Polyisobutylene: fractional precipitation from binary solvent induced by non-solvent addition

M. Sauviat and J. P. Cohen-Addad
Laboratoire de Spectrométrie Physique associé au CNRS, Université Scientifique et Médicale de Grenoble, B.P. 53 *X,* 38041 *Grenoble Cedex, France*

(*Received* 14 *July* 1980)

Large fractions of polyisobutylene chains may be obtained from precipitation induced by acetone added to solutions of polymer in a binary mixture (chloroform and dichloromethane). Fractions were characterized by weight average molecular weights, $\overline{M}_w$, and average radii of gyration, $\overline{R}_G^2$, obtained from light-scattering measurements performed on a good solvent (cyclohexane); the product $\overline{M}_w \times \overline{R}_G^2$ was found to vary according to the formula:

$$\overline{M}_w \times \overline{R}_G^2 = 1.33 \times \overline{M}_w{}^m$$

with $m = 2.22$; while the intrinsic viscosity of fractions was found to vary as:

$$[\eta] = 1.11 \times 10^{-4} \times \overline{M}_w^n$$

with $n = 0.76$. Considering that $m = 2\nu + 1$ and $n = 3\nu - 1$, where v is the critical exponent associated with the description of properties of polymer chain solutions; values of ν derived from m and n were found to be 0·61 or 0·58, respectively; the theoretical value is known to be 0·588. Polydispersity indices, I, were obtained from g.p.c. measurements: $1.1 < I < 1{\cdot}3$.

INTRODUCTION

It has been shown recently that relaxation processes of the transverse magnetic component of protons bound to polyisobutylene chains in solution are sensitive to chain molecular weight variations. This property was interpreted as reflecting low frequency relaxation processes of polymer chains and, more precisely, slow chain diffusion through entanglements[1,2]. More n.m.r. investigations of such basic properties require the availability of relatively large fractions with narrow and well-defined distributions of molecular weights.

The purpose of the present work was firstly to show that fractions of polyisobutylene chains may be conveniently obtained using a nonsolvent addition method. Secondly, the chain distribution within each fraction was considered as narrow enough to determine the critical exponent value characterizing the dependence of the intrinsic viscosity and radii of gyration upon the average chain molecular weight.

Column separation procedures are used on a preparative scale for the fractionation of a wide variety of high *MW* polymers. Temperature and elution gradient chromatography is more often used than gel permeation chromatography (g.p.c.) because it can be carried out on a preparative scale with a smaller cost than preparative g.p.c. This method, first described by C. A. Baker and R. J. P. Williams[3], is based on polymer solubility dependence upon chain length. This procedure has been used for the fractionation of high *MW* polyisobutylene (PIB)[4-7]. Difficulties have been encountered for the separation of the highest *MW* fractions[5,7]. Inversion of *MW* occurs in the last fractions, probably caused by adsorption of polymer on the glass carrier.

In the present paper, we describe a low cost fractional precipitation procedure, based upon simple operations, which does not require the use of elaborate equipment. Using this procedure, it was possible to fractionate samples of 15 g of high *MW* PIB. Polydispersity indices of the fractions ($I = \bar{M}_w/\bar{M}_n$) were evaluated from g.p.c. measurements and were found to be between $I = 1.1$ and 1.3.

DESCRIPTION

A procedure of fractional precipitation by addition of non-solvent or precipitant (or coacervation) was used. In a binary system polymer–solvent characterized by the polymer–solvent interaction constant χ, a phase separation occurs when $\chi > \chi_c$ a critical value which depends on the *MW* of the dissolved polymer. It has been shown by Flory[8] that:

$$\chi_c = \frac{1}{2}\left(1 + \frac{1}{\sqrt{x}}\right)^2 \simeq \frac{1}{2} + \frac{1}{\sqrt{x}}$$

where x is the segment number.

The fractionation by non-solvent addition method can be explained in the following manner: the gradual addition of a non-solvent (with a large χ value) will cause the χ value of the system to exceed the χ_c value for each component. The precipitation will occur in the order of decreasing values of x. In the present procedure a binary

0032-3861/81/040461-04$02.00

solvent (chloroform and dichloromethane) was used for convenience. The thermodynamics of coacervation in ternary systems in special simple cases has been elucidated by Tompa[9].

EXPERIMENTAL

Fractionation

The technical material studied was commercially available Vistanex MML 80 supplied by BASF.

A 1:3 chloroform–dichloromethane mixture was used as solvent, the nonsolvent was acetone, and the temperature of fractionation was 30±0.1°C. The fractionation was carried out in a separatory funnel of 5 l with a teflon cock at the bottom enabling the dense dilute solution to be separated easily. The apparatus was thermostated by a liquid circulating in a double jacket.

A sample of 15 g of polymer was dissolved in a mixture of 1 l of chloroform and 3 l of dichloromethane, at 30°C. After complete mixing, the flask was allowed to stand at least overnight. The first fraction was obtained by slow addition of non-solvent to the vigorously stirred solution. The mixture was then allowed to stand overnight at the same temperature. The separation was carried out by decanting the polymer-rich upper layer. The solvent-rich layer, maintained at 30°C, was then treated with a further volume of acetone, using the procedure described above, to obtain the next fraction.

The first fraction was obtained with 195 ml of acetone, the second with 5 ml, then the following ones with increasing volumes of non-solvent, until the fractionation was completed. Using this procedure, it was possible to separate the polymer sample into 18 fractions. The procedure was reproducible.

From the precipitated fractions, the polymer was recovered either by solvent evaporation under vacuum of 50°C, or by freeze-drying from cyclohexane solutions, until a constant weight was obtaiined. Fraction weights lie between 90 mg and 1.5 g and the total recovery of the polymer is 95–98%.

Fraction characterization

The fractions were investigated by light scattering, viscosimetry and gel permeation chromatography.

Light-scattering measurements Measurements were made with a Sofica PGD 42000 photometer. The instrument was calibrated with pure benzene for which the Rayleigh ratio is known. Data were taken at 11 scattering angles between 30 and 150° with unpolarized light of wavelength 436 mm. Measurements with cyclohexane solutions were carried out at 25°C. The specific index increment dn/dc was given the known value 0.105 ml g^{-1} (ref 10).

The solvent and the initial polymer solutions were filtered through a Millipore Teflon filter (porosity = 1 μ). For a polymer sample, the solutions were diluted to obtain five different concentrations. Solutions were centrifuged at about 12.000 pm (18400 g) for one hour, and directly pipetted into the light scattering cells.

The values of the wt average molecular weight $\bar{M}_w$ and the mean square radius of gyration (R_G) were determined following the Zimm graphical method[11].

Viscosimetry A Fica MS capillary viscosimeter (Ubbelohde type) with an automatic dilution device was used. The measurements were carried out with dilute cyclohexane solutions at a temperature of 25°C ± 0.2°C. Data on six concentrations of each sample were plotted against the concentration c to obtain the intrinsic viscosity $[\eta]$ and the Huggins constant k'.

Gel permeation chromatography Measurements were performed on Styragel columns (porosities 250, 10^3, 3×10^4 and 10^5 Å), using tetrahydrofuran as solvent, at a temperature of 25°C. The determination of *MWD* was achieved by use of a computer routine taking in part g.p.c. data given by a refractometric detection, the universal calibration curve of the apparatus with isomolecular polystyrene samples, and the intrinsic viscosities of PIB samples measured with a Fica capillary viscosimeter[12].

RESULTS AND DISCUSSION

Simple fractionation

The results of the fractionation in the form of cumulative weight distribution data, constructed in the usual way[13], are shown in *Figure 1A*. It gives the plot of the average cumulative wt %, Q, for a given fraction *versus* its intrinsic viscosity.

Experimental points representing two different fractionations fall along a single distribution curve, showing the reproducibility of the fractionation procedure.

The intrinsic viscosities of the fractions lie between 6.37 dl g^{-1} for the first fraction and 0.81 dl g^{-1} for the 18th one. Calculating the sum

$$\sum \omega_i[\eta_i]$$

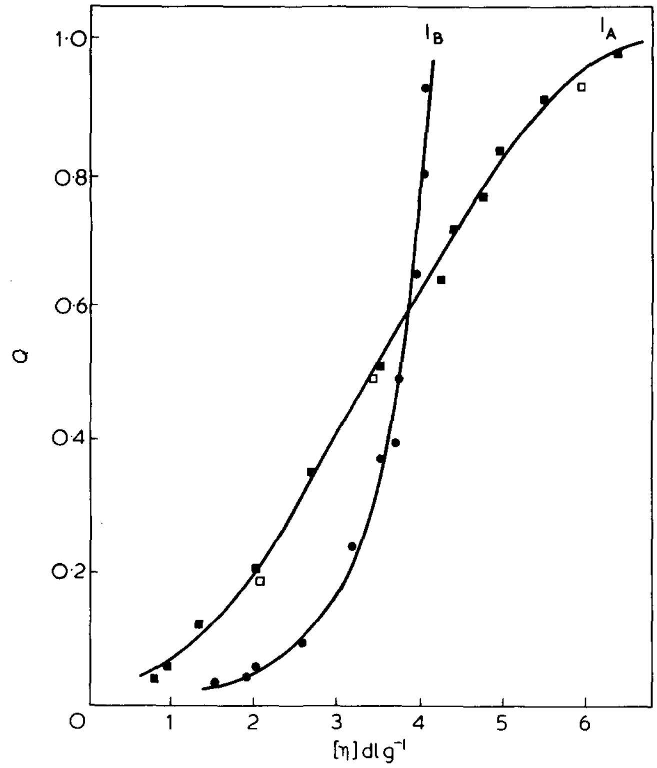

Figure 1 Integral *MWD*, *Q*, of PIB fractions *versus* intrinsic viscosity measured in cyclohexane at 25°C. (■, □), I_A Simple fractionation (the two symbols correspond to two different fractionations following the same procedure); (●), I_B Double fractionation

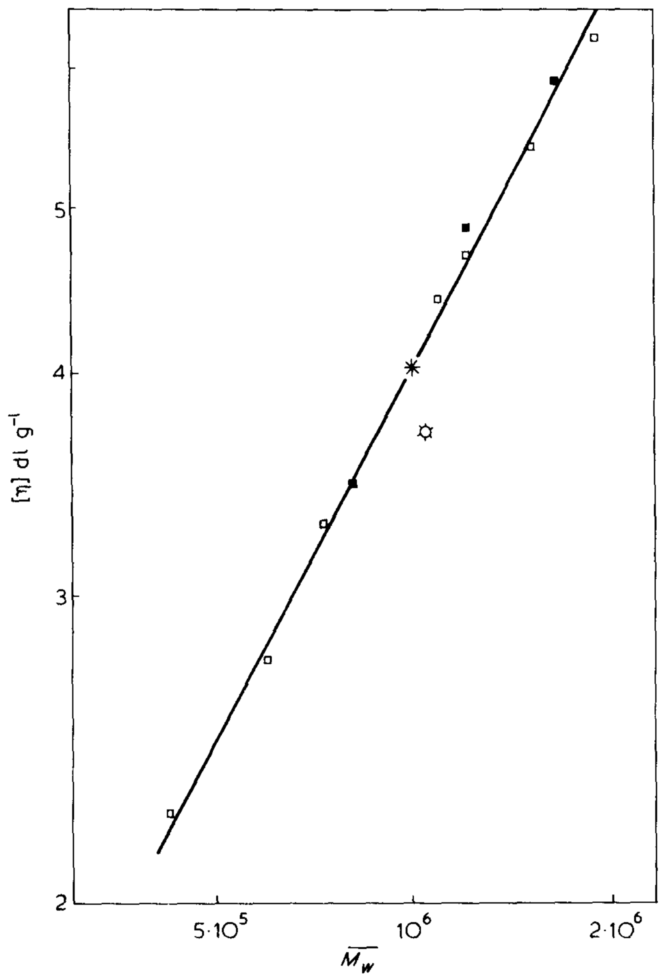

Figure 2 Double logarithmic plots of [η] versus $\bar{M}_w$ for PIB fractions in cyclohexane at 25°C. (■, □), simple fractionation. (The two symbols correspond to two different fractionations following the same procedure); (*), double fractionation; (O), unfractionated original sample

for the recovered polymer (ω_i being the weight per cent for a given fraction, and $[\eta_i]$ its intrinsic viscosity) a value of 3.43 dl g^{-1} was obtained, which is only slightly smaller than the value $[\eta]_0 = 3.59$ dl g^{-1} of the original sample MML 80. Therefore, only limited degradation takes place during the precipitation procedure.

Double fractionation

The fraction 8 was refractionated following the same procedure described above. It was possible to separate 13 fractions. *Figure 1B* gives the distribution curve for this double fractionation.

These distribution curves give an approximate illustration of the *MWD* in a polymer sample; the comparison of curves IA and IB shows that the fraction 8 exhibits a much lower polydispersity than the original sample, 40 wt % of the fractions obtained by the double procedure having an intrinsic viscosity close to 4 dl g^{-1}. However, it can be seen that the double fractionation enables the separation of lower *MW* species.

Fraction characterization

Viscosimetry and light-scattering measurements. Figure 2 shows the log–log plot of the intrinsic viscosity [η] in cyclohexane *versus* the wt average molecular weight $\bar{M}_w$ obtained from light-scattering data, using the first twelve fractions. It was not possible to carry out light-scattering measurements corresponding to the last six fractions, because their weight was too low.

The set of data points for two different fractionations may be fitted by a straight line, yielding:

$$[\eta] = 1.11 \times 10^{-4}\ \bar{M}_w^n$$

when [η] is expressed in dl g^{-1}, $n = 0.76$.

The experimental point (x) corresponding to a polymer sample obtained from double fractionation procedure falls on the same curve; while the experimental point corresponding to unfractionated MML 80 original polymer (*) falls apart from this curve, illustrating the great polydispersity of this sample. The intrinsic viscosity may be expressed as a molecular weight function according to the following formula:

$$[\eta] \propto M^{3\nu - 1}$$

where ν is the critical exponent involved in the descriptions of polymer chain solutions derived from critical phenomena theories[14]: $\nu = 0.588$ and $3\nu - 1 = 0.764$. Although the agreement between n and $3\nu - 1$ is probably fortuitous, it indicates that chain length distribution within each fraction is narrow. Polyisobutylene fractions have been obtained by using the theta column elution technique with benzene[6]; the corresponding exponent characterizing the intrinsic viscosity in cyclohexane has been found equal to 0.76; accordingly elution technique and partial precipitation method give about the same chain length distribution.

The mean square radius of gyration was obtained from light-scattering measurements performed on polymer solutions in cyclohexane:

$$\bar{R}_G^2 \propto \left(\sum_N N\Pi(N) R_G^2(N)\right)\left(\sum_N N\Pi(N)\right)^{-1}$$

where Π(*N*) is the normalized weight distribution function of the degree of polymerization; the exponent value characterizing the wt average *MW* dependence of $\overline{R_G^2}$ was found to be 0.66, to be compared with 0.59 — there is a slight discrepancy. The mean square radius of gyration was multiplied by $\bar{M}_w$ to obtain a direct approach to the average procedure:

$$\overline{R_G^2} \times \bar{M}_w \propto \left(\sum_N N^{2\nu} N^2 P(N)\right)\left(\sum_N N P(N)\right)$$

where $P(N)$ is the number of chains of degree of polymerization, N, in the sample. *Figure 3* shows the log–log plot of $\overline{R_G^2} \times \bar{M}_w$ as a function of $\bar{M}_w$:

$$\overline{R_G^2} \times \bar{M}_w = 1.33 \times \bar{M}_w^m$$

with $m = 2.22$; considering that m should be equal to $2\nu + 1$ for monodisperse chains, the critical exponent value derived from m is now equal to 0.61. The better agreement with the theoretical value 0.59 is probably due to compensation of errors obtained by multiplying $\overline{R_G^2}$ by $\bar{M}_w$.

Gel permeation chromatography Four samples were investigated by g.p.c.: fractions 10–14–17 obtained by the simple separation procedure, and a fraction 8_9 obtained by the double procedure (fraction 9 from the refractio-

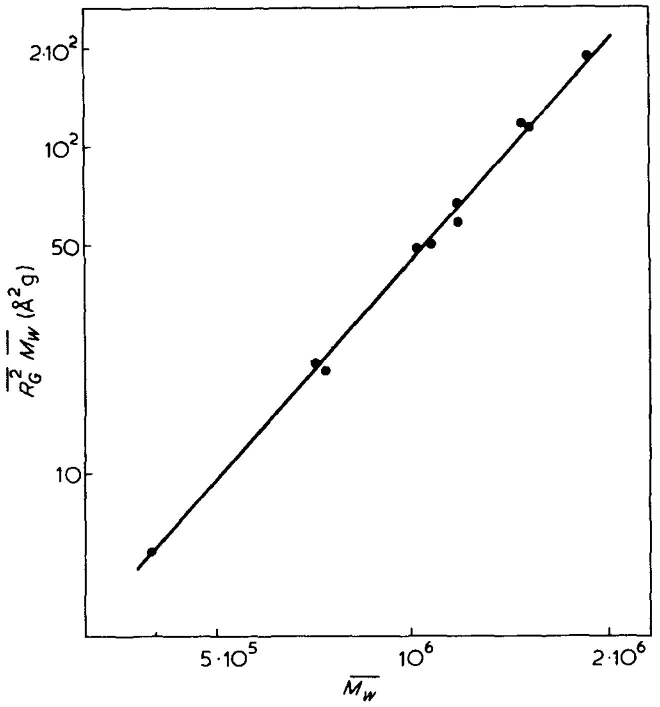

Figure 3 Double logarithmic plots of $\overline{R_G^2} \times \bar{M}_w$ *versus* $\bar{M}_w$ for PIB fractions in cyclohexane at 25° C

nation of the fraction 8). Results are summarized in *Table 1*.

CONCLUSION

The purpose of the present work was to show that large fractions of polyisobutylene chains may be obtained by precipitation from a ternary solution. A binary mixture was used instead of benzene as a good solvent above the theta temperature. The chain *MWD* was found to be narrow enough to permit n.m.r. studies of low frequency relaxational processes characterizing slow chain diffusion through entanglements.

Table 1 Polydispersity indices characterizing several fractions of polyisobutylene chains

Fraction	$\bar{M}_w$ 10^5	$\bar{M}_n$ 10^5	$I = \frac{\bar{M}_w}{\bar{M}_n}$
10	7.08	5.53	1.28
14	2.86	2.58	1.11
17	1.69	1.52	1.11
8_9	7.81	6.12	1.28

ACKNOWLEDGEMENTS

The experimental procedure used to obtain partial fractionation of polyisobutylene was proposed by Dr H. Cheradame (Laboratoire de Chimie des Polymeres de l'Ecole francaise de Papeterie, Grenoble).

REFERENCES

1 Cohen-Addad, J. P. *J. Chem. Phys.* 1979, **71**, 3689
2 Cohen-Addad, J. P., Guillermo, A. and Messa, J. P. *Polymer* 1979, **20**, 536
3 Baker, C. A. and Williams, R. J. P. *J. Chem. Soc.* 1956, 3252
4 Cantow, M. J. R., Porter, R. S. and Johnson, J. L. *J. Polym. Sci. Part C1* 1963, 187
5 Panton, J. C., Plesch, P. H. and Rutherford, P. P. *J. Chem. Soc.* 1964, 2586
6 Matsumoto, T., Nishioka, N. and Fujita, H. *J. Polym. Sci. Part A2* 1972, **10**, 23
7 Mokhtar-Nejad, E., Berger, K., Hammel, R. and Lederer, K. *Makromol. Chem.* 1978, **179**, 159
8 Flory, P. J. 'Principles of Polymer Chemistry' Cornell Univ. Press, Ithaca, NY, 1953
9 Tompa, H. *Trans. Faraday Soc.* 1949, **45**, 1142; Tompa, H. and Bamford, C. H. *Trans. Faraday Soc.* 1950, **46**, 310
10 Huglin, M. B. 'Light Scattering from Polymer Solutions' Academic Press, NY, 1972
11 Zimm, B. H. *J. Chem. Phys.* 1948, **16**, 1093, 1099
12 Busnel, J. P., Orvoen, J. B. and Bruneau, C. M. *Analysis* 1978, **6**, 6, 255
13 Schulz, G. U. and Dinglinger, A. *Z. Phys. Chem. B.* 1939, **43**, 47
14 Des Cloizeaux, J. *J. Phys. Lett.* 1978, **39**, L131