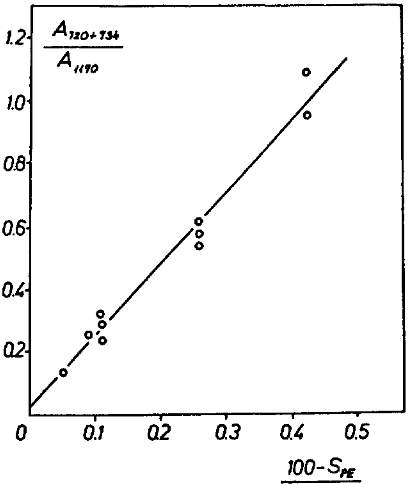

Figure 2.
The IR Calibration curve obtained by PE and PP mixtures (S_{PE} = wieght % PE in PE and PP mixtures).

For determination of the dependence of the copolymer composition on the molecular weight, EP fractions with different moleular weights were prepared by GPC. Figure 3 shows the GPC curve of an EP-2 sample and the four elution volume ranges which corresponde to the four copolymer fractions obtained by GPC fractionation. For IR measurements, films were pressed as described in the Experimental. Chemical compositions of fractions were calculated by the use of the IR calibration curve. It was found that the PE content of the fractions of the same copolymer agreed within experimental error, i.e., the chemical composition is independent of molecular weight.

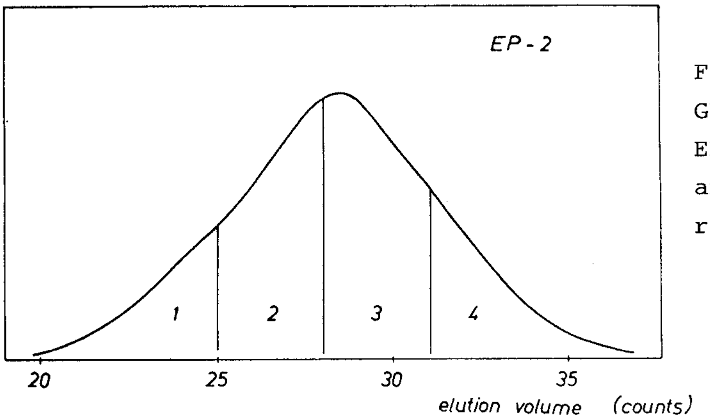

Figure 3. GPC trace of EP-2 copolymer and fractionation ranges

B. Determination of molecular weights

According to the IR results the composition of the investigated EP copolymers is independent of molecular weight. Thus, the universal calibration concept (GRUBISIC et al., 1967) may be used without modification for determination of molecular weight averages of molecular weight (SAMAY, 1977). Since the Mark-Houwink constants of EP's are not known, intrinsic viscosity ($[\eta]$) of EP's has also been determined (cf. Table I).

The Mark-Houwink relationship for the i-th fraction (assumed to be a monodisperse polymer) is

$$[\eta]_i = KM_i^a \qquad (1)$$

where K and a are the Mark-Houwink constants and M_i stands for the molecular weight of the i-th fraction. The intrinsic viscosity ($[\eta]$) of the non-fractionated polymer is

$$[\eta] = \Sigma w_i [\eta]_i, \qquad (2)$$

where w_i stands for the weight fraction, which may be obtained from the GPC curve.

The universal calibration curve is described by the equation

$$\log ([\eta]_i \cdot M_i) = f(v_i), \qquad (3)$$

where v_i stands for the elution volume of the i-th fraction. Introducing the notation

$$J_i = [\eta]_i \cdot M_i, \tag{4}$$

and combining equations (1),(2), and (4), we obtain

$$K = \left| [\eta] \frac{1}{\Sigma w_i J_i^{a/(1+a)}} \right|^{1+a} \tag{5}$$

Since $[\eta]$ is known from the viscosity measurements, w_i from the GPC curves, and J_i from the universal calibration curve, value of K corresponds to an "a" and may be determined. Then, by substituting these a-K pairs into the equation of the universal calibration curve (eq.(3)) MWD and molecular weight averages may be obtained. Similar calculations have been carried out for homopolymers (poly(vinyl chloride), polystyrene, polybutadiene) by AMBLER (1973), who found that deviations of the median value of $\bar{M}_w$'s and $\bar{M}_n$'s for the range of $0.66 < a < 0.80$ are less than ±1 % and ±11 %, respectively. For sake of simplicity, this method may be called as median value method (MV method).

Thus, according to this method, for determination of MWD's of our EP copolymers, a's were varied from 0.66 to 0.80 by a step of 0.01 in a computer program used for MWD determination of polymers from GPC curves. Then the median values of $\bar{M}_w$'s and $\bar{M}_n$'s were determined, and it was found that the MV method used in the case of EP copolymers gave $\bar{M}_w$ values with ±1 % and $\bar{M}_n$ values with ±11 % deviation. Table I shows the median values of $\bar{M}_w$'s, the corresponding $\bar{M}_w/\bar{M}_n$ data, and the Mark-Houwink constants, a and K, obtained by the MV method.

Mark-Houwink constants and molecular weight averages have also been calculated by using the following equations of OGAWA and INABA (1977):

$$a_{EP} = \sqrt{a_{PE} \cdot a_{PP}}, \tag{6}$$

$$K_{EP} = \alpha \cdot K_{PE} + (1-\alpha) K_{PP} - 2\alpha(1-\alpha) \sqrt{K_{PE} K_{PP}} \tag{7}$$

where K_{PE}, K_{PP}, a_{PE} are reported data (OGAWA and INABA, 1973), and α stands for the weight fraction of PE in EP copolymers. This method is called as OI method. As it can be seen in Table I the OI method gives the same a_{EP} value for each EP's and leads to significantly higher $\bar{M}_w$'s than that of obtained by the MV method. But both methods result in quite the same polydispersities.

In conclusion, GPC combined with viscometry and IR spectroscopy may be applied for determination of MWD, molecular weight averages and corresponding Mark-Houwink constants (a and K) in 1,2,4-trichlorobenzene at 135 °C (useful in subsequent investigations - LÁSZLÓ-HEDVIG et al., 1981), of ethylene-propylene copolymers for which the chemical composition is independent of the molecular weight. The MV method based on the universal calibration concept yields significantly lower molecular weight averages than the OI method. However, polydispersities ($\bar{M}_w/\bar{M}_n$) are practically the same.

Table I. Composition, intrinsic viscosity, Mark-Houwink constants, and molecular weight data of ethylene-propylene (EP) copolymers

Samples	Composition (PE weight %)	$[\eta]$ (dl/g)	$K \cdot 10^4$		a		$\bar{M}_w \cdot 10^{-3}$		$\bar{M}_w/\bar{M}_n$	
			OI method	MV method	OI method	MV method	OI method	MV method	OI method	MV method
EP - 1	8	2.01 ± 0.1	0.99	2.28	0.76	0.74	460	318	7.54	7.39
EP - 2	18	1.94 ± 0.07	1.04	2.97	0.76	0.73	408	265	9.30	9.46
EP - 3	29	2.16 ± 0.05	1.22	5.06	0.76	0.69	465	302	11.40	10.80

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