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Excluded volume and hydrodynamic properties of polystyrene in non-ideal solvents

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ABSTRACT

At 298 K, intrinsic viscosity, [η], has been measured for fifteen polystyrene, PS, samples of different relative molar masses M in pure toluene, T, and seven different binary solvents. These solvents were toluene / methanol (MeOH) mixtures having different volume fractions of MeOH. The θ - composition for the binary solvent system was found to be 77% T / 23% MeOH at 298 K. The dependance of excluded volume of polymer molecules on M and the solvation power was demonstrated. A constant value of 0.633 nm for the effective unit length, b, was obtained under θ - condition. Meanwhile a non-constancy of b, obtained in case of thermodynamically good solvents, was attributed to the neglect of excluded volume effect.

Key words

polystyrene, hydrodynamic, excluded volume, binary solvents, viscosity, θ-condition

INTRODUCTION

In an extended series of publications [1-9], the viscometric behavior and unperturbed dimensions of polystyrene in mixed solvents were studied. The obtained results were compared with the literature data [10-17].

When a single solvent is not available to yield a convenient θ-temperature, recourse is frequently made to binary solvent mixtures the variable composition of which affords, in principle, a range of different θ-temperatures. At a fixed temperature, of course, there are numerous pairs of liquids [18, 19] capable of yielding θ-compositions.

The intrinsic viscosity of polymer solutions [20] was constructed on the assumption of Gaussian statistics for bundle, i.e., without taking account of volume effects. Subsequent experimental [21, 22] and theoretical [23-25] investigations have shown that in good solvents the ratio between intrinsic viscosity and the dimensions of the hydrodynamically unpermeable macromolecules differs considerably from that predicted by the Kirkwood-Riseman theory.

The effect of the solvent on hydrodynamic properties of polystyrene is one of the most interesting but least investigated phenomena of intermolecular reactions which take place in polymer solutions. The work described here deals with the properties of polystyrene in a series of solvents exhibiting a systematic variation of solvent-solute interaction. Such a variation is obtained by varying the composition of two-component solvent, viz., toluene (T) and methanol (MeOH). The effect of this variation on the hydrodynamic properties of polystyrene is also considered.

EXPERIMENTAL

Materials

All solvents were dried over anhydrous Mg SO_4 and distilled at atmospheric pressure. The polystyrene (PS) samples of nominal polydispersity indices M_w / M_n < 1.09 were obtained from Polymer Laboratories Ltd., Church Stretton, Shropshire, UK and Pressure Chemical Company, Pittsburg, Pa. The quoted relative molar masses M x 10^{-5} for the fifteen polymer samples were 1.06, 1.10, 1.77, 2.00, 2.75, 2.94, 3.79, 3.90, 4.20, 5.05, 6.19, 6.40, 7.70, 9.6 and 11.0 for samples PS1 -PS15.

Techniques

Details of the preparation of solutions as well as measurements of $[\eta]$ have been described elsewhere [4-6].

The θ- composition for polystyrene (PS) in T / MeOH solvent mixture was determined by applying the Cornet and Ballegooijen method [26] at 298 K.

RESULTS AND DISCUSSION

θ - composition

The Cornet and Ballegooijen method [26] was employed to establish the θ - composition for PS5 in mixed solvents, the constant temperature maintained being 298 K. The volume fraction of non-solvent (MeOH) necessary for incipient precipitation was plotted versus the logarithm of the corresponding volume fraction of PS. The extrapolation of the linear dependence to pure polymer yielded the θ - composition which correspond to 77% T and 23% MeOH. the θ - composition was confirmed by treating the experimental viscometric data, measured at 298 K in this mixed solvent, according to the well known Mark - Houwink relation (MHS) as well as the Stockmayer - Fixman plot [27]. The derived values of the MHS exponent ν and the Stockmayer - Fixman slope obtained by least squares analysis were 0.5 and zero, respectively, which confirm the existence of θ - condition. The resultant θ- composition lies in excellent agreement with the volume / volume composition of 76.9 T / 23.1 MeOH reported by Marzolph and Schulz [28], and by Rossi et al. [29]. Other θ - composition of 80% T / 20% MeOH have been reported by Oth and Desreux [14].

Excluded volume

The values of intrinsic viscosity, $[\eta]$, for the fifteen PS samples in pure T and seven mixed solvents comprise T and MeOH ranged from 29.3 dm3 kg-1 , for the sample of lowest M (PS1) in the worst solvent (θ- solvent, 23% MeOH), to 262.9 dm3 kg-1 , for the sample of highest M (PS 15) in the best solvent (0% MeOH). The obtained results were found to be in a good accord with that reported by Bawn et al. [31]. The plot of intrinsic viscosity in a mixed solvent vs. intrinsic viscosity of the same samples in the single solvent should exhibit very little scatter. A combination of bilogarithmic coordinates with the Zimm - type double correlation is used here to represent the viscosity data according to the method proposed by Munk et al. [14]. In Fig. 1 the data are plotted as log $[\eta]$ vs. (log $[\eta]_T$ + 2ϕ $_{MeOH}$). Here $[\eta]$ is the intrinsic viscosity of the polymer sample dissolved in mixed solvent and $[\eta]_T$ is the intrinsic viscosity of the same sample in toluene.

Mark - Houwink plots according to Eqn. (1)

$$[\eta] = K_m M^{\nu} \qquad (1)$$

yielded the derived values of the constants K_m and ν via the least squares analysis. The obtained constants for all the mixed solvents and pure T are given in Table (1). The standard deviation of the least squares analysis for each solvent is also listed in the last column of the same table.

From the viscosity measurements, the chain expansion factor α was obtained as $([\eta] / [\eta]_\theta)^{1/3}$ where $[\eta]_\theta$ is the intrinsic viscosity of PS in θ- solvent (solvent h) at 298 K. The dependance of the excluded volume on the composition of the solvent and molecular weight is illustrated in Fig. (2). In this figure the excluded volume is plotted as a function of ϕ $_{MeOH}$. and M of polymer samples in a Zimm - type double correlation plot. It can be easily seen that, for each M and for a given polymer -solvent systyem,, the excluded volume (α^5-α^3) is decreasing smoothly with increasing the content of the precipitant, ϕ $_{MeOH}$. and decreasing M respectively. The present results reinforces the growing body of evidence that the compactness of the polymer molecules increases as (1) the solvation power

Fig. (1) Double correlation of log [η] as a function of log $[\eta]_T$ + volume fraction of MeOH for PS samples in T/MeOH binary mixture.

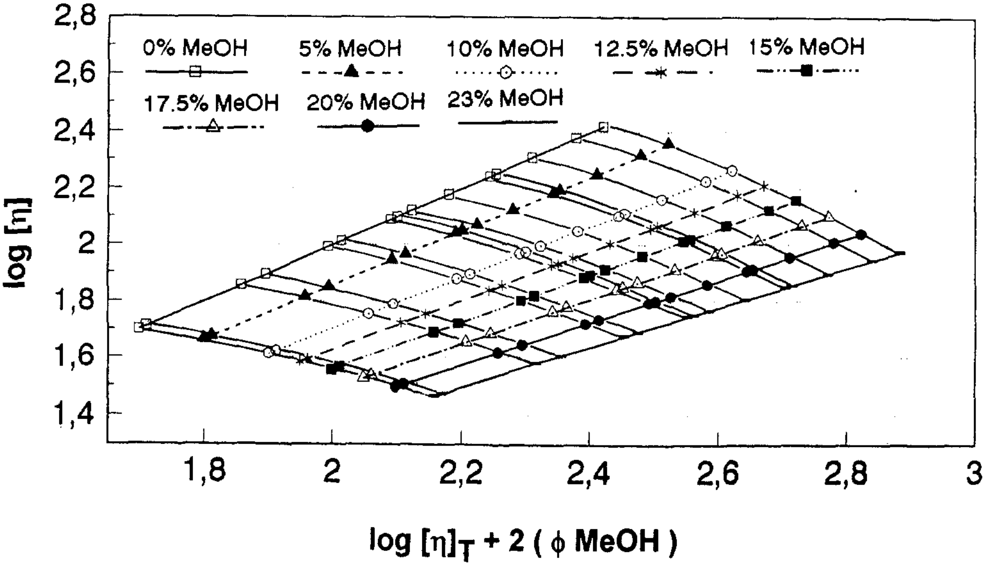

Fig.(2) Double correlation of excluded volume as a function of volume fraction of MeOH + (M x 10 $^{-5}$)

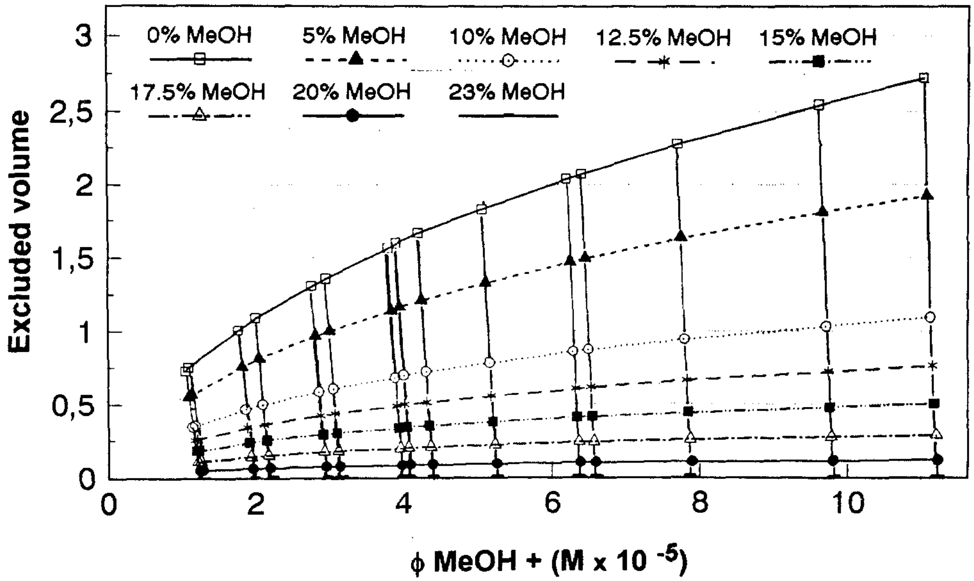

Table (1) Mark-Houwink-sakurada constants of PS in T/MeOH at 298 K

solvent		Mark-Houwink constants		standard
No	% of MeOH	K_m (x 10^3 dm^3kg^{-1})	ν	deviation x10^4
a	0.0	13.5	0.710	4.3
b	5.0	16.8	0.684	1.01
c	10.0	23.7	0.664	4.1
d	12.5	29.3	0.620	4.38
e	15.0	36.8	0.595	3.57
f	17.5	48.1	0.566	3.76
g	20.0	65.0	0.534	3.44
h	23.0	90.0	0.500	5.93

of the solvent decreases, i.e., with increasing the MeOH content; (2) molecular weight decreases and consequently, the excluded volume decreases. This speculation is based on the perturbation theories and Monte Carlo calculation techniques which carefully described by Munk [32]. These theories show the effect of molecular weight, polymer-solvent interaction parameter and concentration of the polymer solution on the volume of sphere occupied by a molecule.

Hydrodynamic properties

The effective hydrodynamic radius, R_e, of a polymer coil, which is swollen but impermeable to the rest of the solvent, has been expressed by Peterlin [33] as

$$R_e = 0.11 \{ [\eta] M / (1-\nu) \}^{1/3} \quad (2)$$

(where intrinsic viscosity is in dm3 kg-1 and R_e in nm). The Kirkwood - Riseman [20] theory gives equation (3) where Z is the degree of polymerization and b is the
effective length of the monomer unit :

$$R_e = Z^{1/2}\ b \quad (3)$$

Using equations (2) and (3), values of R_e and b were calculated for each molecular weight and each ϕ_{MeOH}. Detailed results are tabulated in Table (2). It can be seen that the overall trend is as follows : (1) for a particular M an increase in solvent power leads to an increase in b; (2) for a particular ϕ_{MeOH}

Table (2) Hydrodynamic properties (in nm) for PS in T/MeOH solvents

sample		solvent							
		a	b	c	d	e	f	g	h
PS1	Re	28.955	27.385	25.287	24.206	23.233	22.188	21.184	20.221
	b	0.907	0.858	0.792	0.758	0.728	0.695	0.664	0.633
PS2	Re	29.587	27.965	25.809	24.698	23.695	22.618	21.583	20.588
	b	0.910	0.860	0.794	0.759	0.729	0.695	0.664	0.633
PS3	Re	38.782	36.514	33.498	31.949	30.505	28.994	27.514	26.138
	b	0.940	0.885	0.812	0.774	0.739	0.703	0.667	0.633
PS4	Re	41.595	39.107	35.827	34.119	32.556	30.900	29.293	27.764
	b	0.949	0.892	0.817	0.778	0.742	0.705	0.668	0.633
PS5	Re	49.859	46.767	42.658	40.526	38.552	36.509	34.482	32.571
	b	0.970	0.909	0.830	0.788	0.750	0.710	0.671	0.633
PS6	Re	51.799	48.548	44.245	42.011	39.952	37.800	35.682	33.676
	b	0.974	0.913	0.832	0.790	0.751	0.711	0.671	0.633
PS7	Re	59.875	55.981	50.852	48.190	45.734	43.145	40.617	38.234
	b	0.992	0.927	0.842	0.798	0.758	0.715	0.673	0.633
PS8	Re	60.854	56.892	51.651	48.938	46.432	43.810	41.226	38.786
	b	0.994	0.929	0.843	0.799	0.758	0.715	0.673	0.633
PS9	Re	63.479	59.304	53.788	50.930	48.293	45.535	42.809	40.245
	b	0.999	0.933	0.846	0.801	0.760	0.717	0.674	0.633
PS10	Re	70.503	65.778	59.506	56.265	53.273	50.121	47.048	44.146
	b	1.012	0.944	0.854	0.807	0.765	0.719	0.675	0.633
PS11	Re	79.190	73.742	66.523	62.794	59.357	55.755	52.211	48.863
	b	1.026	0.956	0.862	0.814	0.769	0.723	0.677	0.633
PS12	Re	80.797	75.128	67.756	63.938	60.407	56.726	53.099	49.687
	b	1.029	0.958	0.864	0.815	0.770	0.723	0.677	0.633
PS13	Re	89.682	83.344	74.976	70.658	66.650	62.483	58.365	54.506
	b	1.042	0.969	0.871	0.821	0.775	0.726	0.678	0.633
PS14	Re	101.681	94.333	84.617	79.583	74.941	70.100	65.332	60.858
	b	1.058	0.982	0.881	0.828	0.780	0.730	0.680	0.633
PS15	Re	109.898	101.815	91.160	85.654	80.574	75.248	70.049	65.141
	b	1.069	0.990	0.886	0.833	0.783	0.732	0.681	0.633

For composition of solvents a - h see Table (1)

there is an increase in b with increasing M, this increase being most significant in good solvents (i.e. large ν and small ϕ_{MeOH}); (3) in solvent h (θ- solvent, $\phi_{MeOH} = 0.23$) the value of b remains constant (= 0.633 nm) at all molecular weights.

Diffusion and sedimentation experiments of Klenin and Ptitsyn [34] afforded values of b for PS in different single solvents for which ν = 0.50, 0.66 and 0.74. The general changes of b with M and with solvent power were the same as observed here, although the value of b in the (unnamed) θ- solvent was somewhat lower (0.55nm). Satisfactory agreement is observed between the value obtained in the present study in θ- solvent (b=0.633) and the value of b = 0.62 nm reported by Abdel-Azim and Huglin [5] for PS in cyclohexane at 307.5 K (θ- solvent). Apart from b under θ- conditions the non-constancy of b is clearly attributable to neglect of excluded volume effect.

It can be clearly seen, from Table (2), that the value of R_e increases with increasing the molecular weight of the polymer in the particular solvent and with increasing the volume fraction of T. This behavior is attributable to the dependance of [η] on the molecular weight of the polymer and the thermodynamic quality of the solvent.

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