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# Infrared Detection of Polymers in Gel Permeation Chromatography

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## Synopsis

A gel permeation chromatograph equipped with an on-line Grubb-Parsons infrared spectrometer is described. The versatility, specificity, sensitivity, and limitations of such an infrared detector are discussed with particular reference to spectrometer specification, eluent absorbance, and solute absorbance. A stable baseline is produced when this detector is operated at high temperatures, e.g., for the separation of polyethylene in *o*-dichlorobenzene at 135°C. Individual functional groups in a chemically inhomogeneous solute, such as a copolymer, may be monitored by repeated injections of the solute, changing the wavelength setting between separations. This procedure is illustrated with AB poly(styrene–*b*–*t*-butyl methacrylate) block copolymer in trichloroethylene at 35°C.

## INTRODUCTION

Since Moore[1] demonstrated the controlled preparation of macroporous crosslinked polystyrene gels for the molecular size fractionation of polymers in organic solvents, analytical gel permeation chromatography (GPC) has been employed widely in polymer science. An important contribution to the rapid acceptance of the technique, also provided by Moore, was the use of a differential refractometer with a flow-through cell for monitoring continuously the concentration of polymer in the solvent eluting from a column of gel. The time-consuming steps, involving isolation and characterization of fractions, commonly required in classical fractionation methods are thus avoided.[2] The differential refractometer was a major component of the first instrument marketed by Waters Associates[3] and currently is the most widely used detector in GPC.

The ideal detector should have high sensitivity, should be versatile, i.e., applicable to a wide range of polymer–solvent systems, and should be capable of monitoring specific functional groups in a solute as well as the solute concentration. The differential refractometer is very versatile and very sensitive if the eluent has an appropriate refractive index. However, the refractive index of a solvent or a solution is influenced by minor changes in solvent purity and by temperature fluctuations. At high temperatures, e.g., 130–140°C for sepa-

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rations of polyethylene in *o*-dichlorobenzene, the response of a differential refractometer is particularly sensitive to changes in temperature, column pressure drop, and eluent flow rate, so that baseline drift and noise often appear on gel permeation chromatograms. Further, the refractive index difference of a solute in a solvent depends on chemical composition, and refractometry, therefore, cannot discriminate between different chemical groups in copolymers or in a mixture of homopolymers. Consequently, copolymer composition analysis has been performed with multiple detectors,[4–8] using a differential refractometer and ultraviolet photometer in series. An ultraviolet photometer has high sensitivity for aromatic and carbonyl bands and, in common with other detectors monitoring a specific functional group in a solute, is rarely influenced by environmental factors. This specificity, however, limits the number of polymers which can be examined, and clearly an ultraviolet photometer is unsuitable for polyolefins.

Infrared absorption may also be used to monitor functional groups but is less sensitive than ultraviolet absorption. Organic compounds have several fundamental infrared absorption bands, and good sensitivity is generally possible with a strongly absorbing solute band in a region of high solvent transmittance. Therefore, it is surprising that on-line infrared spectrophotometric detectors are not widely used for the direct and continuous measurement of solute concentration in the GPC eluent. No reference to infrared detectors is given in two recent textbooks on conventional liquid chromatography[9,10] in which differential refractometry and ultraviolet photometry are mainly used, although preliminary results of GPC separations with Beckmann and Perkin-Elmer infrared spectrometer detectors have been reported by several workers.[11–17] In particular, Ross and Casto[15] showed that infrared detection has high sensitivity in GPC separations of polyethylene at 110°C. They also demonstrated that the detector response is directly proportional to polymer concentration but is independent of polymer molecular weight and environmental factors.

In this paper, we describe the use of a Grubb-Parsons Spectromaster as an infrared detector in GPC. In addition to adequate detection of polyolefins at high temperatures, we required accurate determinations of the individual functional groups in a chemically inhomogeneous solute such as a copolymer. Infrared absorption is the *only* single detector sufficiently versatile to meet these two objectives. Copolymer composition distributions are obtained by repetitive injections of the same sample, changing the infrared wavelength setting between fractionations in order to monitor specific functional groups separately. The importance of correct choice of solvent to match the wavelength settings for functional groups in polymers and copolymers is emphasized.

## EXPERIMENTAL

### Infrared GPC Instrument

The Grubb-Parsons Spectromaster was part of an instrument containing an automatic injection valve and stainless steel components which was constructed at the I.C.I. Corporate Laboratory in 1969. The schematic flow di-

agram of this infrared GPC instrument is essentially the same as that given by Ross and Casto[15] but is somewhat simpler than that of the Waters instrument,[3] since a stream of flowing solvent through reference columns is not required for infrared detection. The components in the solvent pumping unit, sample injection/column unit, and detection/recording unit are described in turn. Full details of the infrared GPC instrument are given elsewhere.[18]

In the solvent pumping unit, the capacity of the reservoir and surge tank is 16 $dm^3$ and 1 $dm^3$, respectively. The metering pump, supplied by Research Equipment (London) Limited, is capable of delivering solvent at a constant preselected flow rate of 0 to 5 $cm^3$/min, using a maximum pressure in the instrument of $1.45 \times 10^6$ N $m^{-2}$. All studies in this paper were performed with a flow rate of 1 $cm^3$/min.

The sample injection/column unit consists of a manual injection valve, an automatic injection valve, a manual/switching valve, and chromatographic columns, all enclosed within a thermostatted air oven. Because reference columns are not required when using infrared detection, the oven (152.5 cm × 25.4 cm × 25.4 cm) is smaller in volume than the oven in the Waters Model 200 instrument. The valves and columns in the oven can be maintained at any selected temperature betwen 0° and 200 ± 1°C. The electronics and mechanics of the automatic injection valve[19] have been incorporated into instrumentation marketed by Applied Research Laboratories, Limited.[20] The manual injection valve is operated as on a Waters instrument, when the automatic injection valve is isolated from flowing solvent by the manual/automatic switching valve. When flowing solvent bypasses the automatic injection valve, the seven sample loops, each 2 $cm^3$ in volume, are filled in turn by manual rotation of the automatic injection valve. Moving the manual/automatic switching valve directs flowing solvent through one loop in the automatic injection valve, so that the sample solution is carried to the chromatographic columns. When this first injection occurs, the automatic electronics control is switched on to monitor the volume of solvent, as defined by 5-$cm^3$ counts produced by the siphon. After a chosen number of counts, preset on the injection interval control (e.g., 30 counts for four 122-cm columns), the automatic injection valve rotates, so that flowing solvent is directed through the next sample loop. In this way, the automatic injection valve rotates automatically at regular intervals, so that all seven samples are injected without operator attention.

The Spectromaster infrared detector was set up and operated by the procedures described in the Grubb-Parsons instruction manual. The Spectromaster is based on the double-beam, null-balance principle, having accurate and reproducible *manual* adjustment of wavelength to at least 0.006 $\mu$m in the range 0.6 to 15 $\mu$m and of slit width in the range of 0 to 1.5 mm.

After fractionation on the GPC columns the dissolved polymer is transported from the column oven to the detector cell through stainless steel tubing which is resistance heated with a Primatron transformer controlled by a Variac. The location of the cells in the Spectromaster is shown in Figure 1. The cells are mounted in a heated block which is painted black to minimize light reflections. In Figure 1, the nearer cell is a continuous flow-through sample cell while the cell further away is the static reference cell, which is of similar construction to the sample cell. The dimensions of the rock-salt cells

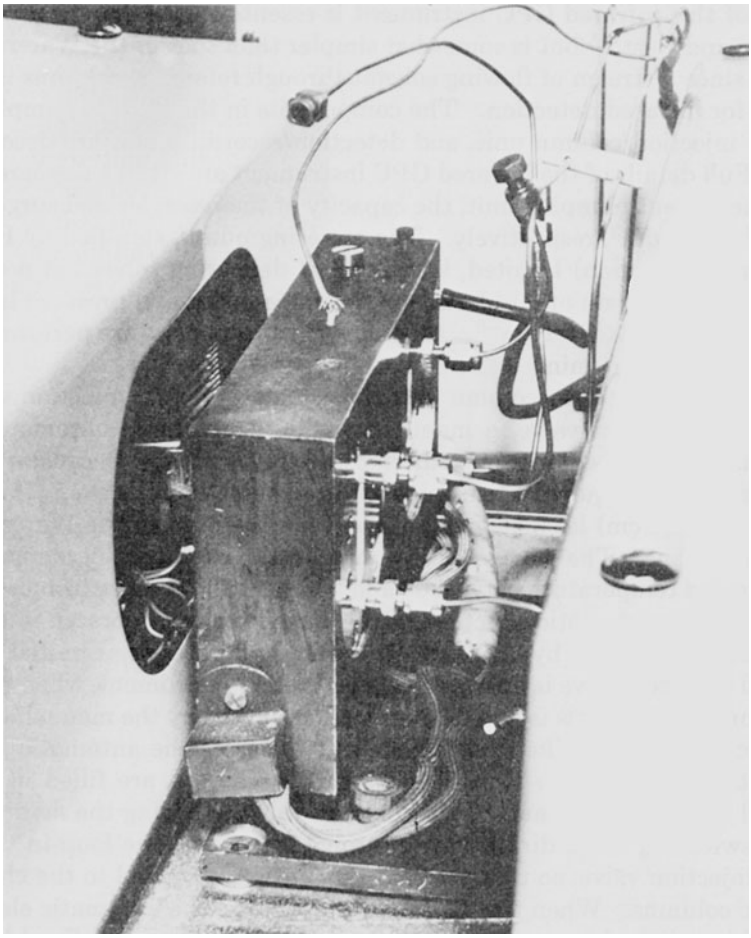

Fig. 1. Detector cell heating block, showing location in Grubb-Parsons double-beam spectrophotometer.

(1 mm path length, 3 mm wide, 2 cm high) are determined by a PTFE spacer. Other PTFE gaskets are included to withstand the pressure required to seal the cell for high-temperature operation. The Spectromaster wavelength and slit-width settings for each functional group are listed in Table I. The Spectromaster is set to an appropriate wavelength, and when polymer enters the cell, the imbalance of the two beams due to absorption causes the servomotor to drive a comb into the reference beam until equilibrium is restored. The

TABLE I
Spectromaster Wavelength and Slit Settings

| Functional group | Wavelength, $\mu$m | Slit width, mm |
|---|---|---|
| Saturated CH stretch | 3.41 | 0.60 |
| Out-of-plane aromatic CH deformation | 14.35 | 0.60 |
| >C=O stretch | 5.80 | 0.20 |
| Si—O—Si bend | 9.30 | 0.18 |

potentiometer fixed to the shaft of the comb translates the required reference beam attenuation into a d.c. voltage which displaces the pen of the chart recorder from a continuous baseline. Retention volumes were obtained by measuring continuously the volume of eluent flowing through the columns as a function of time using a siphon (5 $cm^3$) arrangement as on Waters instruments.

### Materials

The narrow molecular weight distribution polystyrene standards were supplied by Pressure Chemical Company, Pittsburgh. The molecular weight data for the six standards, labeled PS1 to PS6, are given in a previous paper.[21]

The preparation and characterization of the poly(dimethylsiloxane) fractions have been described elsewhere.[21-23]

The linear polyethylenes were commercial Phillips-type Rigidex samples.

Samples of AB poly(styrene–*b*–*t*-butyl methacrylate) block copolymer and poly(*t*-butyl methacrylate) were prepared in this Laboratory by Dr. R. Denyer employing an anionic catalyst.

The *o*-dichlorobenzene, supplied by I.C.I. Mond Division, was 99% pure and contained Topanol OC (0.1% w/v) as antioxidant. The trichloroethylene, supplied by I.C.I. Mond Division, was 99.9% pure and contained triethylamine (200 ppm) as alkaline stabilizer.

### GPC Columns

Crosslinked polystyrene gel columns packed by a technique employing nonswelling liquids[24] were used to obtain all of the results. For both *o*-dichlorobenzene and trichloroethylene, the column combination was $10^5$, $10^4$, $10^3$, and $10^2$ nm (Waters designation). Toluene (Analar) was employed for plate count determinations by injecting a 1% solution for 15 sec. The plate counts (plates per foot) were 900 (trichloroethylene, 35°C), 1200 (*o*-dichlorobenzene, 135°C), and 880 (*o*-dichlorobenzene, 87°C). These results show that the infrared instrument produces plate counts which are equivalent to those (900–1200 in this laboratory[24]) determined on a Waters instrument. The decrease in plate count when the temperature of *o*-dichlorobenzene is reduced from 135° to 87°C is due to the increase in eluent viscosity.[21] The polymer solution concentration was normally 0.25% (w/v). The dependence of detector response on injected weight of polymer was studied with solutions having polymer concentrations in the range of 0.05 to 0.50% (w/v). Number-average, viscosity-average, and weight-average molecular weights ($\bar{M}_n$, $\bar{M}_v$, and $\bar{M}_w$, respectively) were determined as described previously.[21-23]

## RESULTS

### Spectrometer

An infrared spectrometer must have the following features in order to function adequately as a GPC detector: (1) high signal-to-noise ratio; (2) electrical balance system which is stable over long periods of time; (3) detection of very small changes in transmittance.

The Spectromaster has a high-quality amplifier with scale expansion and

backing-off facilities. This ensured high signal-to-noise ratios at low- and medium-scale expansions, but baseline noise was too great at high-scale expansions. To reduce this electronic noise, the chromatogram was expanded mechanically by removing alternate teeth from the reference beam comb and operating the amplifier at a medium or low expansion. Typically, the amplifier was operated with gain setting 3.5 and with scale expansion on position 2 (twofold expansion) or 3 (fivefold expansion).

The cheaper type of spectrometer is generally a rapid scan instrument, having a coarse servosystem which may require a 0.2% transmittance change in signal before deviation. With changes which occur over a long period of time, stepped chromatograms may result. With the Spectromaster, stepped curves were due to the uneven operation of the servomotor controlling the reference comb. Smooth attenuator response was obtained by using a carbon-resistance potentiometer detached from the servomotor; this unit is not included in the standard Spectromaster but was developed for a milk analyzer.[25]

## Eluent

In order to maximize detector sensitivity, the solvent must have a low absorbance at the wavelength employed for monitoring the eluting solute. GPC solvents having simple infrared spectra with transmission windows can be chosen for many polymers. Examples are shown in Figure 2 for the eluents used in the infrared GPC instrument in this laboratory. From the

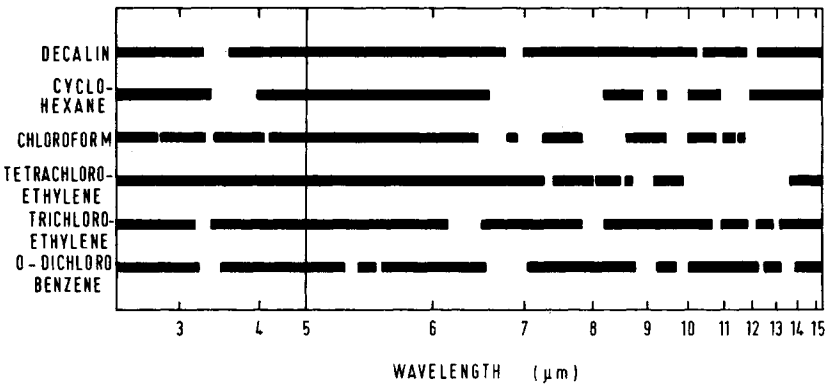


Fig. 2. Solvent transmission windows; bars show regions in which transmission exceeds 30% in 1-mm path length NaCl cell.

wavelengths of the functional groups in Table I, it is clear that *o*-dichlorobenzene is "transparent" for monitoring polystyrene and polyethylene and that trichloroethylene is "transparent" for polystyrene, poly(dimethylsiloxane), and poly(*t*-butyl methacrylate).

## Solute Absorbance

For quantitative GPC work, the detector output must be linearly proportional to the solute concentration. In the infrared GPC instrument, the

wavelength is fixed at a solute absorption band. The absorbance $A$ is given by Beer's law:

$$A = \log_e\left[\frac{I_0}{I}\right] = \epsilon_\lambda cl \tag{1}$$

where $\lambda$ is the fixed wavelength, $I_0$ is the intensity of incident radiation, $I$ is the intensity of transmitted radiation, $c$ is the concentration of functional groups in the solute, $l$ is the path length of the detector cell, and $\epsilon_\lambda$ is the extinction coefficient of the solute absorption band. Since the Spectromaster output was transmittance $(I/I_0)$, it follows from eq. (1) that the detector response will not be linearly related to $c$ over a wide polymer concentration range. GPC separations are performed at low solute concentrations, typically 5 mg polymer eluted in 20 to 100 $cm^3$ solvent depending on the molecular weight distribution and the number of columns. The chromatogram transmittance is then in the range of 90% to 100% of the transmittance value at the baseline. With the baseline set at 100% transmittance, transmittance values in this range are linearly related to absorbance values. Therefore, the chromatogram output in transmittance gives a direct measure of solute concentration. This was confirmed by injecting polymers having various concentrations in the GPC solvent onto the columns and measuring the areas of the resulting infrared chromatograms with a planimeter. Results are shown in Figure 3 for polystyrene and poly($t$-butyl methacrylate) at various wavelengths.

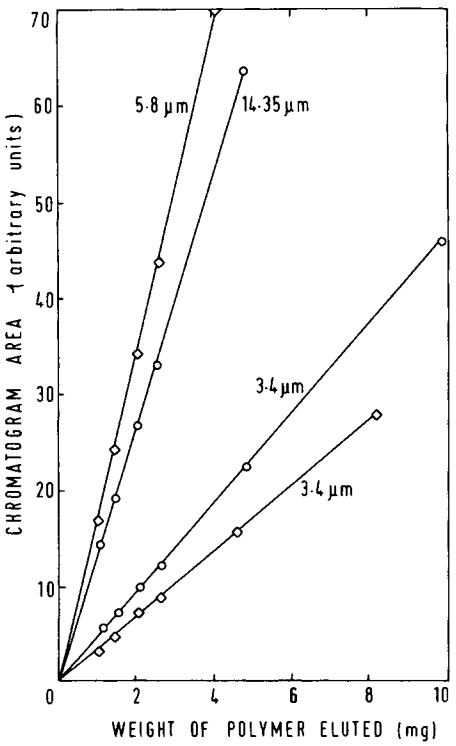


Fig. 3. Chromatogram area vs. weight of eluted polymer plot for polystyrene standard PS 3 (○) and for poly($t$-butyl methacrylate), $\bar{M}_w$ = 112,000 and $\bar{M}_w/\bar{M}_n$ = 1.29 (◇) in trichloroethylene at 35°C.

TABLE II
Average Molecular Weights for Poly(dimethylsiloxane) Fractions

| Fraction | $\bar{M}_v$[a] | Waters GPC Instrument | | | | Infrared GPC Instrument | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\bar{M}_n$ | $\bar{M}_v$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | $\bar{M}_n$ | $\bar{M}_v$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ |
| C7 | 28,000 | 21,700 | 25,800 | 26,900 | 1.24 | 23,000 | 27,000 | 28,000 | 1.22 |
| D9 | 34,500 | 29,600 | 33,500 | 34,200 | 1.16 | 26,900 | 30,800 | 31,500 | 1.17 |
| D8 | 42,000 | 36,500 | 42,000 | 43,000 | 1.18 | 33,800 | 39,000 | 39,700 | 1.17 |
| C1 | 800,000 | 390,000 | 615,000 | 729,000 | 1.67 | 520,000 | 740,000 | 830,000 | 1.60 |

[a] Determined experimentally by dilute solution viscometry.

For the range of eluted polymer from 1 to 10 mg, it is clear from Figure 3 that the linear relation between $I/I_0$ and $c$ is valid for the dilute solutions used in GPC. This is confirmed by comparing values of $\bar{M}_n$, $\bar{M}_v$, and $\bar{M}_w$ for poly(dimethylsiloxane) fractions determined with the infrared and the Waters instruments, see Table II. For a band with a low $\epsilon_\lambda$ value, the relation between transmittance and solute concentration remains linear up to high $c$ values. At high solute concentrations, the dependence of infrared transmittance on $c$ was examined by placing directly into the detector cell a series of solutions of polystyrene PS3 in trichloroethylene, see the results in Figure 4. The transmittance values show that deviations from linearity are not serious for the 3.4 and 14.35 $\mu$m bands.

The molecular weight independence of infrared transmittance was checked for each polymer–solvent system. Typical results for polystyrene standards (14.35 $\mu$m band) in trichloroethylene are given in Table III, showing that the ratio of chromatogram area to polystyrene concentration is a constant. Ross and Casto[15] also found that the infrared detector response was independent of molecular weight for polystyrene standards monitored at 3.4 $\mu$m. This represents an advantage of infrared detection over differential refractometry, since it has been shown that the refractive index of polystyrene in solution varies significantly with molecular weight.[26,27] For molecular weights below 5000, the evaluation of refractometer response as a function of molecular weight is necessary for quantitative determinations of molecular weight distributions from chromatograms.

Since GPC separations are performed at low solute concentrations, good detector sensitivity is required, otherwise the detector cell volume becomes

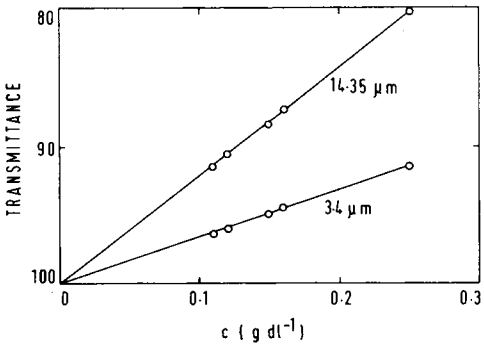


Fig. 4. Infrared transmittance vs. concentration plot for solutions placed in the detector cell of polystyrene standard PS 3 in trichloroethylene at 35°C.

TABLE III
Area of Chromatograms (at 14.35 μm) for Trichloroethylene Solutions of Various Polystyrene Standards

| Standard | Molecular weight | Concentration, % w/v | Area, cm² | Area/concentration |
|---|---|---|---|---|
| PS 1 | 160,000 | 0.246 | 25.85 | 100.50 |
| PS 2 | 98,200 | 0.248 | 25.95 | 100.45 |
| PS 3 | 51,000 | 0.252 | 26.05 | 100.35 |
| PS 4 | 19,800 | 0.261 | 26.95 | 100.35 |
| PS 5 | 10,300 | 0.243 | 25.40 | 100.45 |
| PS 6 | 3,700 | 0.243 | 25.10 | 100.35 |

too large when gel permeation chromatograms are broadened due to solute mixing in the cell. As the infrared absorption flow-through cell was larger in volume than the present-day microcells employed in refractive index and ultraviolet absorption detectors, a comparison was made of the resolution of the infrared instrument and that of the Waters Model 200 gel permeation chromatograph, using poly(dimethylsiloxane) fractions studied extensively in this laboratory. In conjunction with the plate count data, the polydispersity results in Table II show that chromatogram broadening must be very similar in the two GPC instruments.

## Polyethylene

Typical chromatograms from the infrared GPC instrument are shown in Figure 5 for a commercial linear polyethylene. Here, the baseline stability and noise are not influenced by variations in temperature, pressure, and flow rate because infrared absorption is relatively insensitive to these variables, even at elevated temperatures. No reference columns were employed, al-

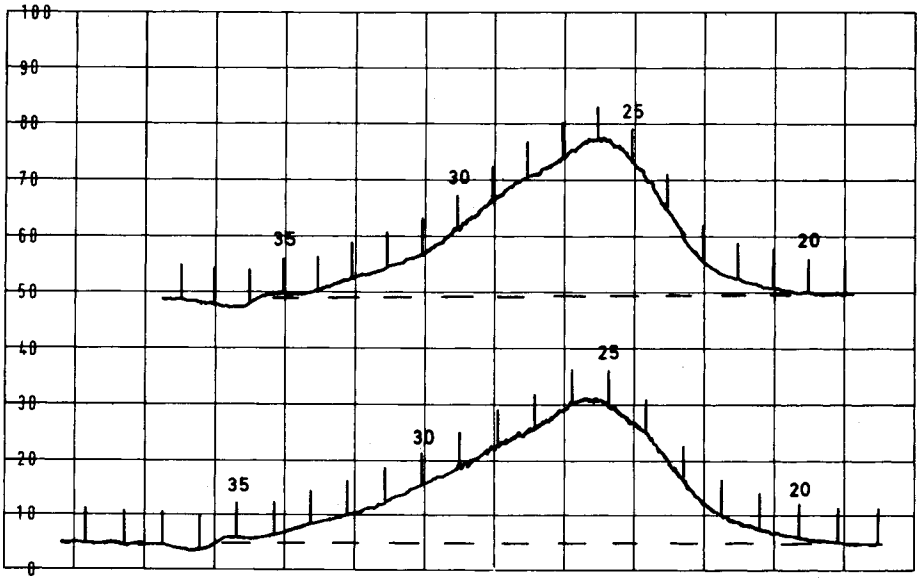


Fig. 5. Infrared gel permeation chromatograms for linear polyethylene (Rigidex 2) in *o*-dichlorobenzene at 135°C.

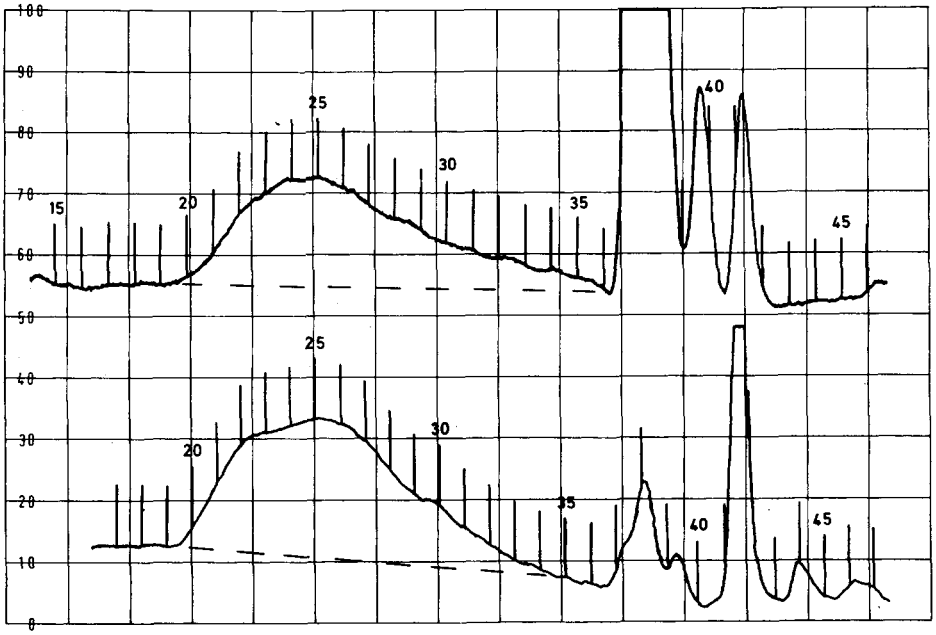


Fig. 6. Differential refractometer gel permeation chromatograms for linear polyethylene (Rigidex 2) in *o*-dichlorobenzene at 135°C.

though double-beam operation was utilized with a static solvent cell in the reference beam. With a refractometer, it is necessary to use two carefully balanced eluent streams (sample and reference). Variations in flow rate are partly caused by the split stream system in the Waters Model 200 instrument, i.e., sample and reference columns fed from a single eluent pump. At high temperatures, the refractometer response is noticeably sensitive to variations in flow rate which can produce temperature fluctuations. Clearly, precise thermal control of the refractometer is essential, which is not easy to achieve at 130°C.

Peaks arising from low molecular weight eluent impurities are virtually absent in Figure 5. Such impurity peaks are invariably present when a differential refractometer is employed, and chromatograms for polyethylene obtained with a Waters instrument in this laboratory are shown in Figure 6. With chromatograms of this latter type, the variation of the baseline gives irreproducible chromatograms and affects the reliability of the molecular weight information determined from the chromatograms, particularly if the low molecular weight tail merges with the instrumental impurity peaks. In our experience, infrared detection is much more reliable and reproducible than differential refractometry; this conclusion is supported by the work of Ross and co-workers.[15,16]

## Block Copolymers

For solutes containing several functional groups, the concentration of each group can be determined, provided there is no overlap between infrared bands and there are solvent windows at the bands corresponding to the func-

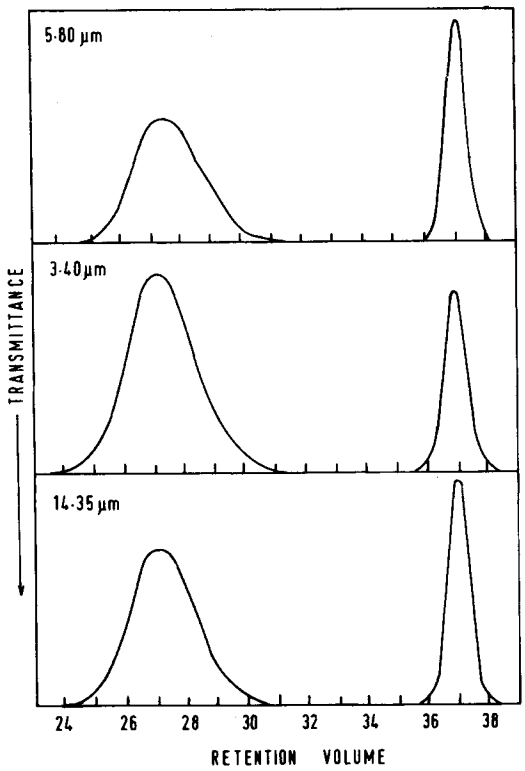


Fig. 7. Chromatograms for AB poly(styrene–*b*–*t*-butyl methacrylate) and methyl benzoate, obtained at three fixed wavelengths (see Table I).

tional groups. Then, repeated injection of the same sample into the infrared instrument can be performed with a different wavelength setting on the second injection, and another setting on the third injection, etc. The wavelength may be chosen to monitor both types of repeating unit or only one type of repeating unit in a copolymer in turn. The procedure is illustrated by the chromatograms for AB poly(styrene–*b*–*t*-butyl methacrylate) in Figure 7. This block copolymer ($\bar{M}_n$ = 50,000) was injected into the infrared instrument three times with the wavelength set to monitor the carbonyl group, the aromatic group, and aliphatic C—H. In order to calculate the copolymer composition as a function of retention volume, and therefore molecular weight, an internal standard must be added to each injected copolymer solution. Chromatograms for methyl benzoate at a retention volume of 37 counts are shown in Figure 7.

Therefore, if the conditions of GPC fractionation remain constant, i.e., solvent flow rate, temperature, and column combination, the chromatograms from the independent injections can be combined, so that the concentration and distribution of specific monomer units within a copolymer size distribution can be determined. Copolymer molecular weight and composition distributions can then be determined, if the concentration dependence of the transmittance of each functional group has been obtained by prior calibration with homopolymer samples, e.g., Figure 3. The procedure can be extended to mixtures of homopolymers and to endgroup contents for some homopoly-

mers. An alternative approach, if the detector is a recording infrared spectrometer, is to stop the eluent flow in order to take a spectrum of the eluting solute.[28] The copolymer composition distribution is then determined from spectra obtained at a series of retention volumes.

The skilled work of Mr. J. Williams and Mr. D. Fisher in constructing the GPC instrument is gratefully acknowledged. The authors thank Professor J. C. Bevington of Lancaster University for helpful discussions. The work was undertaken as part of the Research Student Community Scheme at the Corporate Laboratory, Runcorn, and as part of a program to develop GPC for polymer characterization. Techniques and apparatus arising from this program are being developed commercially by Applied Research Laboratories Ltd., Luton, under licence from I.C.I. Ltd.

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