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STRUCTURAL EVALUATION OF COPOLYMERS USING
PREPARATIVE GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

A detailed structural evaluation of a copolymer, or a resin exhibiting a branched structure, is only possible through the analysis of fractions from the parent resin. A description is given of a preparative GPC unit which operates at elevated temperatures and thus may be used in the structural analysis of a wide range of resin types including copolymers. Examples are given of the use of this preparative gel permeation chromatographic technique in the study of ethylene-vinyl acetate copolymers and styrene-butadiene rubbers. Through analysis of fractions by infrared, solution viscosity and analytical gel permeation chromatography, a comprehensive structural evaluation is derived which serves to illustrate the potential of preparative gel permeation chromatography in resin structure studies.

INTRODUCTION

In attempting to obtain polymer structure information one needs to fractionate the polymeric material into its differing molecular weight components on a scale large enough to allow further analysis of the fractions by the many techniques presently available, such as osmometry, solution viscosity, infrared (IR), gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), etc., in order to define the structure and composition of sample. The most commonly used fractionation method has been gradient elution chromatography¹ in which the eluent composition is varied to produce the molecular weight separation. This method has proved very useful but does suffer from some disadvantages such as: (a) the lack of resolution of very high-molecular-weight species, (b) the difficulty of fractionating copolymers such as ethylene-vinyl acetate copolymers or rubber which may differ in composition, as well as molecular weight, and hence have variable solubility, (c) the fact that each different polymer system requires individually tailored solvent/non-solvent mixtures.

GPC with its separation based on the hydrodynamic volume of molecules in solution, provides a very attractive alternative to the gradient elution fractionation method and generally does not suffer from the above problems. For the most part, however, the GPC method has been used as an analytical procedure, fractionating very small samples; only occasionally^{2,3} has the method been applied to large scale

fractionation. In this present paper a description is given of the operation of a high temperature preparative GPC which combines the advantages of the GPC method of separation with those of a preparative technique. Examples are given of how the preparative GPC technique has been used in the study of the structural characteristics of ethylene-vinyl acetate (EVA) copolymers and styrene-butadiene rubbers (SBR).

In designing the preparative GPC described below, the objective was to produce a system which could be readily operated at differing temperatures and with various solvents so as to be suitable for application to a wide range of resins. The ability to provide fractions of sufficiently large size for subsequent study was considered very important. To facilitate the handling of replicate fractionations necessary to produce the required sample sizes, an in-line solvent stripper has been incorporated into the system to reduce the large volumes of the eluent fractions.

EXPERIMENTAL

Construction and operation of preparative gel fractionation equipment

A diagram of the preparative gel fractionation (PGF) equipment is shown in Fig. 1. The solvent is fed, by gravity, to the degasser and then to the metering pump; the flow rate is 40 ml/min. The solvent then flows through the preheater, which is set at the same temperature as the oven and can be varied from ambient to 150°. Two electrically operated solenoid valves switch the solvent stream either through the sample loop to inject a sample, or to bypass the loop as in normal operation. The solvent stream passes through a filter and then through the fractionation columns; these are Waters' preparative GPC columns which measure 4 ft. by 2.4 in. O.D. and are packed with 'Styragel' of differing porosities (see Fig. 1). The solvent stream then passes through a 'Rototherm' ¼ square ft. thin film evaporator, removing approximately 75% of the solvent in the form of vapor, which is condensed and recycled. The concentrated solution is then fed to a fraction collector operating in a time mode, *i.e.*, fractions are collected for 5 min intervals rather than according to volume, so that any fluctuation in rates of evaporation will not influence the fraction collection procedure which is of importance when combining the fractions from several runs.

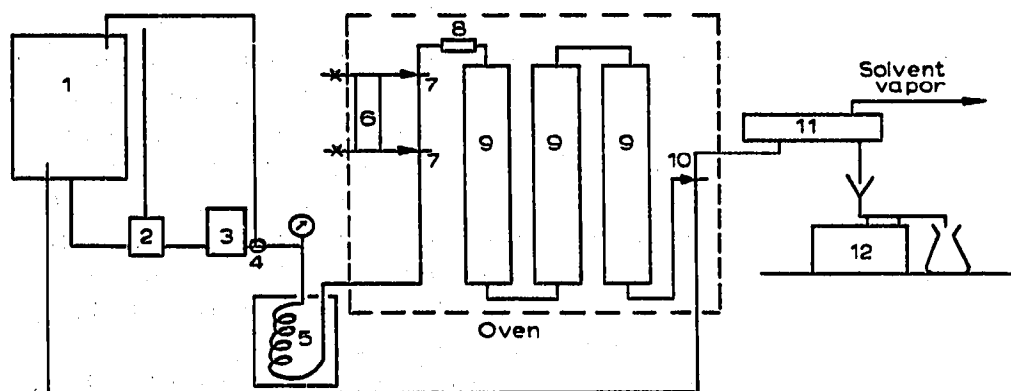


Fig. 1. Schematic diagram of preparative gel fractionator. 1 = Solvent reservoir; 2 = degasser; 3 = metering pump; 4 = pressure relief valve; 5 = preheater; 6 = sample injection system; 7 = 3-way solenoid valves; 8 = filter; 9 = styragel columns, 5×10^3 – 1.5×10^4 , 5×10^4 – 1.5×10^5 , 7×10^5 – 5×10^6 Å porosity; 10 = 3-way air-operated recycle and fail-safe valve; 11 = solvent stripper; 12 = automatic fraction collector.

The fractions obtained are recovered and then analyzed in the usual manner by IR, GPC, solution viscosity and other relevant methods. Since a refractometer or other detection device is not used to monitor the effluent, the choice of solvent depends upon the material being examined, *i.e.*, the best solvent for the polymer can be used which aids in fractionating the materials since the molecules are then fully expanded. The styrene-butadiene rubbers were consequently fractionated using benzene at room temperature and the ethylene-vinyl acetate copolymers were fractionated in xylene at 60°. The materials to be fractionated are made up as 1.5% solutions in the appropriate solvent, filtered, and introduced into the sample loop. The sample is then injected into the solvent stream by energizing the solenoid valves; approx. 1 g of polymer is fractionated at a time.

Polymers to be fractionated are, first of all, analyzed by GPC so that the upper and lower elution volume limits can be determined. The optimum number of fractions to be combined at the beginning and end of the fractionation, to provide sufficiently large samples for analysis, are also determined from this data.

Calibration

In order to calibrate the equipment a mixture of polystyrene, having a broad molecular weight distribution ($M_w/M_n = 30.7$), was fractionated. The fractions were precipitated, dried, weighed, and analyzed by GPC.

The elution volumes of the fractions were then plotted as a function of their extended chain length to provide the calibration curve shown in Fig. 2. In addition,

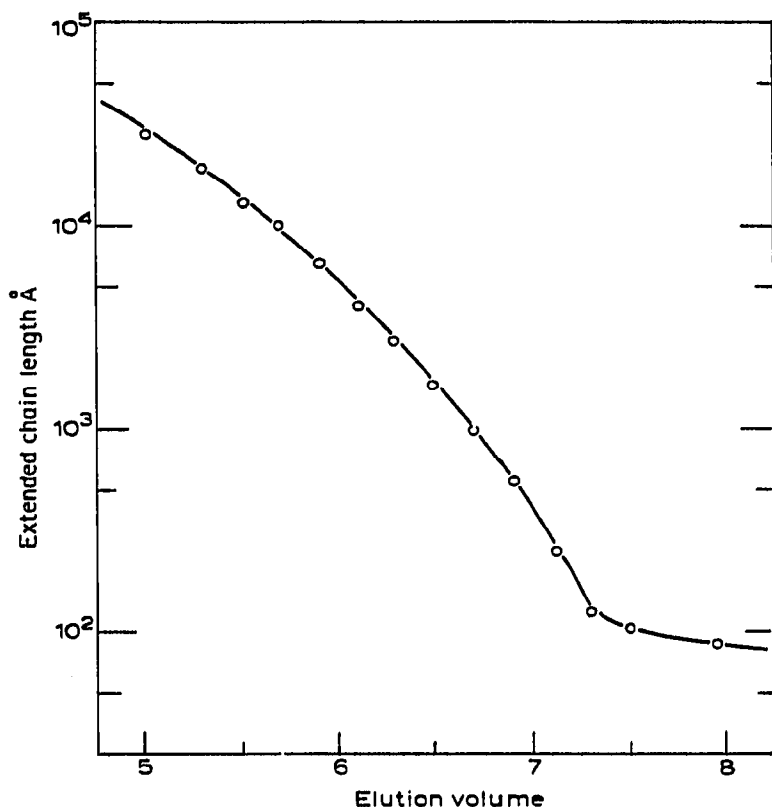


Fig. 2. Calibration curve for preparative gel fractionation using polystyrene in benzene at 25°.

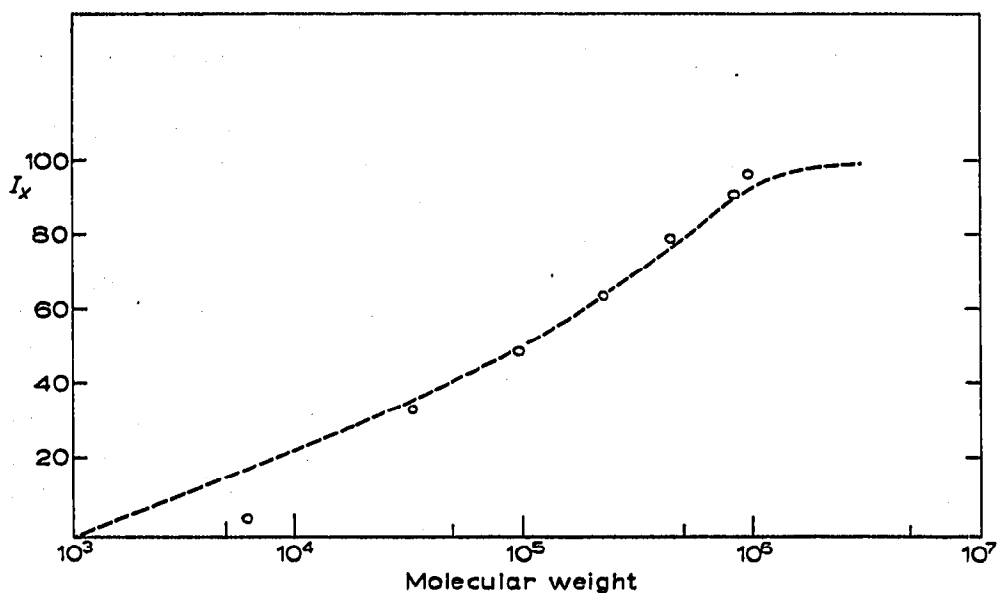


Fig. 3. Comparison of MWD data for polystyrene obtained by analytical GPC and preparative gel fractionation. O = Preparative gel fractionation; - - - - = analytical GPC.

an integral weight *vs.* molecular weight curve was drawn (Fig. 3) and compared with the similar data obtained by GPC analysis of the polystyrene mixture. It is readily apparent that the fractionation achieved by the PGF is quite satisfactory with the possible exception that there is insufficient resolution at the low molecular weight end. (It is planned to install a lower porosity column to rectify this situation.)

CHARACTERIZATION OF FRACTIONS

GPC analysis

A Waters Associates' GPC Model 200 was used to analyze the EVA copolymer fractions. The operating temperature was 140° using trichlorobenzene (TCB) as solvent at a flow rate of 1 ml/min. The porosities of the columns are (1) 7×10^5 – 5×10^6 Å, (2) 5×10^4 – 1.5×10^5 Å, (3) 5×10^3 – 5×10^4 Å, and (4) 5×10^3 – 1.5×10^4 Å.

The rubber fractions were analyzed on a Model 100 GPC using tetrahydrofuran (THF) as solvent at a temperature of 40° and flow rate of 1 ml/min. Five columns were used in this instrument; the porosities of the first three columns were the same as above and the others were (4) 700–2000 Å, and (5) 500/250/100/60 Å.

Solution viscosity measurements

Viscosities were determined as inherent viscosities using a modified Ubbelohde. The viscosities of the EVA fractions were determined in TCB at 140° and of the SBR fractions in THF at 40° .

Molecular weight measurements

The molecular weights of the EVA fractions were determined as number average molecular weights (M_n), by osmometry in toluene at 85° in a Hallikainen automatic osmometer.

Infrared analysis

The ethylene-vinyl acetate copolymers were analyzed for vinyl acetate content by dissolving the material in carbon tetrachloride and measuring the characteristic absorption of the carbonyl group at 5.8μ . The styrene content of the SBR fractions was determined by dissolving the material in carbon disulphide and measuring the absorption band characteristic of various types of unsaturation and also phenyl from which the styrene content and microstructure were calculated.

RESULTS AND DISCUSSION

The two resin types included in this study, ethylene-vinyl acetate copolymer and styrene-butadiene rubber, were chosen as ones which prove difficult to fractionate by gradient elution chromatography. The value of the preparative GPC should be therefore clearly apparent if it proves possible to achieve successful fractionations through its use. The fractionated samples produced by the preparative GPC have been analyzed from the point of view of demonstrating that the technique produces effective molecular weight fractionation while also attempting to determine whether the resins exhibit any structural heterogeneities, such as variations of copolymer content or the presence of long-chain branching.

Examination of ethylene-vinyl acetate copolymers

The first copolymers to be examined were ethylene-vinyl acetate (EVA) resins synthesized in an autoclave reactor. Two resins of differing copolymer content but similar melt index were included in the study: Resin A, containing 16.5% VA and Resin B, with 25.5% VA. By analogy with low-density polyethylenes made by the same process, it was considered likely that these resins would exhibit long-chain branching (LCB) — possibly to differing degrees — and perhaps variations in comonomer content. Certainly simple analytical GPC data (Fig. 4) for the two resins show differences which may be associated with differences in the degree of LCB. In the case

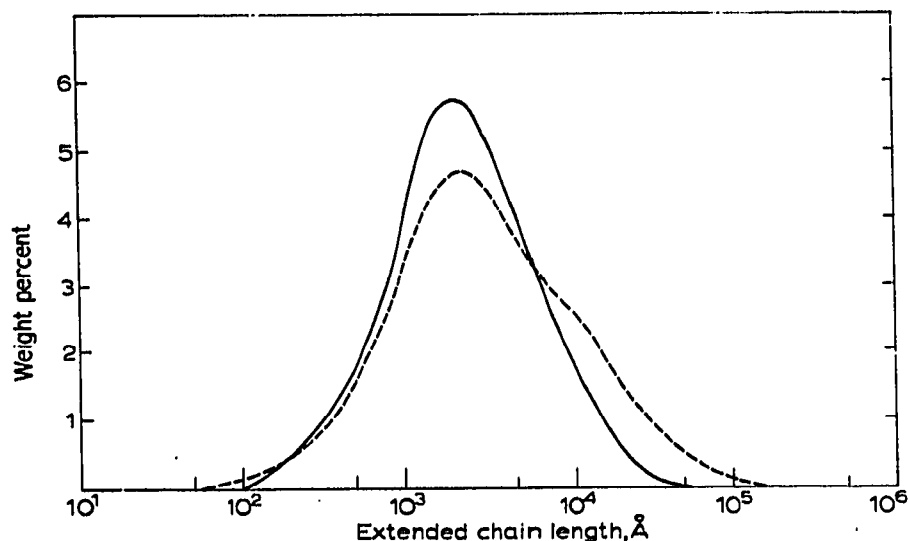


Fig. 4. Molecular size distribution of ethylene-vinyl acetate copolymers A and B. - - - - = EVA copolymer A; ——— = EVA copolymer B.

TABLE I
STRUCTURAL DATA FOR ETHYLENE-VINYL ACETATE COPOLYMER A

Fraction	Inherent viscosity { η } dl/g	Measured $M_n \times 10^{-4}$	Computed $M_n \times 10^{-4}$	$M_w \times 10^{-4}$	R	Percent VA
1	2.36	—	112.3	252.7	2.24	11.0
2	2.07	—	57.5	87.0	1.51	13.8
3	1.76	—	39.0	65.3	1.67	15.3
4	1.57	—	20.1	38.1	1.88	16.4
5	1.35	16.8	14.8	26.8	1.80	16.2
6	1.08	9.03	8.06	15.6	1.93	16.3
7	1.02	8.63	7.23	15.0	2.07	16.8
8	0.898	4.84	4.69	10.1	2.14	16.8
9	0.667	2.32	1.92	4.8	2.68	16.8
10	0.488	1.72	1.34	3.34	2.48	16.2
11 ^a	0.354	1.49	1.26	1.76	1.39	—
12 ^a	0.186	—	0.54	0.77	1.41	17
Whole polymer	—	3.09	1.86	14.4	7.70	16.5

^a Gradient elution fractions.

of low-density polyethylenes, for example, it has been shown⁴ that a distinct high molecular weight shoulder in the GPC trace as shown in the case of Resin A, is usually associated with a high degree of LCB. Consideration of synthesis conditions suggests also that differences in degree of LCB are likely to be present in the two EVA resins.

Fractionation of the EVA resins using the preparative GPC produced fractions which were analyzed by IR, solution viscosity, osmometry, and analytical GPC. The results obtained for fractions from Resin A and Resin B are shown in Tables I and II, respectively. The molecular weight separation is seen to be good except in the low-molecular-weight region, possibly due to the absence of a low porosity column. Because of this difficulty, two or three low-molecular-weight fractions obtained through a gradient elution fractionation⁷ have been included to complete the structural information. The data from these materials are also included in Tables I and II.

TABLE II
STRUCTURAL DATA FOR ETHYLENE-VINYL ACETATE COPOLYMER B

Fraction	Inherent viscosity { η } dl/g	Measured $M_n \times 10^{-4}$	Computed $M_n \times 10^{-4}$	$M_w \times 10^{-4}$	R	Percent VA
1	1.70	—	42.97	60.97	1.41	24.0
2	1.35	16.1	18.24	32.24	1.76	—
3	1.27	10.4	13.32	20.44	1.53	—
4	1.16	—	9.01	15.25	1.69	26.1
5	0.879	6.66	5.64	9.72	1.72	26.0
6	0.743	—	3.72	6.47	1.74	25.8
7 ^a	0.679	—	3.91	5.49	1.40	24.7
8	0.659	2.93	3.36	6.56	1.94	26.8
9	0.573	1.62	1.78	3.83	2.16	26.1
10	0.503	—	1.41	3.58	2.54	26.0
11 ^a	0.432	1.78	1.29	2.66	2.05	26.1
Whole polymer	—	2.70	2.78	10.9	3.90	25.5

^a Gradient elution fractions.

The IR analysis of the fractions shows that the vinyl acetate content is practically constant and exhibits only a very slight decrease in the highest-molecular-weight species. Information of this sort is important when analyzing copolymers by GPC since variations in comonomer content could lead to variations in the refractive index which would give rise to erroneously high or low concentration values and hence yield an erroneous molecular size distribution. It is thought that in this case the fluctuation in vinyl acetate content would have an insignificant influence upon the GPC data. The homogeneous incorporation of the vinyl acetate into the polymer chain as indicated by the copolymer content data is a confirmation of kinetic studies which indicate that ethylene and vinyl acetate are equally reactive with each other at high temperatures and pressures.

If long-chain branching is present in a polymer, the conversion of GPC data into molecular weight distribution (MWD) data becomes complicated because LCB influences the hydrodynamic volume. BENOIT *et al.*⁵ have proposed a Universal Calibration for GPC which takes into account the influence of LCB. It has been demonstrated that this Universal Calibration (elution volume, (C) vs. $[\eta]M$) is applicable to both linear and branched polyethylenes⁶ and should therefore be suitable for EVA resins also.

This Universal Calibration has been applied to fractions from the two EVA resins. A computer program has been set up for this purpose through which values of $[\eta]M_w$ are derived from elution volumes for fractions which allows one to determine M_w using measured values of $[\eta]$. The program is not described here but it does include an iterative analysis aimed at accounting for the presence of polydispersity within the fractions. Analysis of a series of fractions provides information which allows the derivation of a molecular weight calibration (C vs. M) for the particular resin sample being studied from which complete MWD, and hence all molecular weight averages, for fractions and whole polymers, can be computed.

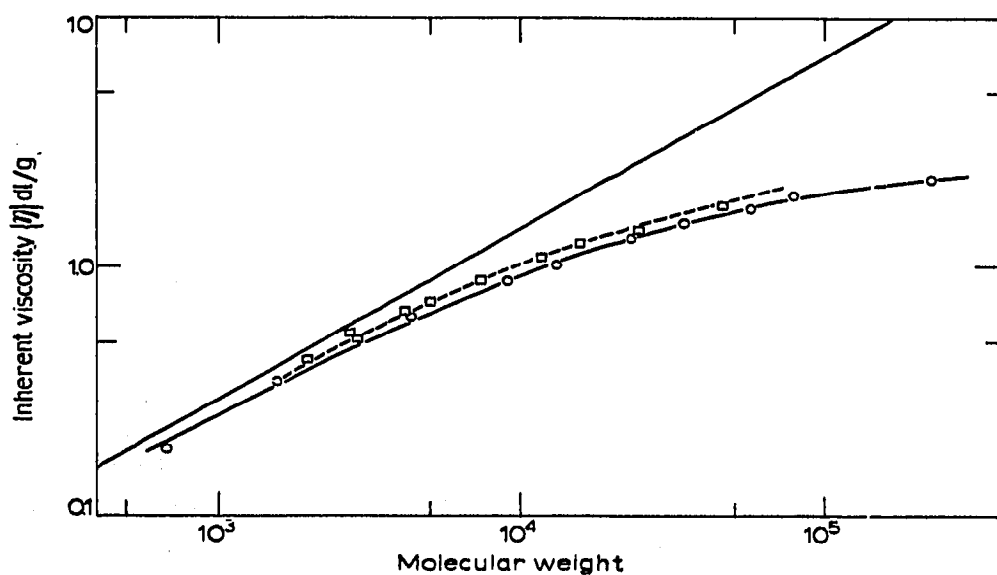


Fig. 5. Solution viscosity-molecular weight relationship for ethylene-vinyl acetate copolymers in TCB at 140°. — = linear polymer; ○—○ = copolymer A; □ --- □ = copolymer B.

TABLE III

STRUCTURAL DATA FOR STYRENE-BUTADIENE RUBBER Y

Fraction	Inherent viscosity { η } dl/g	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	R	Percent styrene
1	5.90	57.0	130.0	2.28	—
2	4.70	47.7	94.0	1.97	—
3	3.86	32.6	67.5	2.07	19.1
4	3.47	17.2	50.5	2.94	19.9
5	2.68	16.2	40.4	2.50	—
6	2.15	11.3	26.7	2.36	—
7	1.86	7.4	23.7	3.21	27.7
8	1.40	4.7	17.1	3.62	—
9	1.04	2.9	14.0	4.81	32.8
10	0.98	1.8	12.0	6.56	32.9

TABLE IV

STRUCTURAL DATA FOR STYRENE-BUTADIENE RUBBER X

Fraction	Inherent viscosity { η } dl/g	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	R	Percent styrene
1	3.71	52.4	73.3	1.4	14.8
2	3.34	30.9	64.9	2.1	18.5
3	2.50	26.7	48.7	1.8	20.8
4	1.95	18.2	23.0	1.3	21.9
5	1.41	11.4	16.4	1.4	22.0
6	1.09	9.4	13.3	1.4	22.1
7	0.99	7.8	11.3	1.4	23.1
8	0.84	6.2	7.9	1.3	24.1
9	0.82	5.9	7.5	1.3	24.3
10	0.78	4.9	7.0	1.4	25.2

Molecular weight data computed in this manner is included in Tables I and II. Also given in these tables are the measured number average molecular weights of the fractions which are found to be in close agreement with the computed values and confirm that the analytical and mathematical procedures used are capable of giving realistic results. From this information the solution viscosity-molecular weight relationship may be determined and compared with the relationship derived for corresponding linear material to show the presence or absence of long-chain branching.

In practice the most suitable way of making such a comparison is by adjusting the EVA data to that for a hypothetical polyethylene using a linear polyethylene [η]- M_w relationship as the reference line. This has been done and the resultant relationships are shown in Fig. 5.

From this data one concludes that the EVA copolymers exhibit relatively high degrees of LCB and in addition that, as expected, the level of LCB present in Resin A is greater than in Resin B.

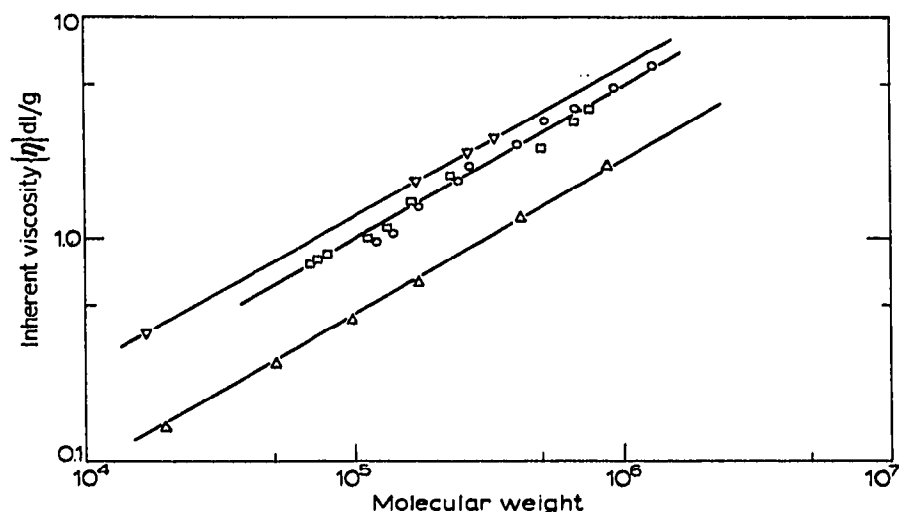


Fig. 6. Solution viscosity-molecular weight relationship for polybutadiene, polystyrene and SBR in THF at 40°. □ = Rubber X; ○ = rubber Y; ▽ = polybutadiene standards; △ = polystyrene standards.

STYRENE-BUTADIENE RUBBER

The two styrene-butadiene rubbers (Resin X and Resin Y) were synthesized using different initiator systems; both rubbers contained approximately 25% styrene. In this case it was again of interest to know whether the comonomer content varied with molecular weight and also whether either of the resins contained any LCB.

Both rubbers were successfully fractionated using the PGF and the fractions analyzed using techniques similar to those used on the EVA copolymers, with the exception of the osmometry measurements.

The information obtained is given in Tables III and IV. It is apparent from the IR analysis of the fractions that the comonomer content of both materials varies considerably and shows a marked decrease in the amount of styrene present as the molecular weight increases. This, of course, means that the raw GPC data for the whole polymer could be misleading because of the unknown influence comonomer content has on the refractive index. Once it has been established that the comonomer content and refractive index vary with molecular weight, then the data may be corrected either by calculation or through measurements on the fractions. This has not been done here and close inspection of Fig. 6 shows a tendency for the copolymer line to converge with that for the polybutadiene at high molecular weight.

It was assumed that the fractions were sufficiently narrow in molecular weight distribution that the slight variation in refractive index within the fraction is negligible, consequently reliable molecular weights are computed via the Universal Calibration iterative analysis procedures.

Using the data presented in Tables III and IV, the molecular weight-solution viscosity relationships for the Rubbers X and Y have been plotted (Fig. 6) together with the similar relationship for polybutadiene and polystyrene. Both the polybutadiene and the polystyrene were polymerized anionically so that they are known to be linear molecules. The fact that the curve for the rubbers falls in between the curves

for polybutadiene and polystyrene and is practically parallel to both, shows that these styrene-butadiene rubbers are also linear materials and do not contain any detectable long-chain branching.

CONCLUSION

The studies described above demonstrate the usefulness of preparative GPC in providing fractions of materials which were previously very difficult, if not impossible, to fractionate by the classical fractional precipitation techniques based on differences in solubility of the fractions. They also illustrate the great potential of the preparative GPC when used in conjunction with a suitably calibrated analytical GPC, as the basis for a rapid and comprehensive structural evaluation for soluble polymers.

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