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Unperturbed chain dimensions of polyisobutylene in different solvents and at different temperatures

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Summary: Intrinsic viscosity of polyisobutylene is determined in different solvents and at different temperatures. The intrinsic viscosity is found to increase with the increase in temperature. These variations are explained in terms of variation in thermodynamic quality of the solvent. From these data, the upertubed parameter (k_0) is determined. It is observed that it firstly increases with temperature and then seems to level off and is found to be different for different solvents. k_0 is also correlated with different thermodynamic parameters like ΔH, δA, ψ and χ .

Introduction

The unperturbed parameter, hereafter designated as k_0, may be used to assess the unperturbed polymer chain dimensions as well as the chain stiffness of randomly coiled polymer. This important configrational factor of a polymer is found to be function of solvent and temperature etc. The way it depends on these parameters is still a mystery and the conclusion drawn by different investigators (1-7) vary from one to another author. The polyisobutylene (PIB), which has a number of industrial and other applications, is very little investigated. The only reference one can find in this respect (as far as the author is aware) is of Bohdanecky (8), who gave the value of k_0 as 9.8×10^{-4}. Therefore one of the aim of this communication is to determine k_0 for PIB using solvents of different thermodynamic quality and at different temperatures. The second objective of this report is to correlate these results with different thermodynamic parameters like, free energy interaction parameter, χ , entropy parameter, ψ , heat of solution ΔH and solubility parameter, δA taken from the literature (9-11).

Experimental

The polymer investigated in this report is polyisobutylene, kindly supplied by BASF, West Germany. The polymer was fractionated with respect to its molecular weight using fractional precipitation method (12). The fractions so obtained were characterized by light scattering and viscometery (12,13).

The viscosity measurements were made by using Ostward type viscometers. Viscometers were chosen so that all solvent flow times ranged between 100 and 200 seconds. The reproducibility of solvents and solution flow times, when coupled with the random errors encounted in the concentration determinations, led to measured values of the intrinsic viscosity that were precise to about ± 1%. The resulting unperturbed chain parameters are thus presented in light of these experimental uncertainties. The solvents used were benzene, toluene, chlorobenzene, cyclohexane and heptane. All the solvents were of E.Merck Brand and were used after drying and distillation of each. The temperature was kept constant at 25± 0.01°C throughout the measurements except in case of benzene. In this case the measurements were made at different (20-45°C) temperature.

Results and Discussion

The intrinsic viscosity of polyisobutylene was obtained by extrapolation method and using the following equation.

$$\eta_{sp}/c = [\eta] + k_1 [\eta]^2 c + \ldots \qquad (1)$$

Here η_{sp} (= η_r-1) is the specific viscosity of the system; $[\eta]$ is the intrinsic viscosity, k_1 is Huggins constant, c and η_r are the concentration of polymer in the solution and relative viscosity of the solution respectively. Neither shear effects nor curvature in the η_{sp}/c vs c plots was observed in these measurements. Linear regression analyses was used in evaluating the dilute solution viscosity data. The results so obtained were plotted versus molecular weight of the polymer on log-log scale (see fig.1), according to following equation (2).

$$[\eta] = k M^a \qquad (2)$$

The values of k and a were obtained by fitting the data to method of least squares and are reported in table 1. Figure 1 shows that the data do not

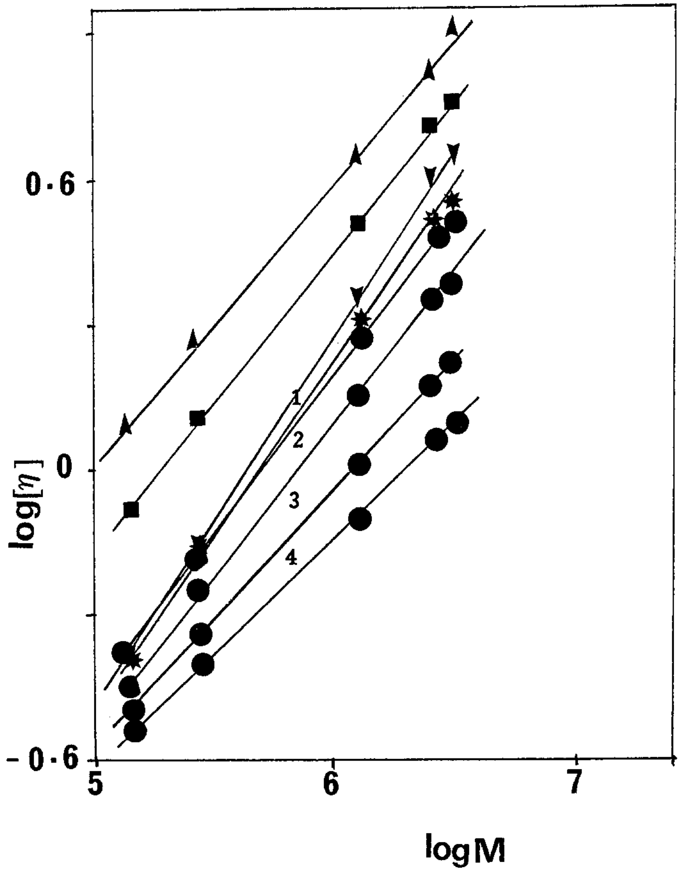

Fig.1. Intrinsic viscosity as a function of molecular weight of polyisobutylene in (▲) cyclohexane; (■) toluene; (▼) chlorobenzene; (✱) heptane and in (●) benzene at (1)45°C; (2)35°C; (3)25°C and at (4)20°C.

Table 1. Mark-Hauwink Sakurada Constants and k_0 of polyisobutylene in different solvents and at different temperatures.

Solvent	Temperature (°C)	k x 10^4	a	k_0 x 10^4
Heptane	25	1.678	0.668	9.5
Cyclohexane	25	16.381	0.563	31.0
Chlorobenzene	25	1.262	0.683	6.6
Toluene	25	33.210	0.485	20.8
Benzene	20	18.790	0.448	7.6
Benzene	25	6.844	0.521	8.5
Benzene	35	2.717	0.612	9.4
Benzene	45	1.347	0.677	9.9

deviate from straight line. Moreover the value of k and a in case of toluene are found to be the same as obtained by others (14). Similarly the data available in literature (9) also fall on the respective plot.

The intrinsic viscosity obtained at different temperatures, using benzene as a solvent is plotted in figure 2. The data show an increase in intrinsic viscosity with temperature as observed by others (8,10,15). The extent of increase is proportional to molecular weight of the polymer. These

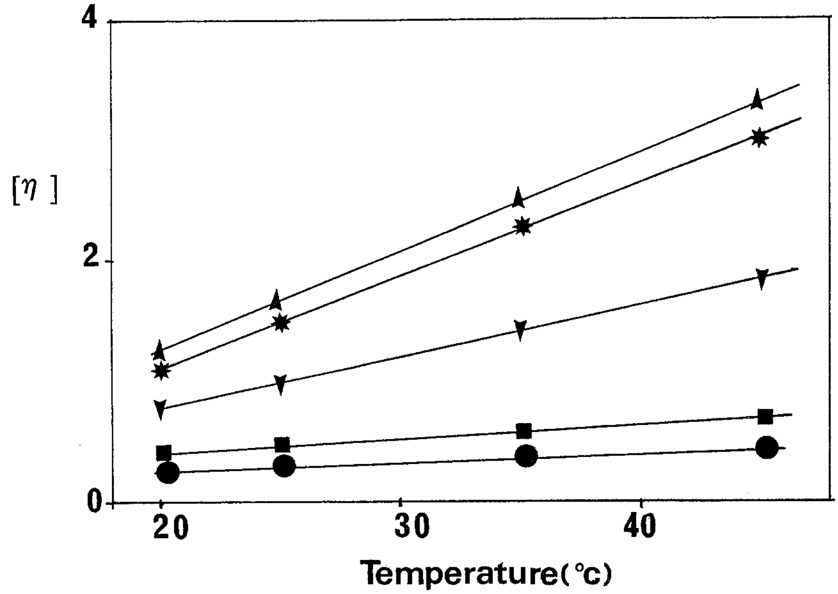

Fig.2. Intrinsic viscosity of polyisobutylene as a function of temperature, having molecular weight equal to (▲) 31.62 x 10^{-5}; (✱) 26 x 10^{-5} (▼)12.69-5; (■)2.82 x 10-5 and (●) 1.41 x 10-5 grams/mole. The solvent used was benzene.

variations in viscosity may be caused by an imporvement of solvent quality with the increase in temperature. The improvement in the quality of the solvent increases solvent/polymer segment interaction and leads to higher viscosities (10). The betterment in the thermodynamic quality of the solvent with temperature is also clear from increasing value of a with temperature (16).

To calculate k_0 from intrinsic viscosity, the data for each solvent and temperature are plotted according to Stockmayer-Fixman (17) (equation(3)) in figure 3.

$$[\eta]/(M)^{\frac{1}{2}} = k_0 + 0.51\ \phi_0\ BM^{\frac{1}{2}} \qquad (3)$$

Here B is a constant and depends on the interactions of the system. ϕ_0 is a universal constant. The required parameter k_0 was obtained by help of their linear regression and are listed in table 1. Figure 3 shows that the data do not deviate from equation (3). The value of B varies from solvent to solvent and increases with the increase in temperature (with the supposition that ϕ_0 is independent of temperature and quality of solvent). k_0 is found to firstly increase with temperature and then levels off (see fig 4) Similarly it is different for different solvents. The reason for such variations in k_0 may be due to the following reason: The chain dimensions of polymer molecules in solution are influenced by both long range(excluded volume) and short range (rotational isomeric) effects (18). Long range effects are result of thermodynamic interactions between polymer molecules and their environments. In a good solvent, where the energy of interaction between polymer and solvent is high, the molecules will tend to expand in order to increase the number of polymer-solvent contacts. As a result,the

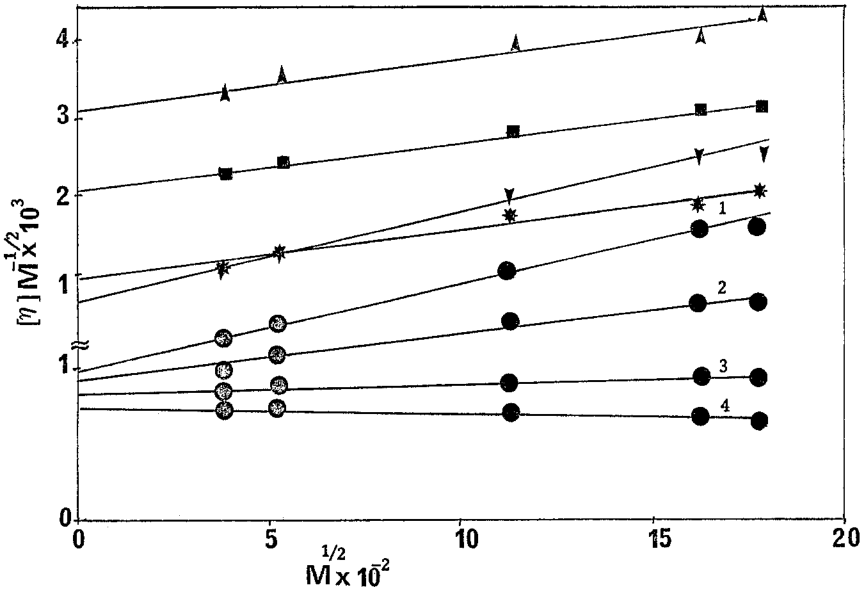

Fig.3 Stockmayer-Fixman plots (equation (3)) of polyisobutylene in different solvents. The symbols have the same meaning as in figure (1).

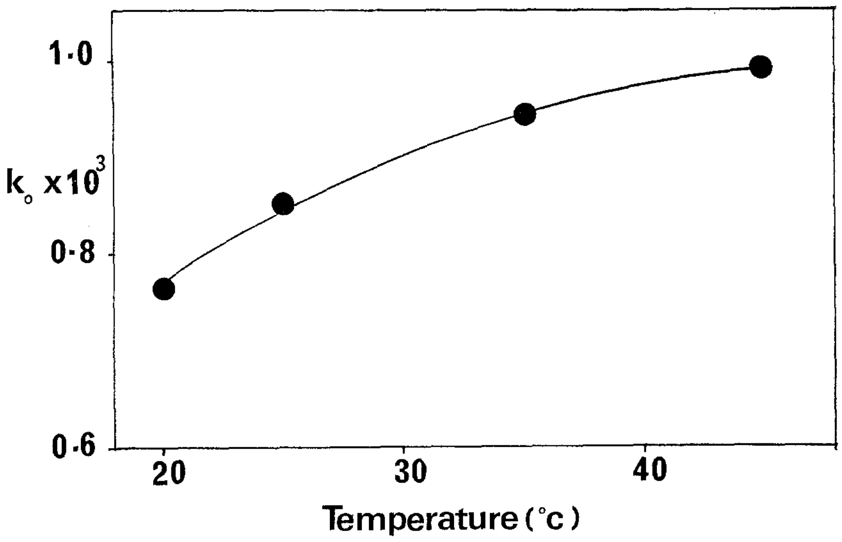

Fig.4 k_o of polyisobutylene in benzene as a function of temperature.

volume which one polymer segment excludes from another is large. In a poor solvent where the energy of interaction is unfavourable, the polymer will contract in order to increase the amount of polymer-polymer contacts.This decreases the amount of polymer-solvent contacts, resulting in a low excluded volume. Under theta conditions, defined as the temperature at which the second varial coefficeint is zero (18), it has been shown that the excluded volume vanishes and the chain is unperturbed by long range interactions. To get an idea about the dependence of k_o on different thermodynamic parameters of the system, obtained from the literature (9-11) and listed in table 2.k_o is ploted versus ΔH and δA in fig.5 The figure shows, k_o decreases with the increase in δA or ΔH of the system, whereas the data are more dispersed in case of ΔH as compared to δA. A try is also made to plot k_o versus ψ or χ parameters, but the trend seemed to be irregular and was not possible to draw any clear conclusion. On the other hand ψ is a function of thermodynamic quality of the solvent

Table.2 k_o and other thermodynamic parameters of the system obtained at 25°C.

Solvent	$k_o \times 10^4$	δA	ΔH	ψ	χ
Heptane	9.5	-	-24(11)	-0.03(9)	-0.15(9)
Cyclohexane	31.0	8.2(11)	-9.0(11)	0.28(9)	0.05(9)
Chlorobenzene	6.6	9.5(11)	160(11)	0.32(9)	0.28(9)
Toluene	20.8	8.9(10)	250(11)	0.32(9)	0.28(9)
Benzene	8.5	9.2(11)	260(11)	0.28(9)	0.29(9)

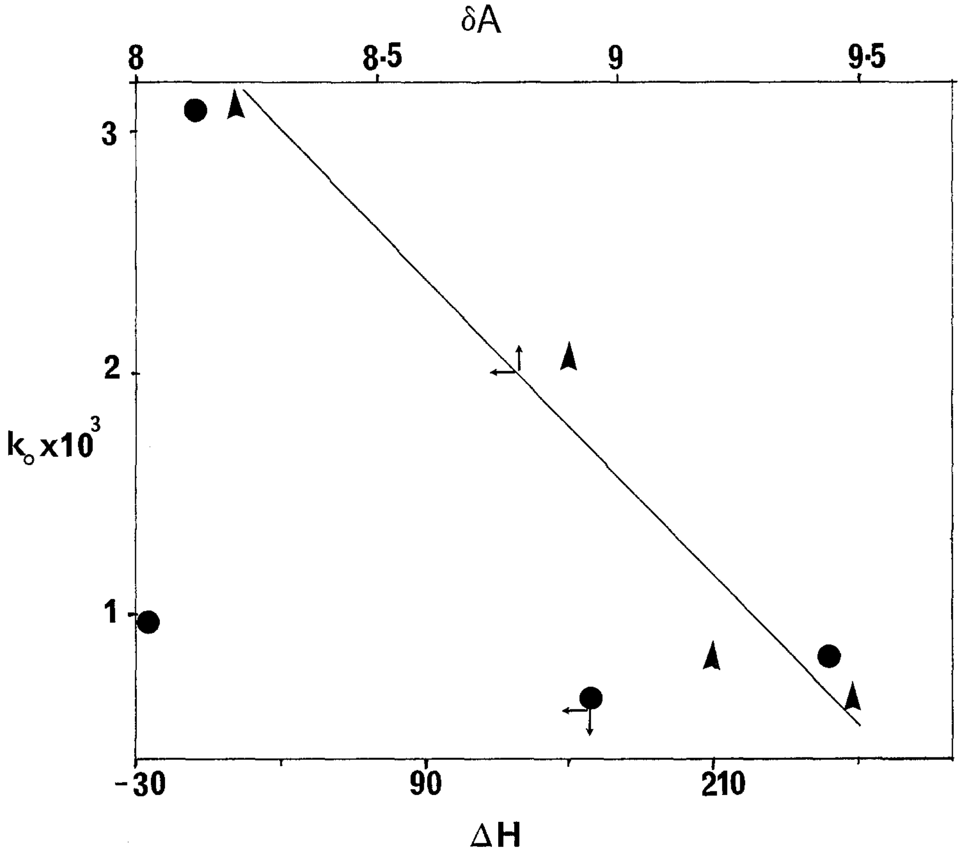

Fig.5 k_o as a function of (▲) δA and (●) ΔH of the system.

and is zero when the measurements are made at theta conditions (19). As it is explained earlier k_o should increase with the increase in thermodynamic quality of the solvent and hence with ψ . Therefore the possible cause of irregular dependence of k_o on ψ may be that the data are obtained at different conditions and most of the data are in higher value of ψ Where it is least sensitive to interactions in the system and k_o etc (19). The above observations conclude that δA or ΔH is more sensitive to quality of the solvent and hence to k_o as compared to χ or ψ parameters.

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