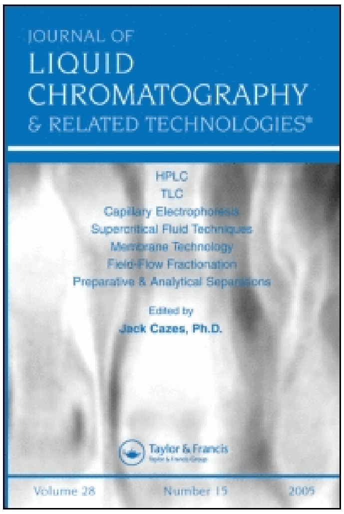

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S. Pokorný[a]; J. Janča[a]; L. Mrkvičková[a]; O. Turečková[a]; J. Trekoval[a]
[a] Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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INVESTIGATION OF HYDROXY-TERMINATED LOW MOLECULAR WEIGHT POLYISOPRENES BY LIQUID CHROMATOGRAPHY METHODS

S. Pokorný, J. Janča, L. Mrkvičková,
O. Turečková and J. Trekoval
Institute of Macromolecular Chemistry, Czechoslovak
Academy of Sciences, 162 06 Prague 6
Czechoslovakia

ABSTRACT

Model samples of low-molecular weight polyisoprenes and polyisoprenes containing one or two hydroxy endgroups were investigated by using various methods of liquid chromatography. Gel permeation chromatography (GPC) was employed in the determination of molecular weights and their distribution. The validity of the principle of universal calibration was confirmed. Under the given GPC experimental conditions separation was unaffected by the adsorption of hydroxylated polyisoprenes on the column packing used. The bonded-phase liquid chromatography method on columns with the amine phase allowed efficient separation to be achieved according to the content of functional groups. Since there also was separation according to molecular weights, the method allowed an estimate to be made of the molecular weights of fractions with various contents of hydroxy groups. The results obtained proved the possibility of a complex analysis of low-molecular weight polymers with functional groups, such as e.g. liquid rubbers; at the same time, the results of bonded-phase column separation indicate the possible use of this modern liquid chromatography method in the analysis of polymers.

INTRODUCTION

Polymers with functional endgroups have been widely used in polymer chemistry and technology. A typical example can be seen in, e.g., liquid rubbers. These materials exhibit two main different features compared with classical polymeric materials. Their molecular weights are rather low, i.e. several thousands or several tens of thousands of daltons; moreover, they contain various numbers of functional groups in their chain which to a large extent determine their physical and chemical character. Important parameters which must be known for the characterization of this type of polymers are average molecular weights and molecular weight distribution (MWD), as well as the distribution of functionality, i.e. the relative fraction of chains containing various numbers of functional groups. All these parameters may be determined by the methods of liquid chromatography. Gel permeation chromatography (GPC)is a convenient tool for the determination of molecular parameters and bonded-phase liquid chromatography for the separation according to the number of functional groups.

Several complicating factors arise in the application of GPC to the determination of MWD of these polyemers. With respect to the content of endgroups, separation may be complicated by undesired interactions of the solute with column packing, as has been observed earlier (1-3). Also, the effective hydrodynamic volume of chains with functional groups may differ from effective dimensions of chains without functional groups; this finding should be borne in mind in the interpretation of experimental data, especially if the principle of universal calibration is used (4). In addition, the validity of constants and exponents of the Mark-Houwink equation reported in the literature and needed for the interpretation of experimental data remains uncertain in the low-molecular weight range under investigation.

Two basic problems must be solved in the application of bonded-phase liquid chromatography, the separation properties of which have been demonstrated using low-molecular weight models of hydroxy and carboxy terminated chains (5). It is necessary to find a suitable system eluent-bonded phase, which would provide good resolution according to the number of functional groups even at a relatively high molecular weight of polymers undergoing separation. It is also important to suppress as much as possible the undesired influence of molecular weights or of their distribution on resolution, as this factor has already been shown to complicate separation in adsorption chromatography (6).

It has been an objective of this study to estimate the possibilities offered by the liquid chromatography methods outlined above for the determination of characteristic quantities, such as molecular weights or their distribution and the distribution of functionality. For this purpose we prepared model samples of low-molecular weight polyisoprene contanining a defined number of hydroxy groups, $n = 0, 1$ and 2, in a sufficiently wide range of molecular weights, with the individual samples having a relatively narrow MWD.

MATERIALS AND METHODS

Preparation of Polymers

The polymers were prepared by the anionic polymerization with organolithium initiators (7,8) in toluene. Polyisoprene without the functional endgroup and α-hydroxypolyisoprene were prepared with n- and sec-butyllithium as initiator; α,ω-dihydroxypolyisoprene was prepared using the dilithiopolyisoprene oligomer obtained from the trans-stilbene-lithium adduct (9). The "living" polymer was transformed into a hydroxy terminated product by reaction with ethylene oxide (10, 11).

Gel Permeation Chromatography

The gel permeation chromatograph was built at this Institute. Four columns, 8 x 1200 mm in size, connected in series and packed with the styrene-divinylbenzene gel Styragel (Waters Associates Inc., Milford, Mass. USA) were used in the experiments, with a differential refractometer R-403 (Waters) serving as detector. Tetrahydrofuran (THF) was the eluent, flow rate 0.35 ml/min, at 25°C. The universal calibration curve (4) was constructed using a series of polystyrene standards (Waters) and the Mark-Houwink equation $[\eta] = 1.17 \times 10^{-4} M^{0.717}$ valid for linear polystyren in THF at 25°C (12). The molecular weights of polyisoprene samples under study with and without functional groups were calculated using GPC experimental data and the equation $[\eta] = 1.77 \times 10^{-4} M^{0.735}$ (13).

Vapour-Phase Osmometry

The measurements were performed with a Hitachi Perkin Elmer 115 osmometer (Hitachi Ltd., Tokyo, Japan) in toluene at 50°C in the concentration range 0.015-0.030 g/cm^3. The apparatus was calibrated by means of benzil and the real constant of the apparatus thus obtained was 1.2x10^4. The number average molecular weights values $\overline{M}_n$ were calculated from the reduced temperature difference extrapolated to zero concentration.

Membrane Osmometry

The measurements were performed with an automatic membrane osmometer (Hallikainen Instruments, Richmond, Ca., USA) at 30°C. The $\overline{M}_n$ values were calculated from the extrapolated reduced pressure to zero concentration.

Light Scattering

The measurements were performed in dried THF with a Photo-Gonio-Diffusometre FICA (Société Française D´Instruments de Controle et d´Analyse FICA, Le Mesnil Saint Denis, France) in vertically polarized light with the wavelength 546.1 nm in the angular range from 30° to 150°. Benzene with the absolute scattering value at 90° $R_{90} = 22.5\times10^{-6}$ cm^{-1} was used as standard. The experimental data were treated by the Zimm method, i.e. by the twofold extrapolation of K_c/R_θ to zero angle and zero concentration. Optically pure solutions in the concentration range 0.005-0.015 g/cm^3 were used. The refractive index increment measured with the Brice-Phoenix differential refractometer (Phoenix Precision Instruments, Gardiner, N.Y., USA) is 0.125 at 25°C and is independent of the number of functional groups in the polymer for n = 0,1,2.

Bonded-Phase Liquid Chromatography

All measurements were carried out with an HP 1084 B liquid chromatograph (Hewlett-Packard, Palo Alto, Ca., USA). A column 4.6x250 mm in size packed with silicagel modified with $-NH_2$ was used in the separation (Hewlett-Packard). The samples were dissolved to c. 0.05 g/cm^3 solutions in n-hexane and injected into the separation column in an amount of 20 microlitres. Various hexane-dichloroethane and hexane-isopropanol mixtures were used as eluents. The flow rate of the eluent was 2 ml/min., temperature 30°C. A Model 2025 differential refractometer (Knauer, Oberursel, FRG) was used for detection.

RESULTS AND DISCUSSION

Using the comparison between the average molecular weights calculated from GPC data by employing the universal calibration method and the values determined by absolute methods (cf. Table 1), it is possible to evaluate the validity of universal calibration and the adequacy of the given Mark-Houwink equation for polyisoprene also in the range of relatively low molecular weights. Simultaneously it is possible to determine the influence of functional hydroxy groups on GPC results. The resulting data show that under the chosen experimental conditions the influence (if any) of interactions of hydroxy groups with the column packing does not play any important role, and that the constants of the Mark-Houwink equation may be used in the molecular weight range under investigation (c. $3x10^3$ - $4x10^4$), regardless of the number of functional groups. Within the limits of experimental error, the weight average molecular weight values $\overline{M}_w$ calculated from GPC data are in good agreement with those obtained by light scattering.

No anomalies could be observed in $\overline{M}_w$ measurements by the light scattering method. The twofold extrapolation according to Zimm was linear (with a positive value of the second virial coefficient) despite the relatively high concentrations of investigated solutions, i.e. no aggregation trends could be observed. Also, it was not necessary to compensate the polyelectrolyte effect in samples with two functional groups.

The agreement of $\overline{M}_n$ values calculated from GPC and obtained by membrane osmometry is also very good. However, $\overline{M}_n$ values obtained by vapour-phase osmometry are lower in most cases than

TABLE 1

Molecular Weights of Polyisoprene Samples with Various Numbers of Hydroxy Endgroups

Sample	GPC data		Light scattering	Osmometry
	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$
		Functionless		
PI-0-1	3 800	1 600		
PI-0-2	5 200	3 200		
PI-0-3	5 400	3 200		2 400[a]
PI-0-4	11 900	9 300	14 700	5 900[a]
PI-0-5	24 100	5 800	30 800	7 700[a]
		Monofunctional		
PI-1-1	3 500	2 600		1 700[a]
PI-1-2	3 500	2 500		
PI-1-3	7 300	5 700	8 500	5 000[a]
PI-1-4	12 000	9 600	-	-
PI-1-5	13 000	10 100	-	-
PI-1-6	13 600	10 400	-	-
PI-1-7	26 200	12 200	29 000	-
PI-1-8	33 200	22 900	-	22 600[b]
		Bifunctional		
PI-2-1	6 100	3 900	-	2 800[a]
PI-2-2	7 600	4 800	-	3 800[a]
PI-2-3	8 700	5 500	-	3 900[a]
PI-2-4	10 200	7 300	11 600	5 000[a]
PI-2-5	12 600	8 600	-	4 600[a]
PI-2-6	15 000	10 100	20 000	8 300[a]
PI-2-7	36 000	26 200	26 000	21 100[b]
PI-2-8	42 300	28 400	41 300	24 500[b]

[a] Values determined by vapour-phase osmometry.

[b] Values determined by membrane osmometry.

those calculated from GPC. This is probably due to the fact that the values obtained by osmometric measurements may be subjected to an error originating from two sources. Firstly, owing to the low real constant of the apparatus a high concentration of solutions (0.015-0.030 g /cm^3) must be chosen, when the concentration gradient is already being formed in the drop on the thermistor, which reduces the measured value. Secondly, it is probable that the polymers under study contain residual low-molecular weight components (catalysts, residual monomers, antioxidants and their transformation products), which again reduce the real average molecular weight of polyisoprene. Under these circumstances, the $\overline{M}_n$ values calculated from GPC data may be regarded as more reliable, because during GPC separation these low-molecular weight components are separated from the polymer itself, and the calculated $\overline{M}_n$ values are not affected by them.

Because of the good solubility of samples in nonpolar n-hexane, separation according to the number of functional groups was carried out on a column with the polar chemically bonded $-NH_2$ phase (LiChrosorb Si 100-NH_2). This column was used in all measurements.

The first successful separation was completed in the system hexane-dichloroethane 80/20 (v/v), where functionless and monofunctional polyisoprenes could be adequately separated in the molecular weight range under study, but the difunctional polymers were not eluted from the column under these conditions (Fig.1). A further increase in the elution power of the eluent, which should lead to the elution of difunctional polyisoprenes, would cause a considerable change in the thermodynamic quality of the solvent compared with pure n-hexane and consequently it would cause the precipitation of the polymers from solution and also lead to some difficulties in detection. For this reason, we looked for a system in which elution could be achieved for all the three types of polymers by adding a small quantity of a second component to n-hexane. The hexane-isopropyl alcohol system appeared to be a suitable choice. Fig.2 (3% v/v of isopropyl al-

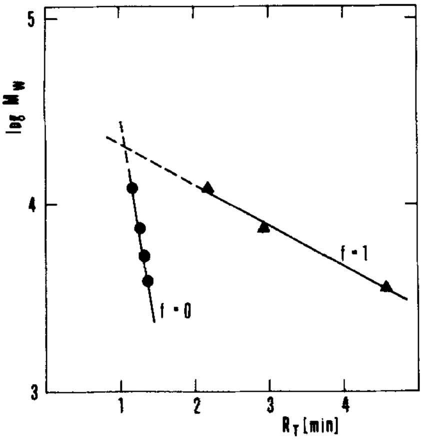

FIGURE 1. The dependence of retention times on molecular weights of samples of functionless and monofunctional polyisoprenes in the elution with hexane-dichloroethane mixture 80/20 (v/v). Conditions: cf. Experimental; f - number of functional hydroxy groups.

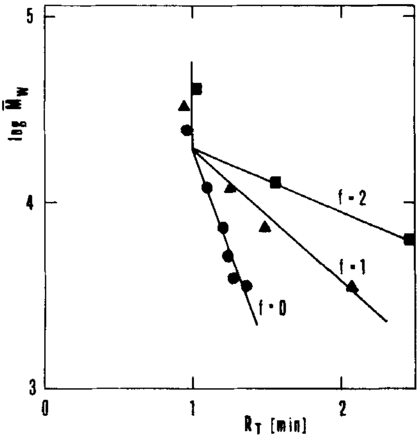

FIGURE 2. The dependence of retention times on molecular weight of polyisoprene samples with 0, 1 and 2 hydroxy endgroups in the elution with hexane-isopropyl alcohol mixture 97/3 (v/v).

cohol in hexane) shows the dependence of the retention data of functionless, monofunctional and bifunctional polyisoprenes on the logarithm of molecular weight. Under such conditions, a sufficient resolution of all three types of polyisoprene can be reached, which makes possible a quantitative evaluation of the distribution of functionality up to a molecular weight of c. 10 000. By lowering the isopropyl alcohol content to 1% (v/v), it is possible to improve the separation of functionless and monofunctional polyisoprenes also in the range of higher molecular weights (above 10 000), but bifunctional polymers are not eluted from the column any more (cf. Fig.3).

An interesting observation in all cases is the considerable dependence of retention times on molecular weight. The separation is consequently reduced to a certain range of molecular weights, but it makes possible not only the determination of the relative amount of polymers with various content of functional groups, but also of their approximate molecular weight. Polyisoprenes with molecular weights higher than approx. 18 000-20 000 cannot be

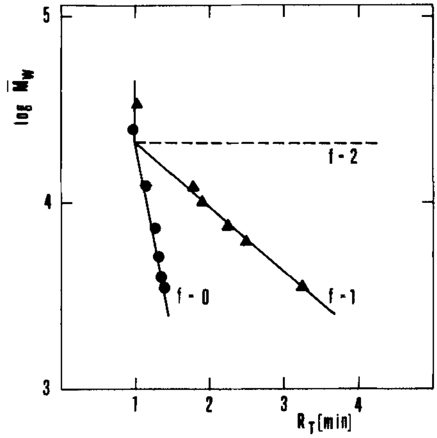

FIGURE 3. The dependence of retention times on molecular weight of polyisoprene samples with 0, 1 and 2 hydroxy endgroups in the elution with hexane-isopropyl alcohol mixture 99/1 (v/v).

separated under our experimental conditions. This limit of molecular weights coincides with the exclusion limit at GPC of polystyrene standards on a silicagel packed column with a similar porosity of 100 Å, as indicated by Fig.4. The likely explanation of this dependence consists in the simultaneous effect of the mechanism of steric exclusion. With increasing molecular weight of the polyisoprene samples, macromolecules penetrate into a smaller pore volume of the column packing, because part of the pores is inaccessible to them for steric reasons, and the surface undergoing interaction with the packing is therefore smaller. Another possible explanation is seen in the reduced chain polarity resulting from increased molecular weight, and consequently in the reduced interaction with the bonded phase which leads to a shorter retention time. Which of these causes is the real one could be decided by using a packing with such a large pore size that the effect of steric exclusion in the molecular weight range under study could not become operative. A study of these aspects is in progress.

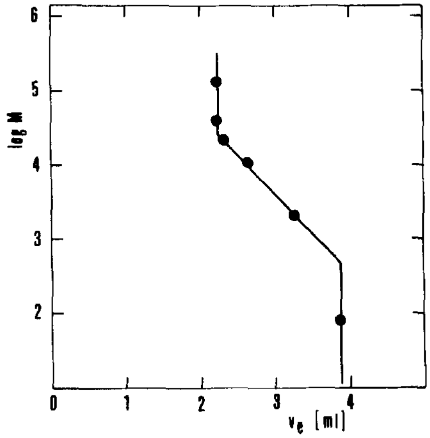

FIGURE 4. The calibration plot of a column packed with Lichrosphere 100 Å using polystyrene standards with tetrahydrofuran as eluent; flow rate of the elution agent 0.5 ml/min.

For a quantitative evaluation of GPC and bonded-phase liquid chromatography results obtained with refractometric detection, it is important to know if the refractive index of polyisoprenes under study depends on molecular weight and on the number of functional groups. Measurements with a differential Brice-Phoenix refractometer and chromatographic measurements have revealed that in the range of molecular weights and of the number of functional groups under investigation the refractive index increment remains constant within the limits of experimental error.

The results reported here show that the liquid chromatography methods may be successfully employed in the characterization of polymers bearing functional groups. GPC can be used in the determination of molecular parameters using the principle of universal calibration within the whole range of molecular weights under study (i.e. c. $3x10^3$-$4x10^4$ daltons). Using bonded-phase liquid chromatography, and under experimental conditions just described, it is possible to determine the quantitative participation of the individual functionalities up to molecular weights of c. 10 000, i.e. within the limits of most frequently occurring values in the case of liquid rubbers. The dependence of retention times on molecular weight makes also possible a direct estimate of molecular weight. It should be stressed that although these conclusions hold only for the hydroxy terminated polyisoprenes with the functionality n = 0-2 investigated in this study, they indicate at the same time the general possibility of use of liquid chromatography also in the study of other polymeric systems with functional groups.

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