Notes and Communications

The Dependence of Cohesive Energy Density on Polymer Stereostructure

THE physicochemical properties of a polymer molecule depend largely on the intermolecular forces and the chain flexibility. The influence of these factors on the hydrodynamic and mechanical behaviour of homologous series of polymers, in which side groups of varying size have been observed to alter the solution properties and glass transition temperatures, has been reported[1-3]. Other workers have shown that the stereoregularity of the polymer chain will also affect these properties and the dependence of unperturbed dimensions and glass transitions on polymer tacticity has been studied for both poly methylmethacrylate (PMMA)[4-7] and poly α-methyl styrene[8] (PMS). Such differences are normally ascribed to changes in chain flexibility but cohesive forces may also influence these properties.

The most widely used method of evaluating intermolecular forces is to estimate the cohesive energy density (CED) of the polymer and by studying polymer solvent interaction for a wide range of liquids it is possible to assign a CED to a polymer by assuming that the best solvent will have a CED equal to that of the dissolved polymer[9].

An estimation of the CED of four PMMA and two PMS samples of varying tacticity has been carried out, in order to ascertain to what extent the CED is influenced by the microstructure of the polymer.

Samples A, B, 8, and S1 were prepared by Dr D. M. Wiles and Dr D. J. Worsfold of the National Research Council of Canada and details can be found in the appropriate references[10-13]. The tacticity of each sample was determined by n.m.r. analysis[10-13]. Sample C was prepared in benzene solution at 60°C with 2,2′-azobisisobutyronitrile initiator. Sample D was obtained by irradiating a solution of 50 per cent monomer in toluene at −78°C for five days using a cobalt-60 source. The sample was fractionated and a fraction of molecular weight $\sim 2 \times 10^6$ was used.

Measurement of the limiting viscosity number $[\eta]$ was made at $30° \pm 0{\cdot}01°C$ in a Cannon–Ubbelohde semimicro dilution viscometer. Solvents were fractionally distilled and middle fractions were used throughout.

The CEDs of fractions A, B, C and D were estimated from the measurements of $[\eta]$ as proposed by Mangaraj et al.[14], who have suggested that if $[\eta]$ is measured in a range of solvents and the maximum value determined, then the CED corresponding to $[\eta]_{max.}$ will be that of the polymer. The value can be obtained more accurately by plotting $\{(V_s)^{-1} \ln ([\eta]_{max.}/[\eta])\}^{\frac{1}{2}}$ against δ_s, where δ_s^2 is the CED, and V_s is the molar volume of the solvent. This should give a straight line with an intercept on the δ_s axis equal to δ_p, the solubility parameter of the polymer.

The choice of solvents for such a determination is important, and it has been emphasized[2] that a homologous series, in which the solvents are structurally similar to a repeating unit in the polymer, should be used. For this

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reason a range of alkyl esters was chosen for the PMMA fractions. Values of the solubility parameter, δ_s, for each solvent, were drawn from the literature[15], and are listed in *Table 1* together with $[\eta]$ measured for each of the four samples.

A group of solvents composed mainly of ring compounds was used to determine δ_p for poly α-methyl styrene. Detailed results are given in *Table 2*.

Table 1. $[\eta]$ for PMMA fractions in an alkyl ester solvent series

Solvent	$\delta_s (cal/cm^3)^{\frac{1}{2}}$	$[\eta]$			
		A	B	C	D
Diethyl phthalate	10·00	0·845	0·415	0·736	0·740
Methyl acetate	9·60	0·925	0·431	0·850	0·806
Methyl/ethyl acetate (3:1)	9·45	0·952	0·434	0·854	0·798
Methyl/ethyl acetate (1:1)	9·32	0·968	0·425	0·809	0·766
Methyl/ethyl acetate (1:3)	9·18	0·917	0·394	0·749	0·755
Ethyl acetate	9·05	0·860	0·375	0·696	0·732
Ethyl/propyl acetate (1:1)	8·90	0·814	—	0·650	—
Propyl acetate	8·75	0·736	—	0·566	—
Propyl/butyl acetate (1:1)	8·60	0·693	—	—	—

Table 2. $[\eta]$ for poly α-methyl styrene in various solvents

Solvent	$\delta_s (cal/cm^3)^{\frac{1}{2}}$	$[\eta]$	
		8	S1
Dioxan	9·80	1·60	2·78
Chlorobenzene	9·50	1·87	3·25
Tetrahydrofuran	9·32	2·01	3·80
Benzene	9·15	2·07	3·42
o-Xylene	9·00	1·77	2·92
Toluene	8·91	1·74	3·09
p-Xylene	8·75	1·60	2·77

Table 3. δ_p for polymethylmethacrylate and poly α-methyl styrene samples

Sample	$\delta_p (cal/cm^3)^{\frac{1}{2}}$	$\delta_{p (calc)}$*	Fraction of syndiotactic diads
PMMA—A	9·28	9·25	0·05
PMMA—B	9·45	9·25	0·41
PMMA—C	9·52	9·25	0·80
PMMA—D	9·55	9·25	0·92
PMS—8	9·20	9·22	0·67
PMS—S1	9·30	9·22	0·90

*Calculated from Small's tabulated group values (ref. 16).

The Mangaraj plot, shown in *Figure 1* allows assignment of the δ_p values listed in *Table 3*. If the stereoregularity of the samples is expressed in terms of the fraction of syndiotactic diads present in the chain, it can be seen that δ_p increases with increasing syndiotacticity for both polymers. The error in δ_p was adjudged to be ± 0.05 (cal/cm^3)$^{\frac{1}{2}}$, between the results quoted.
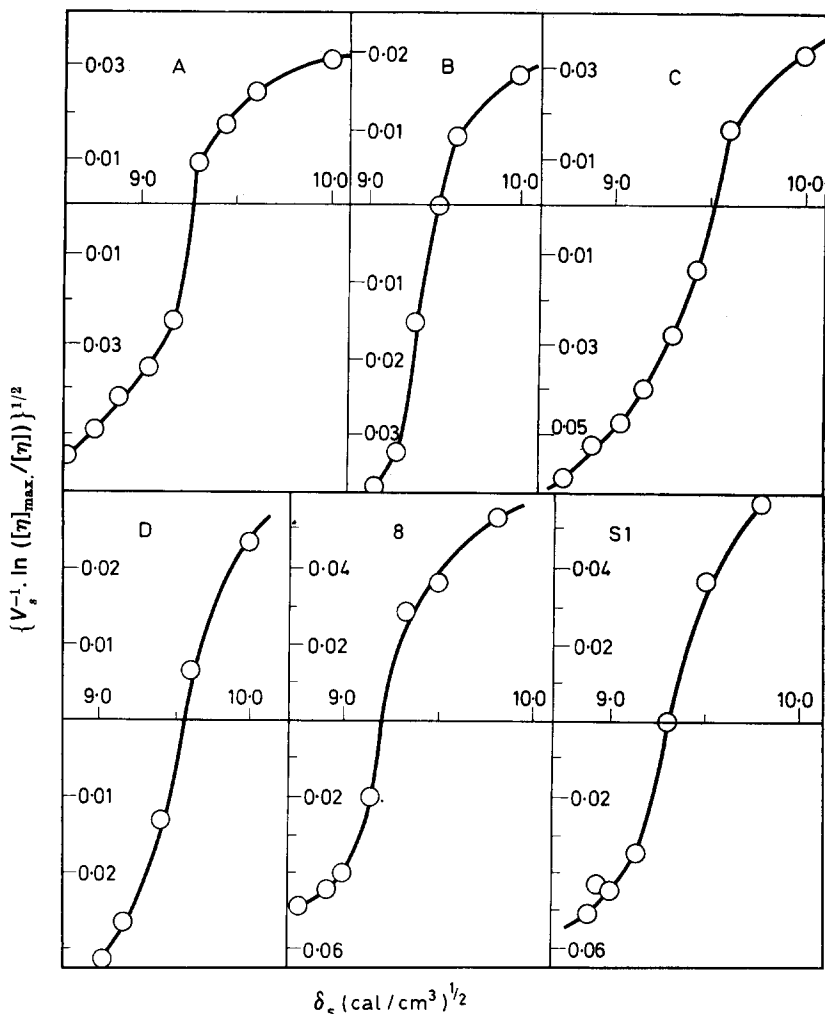
Figure 1—Estimation of δ_p for polymethylmethacrylate and poly α-methyl styrene

The experimental evidence suggests that there is a variation in CED with polymer microstructure. The obvious objection to such a statement is that the tactic forms of the polymer are chemically similar and should have the same value of CED. If, however, isomers such as *o*-, *m*- and *p*-xylene are considered, it is observed that CED is different for each one, thus by analogy with these simple isomers, the CED of a polymer could depend on the stereoregularity of the polymer chain. As the conformations of PMMA and PMS have been shown to vary with tacticity it is not unreasonable to propose that the CED will be a function of the microstructure as the results suggest.

However, it should be stressed that as the observed differences in CED are small, confirmation of the data by estimations of these intermolecular forces using other methods is both necessary and desirable.

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Approximate Calculation of Equilibrium Modulus Factors for Rubber Networks from Swollen Compression Data

IT IS generally accepted that, in contrast to unidimensional extension data, compression stress/strain measurements on partially or fully swollen rubber networks can be fitted by the gaussian expression

$$f = A_0 G_c v_r^{-\frac{1}{3}}(\lambda^{-2} - \lambda) \tag{1}$$

where f is the compressive force with reference to the unswollen cross-sectional area (A_0), v_r is the volume fraction of rubber in the swollen network, G_c is the compression modulus factor, and λ represents the actual compression ratio of the swollen sample, defined by

$$\lambda = \frac{\text{Compressed swollen height } (h_c)}{\text{Uncompressed swollen height } (h_s)}$$

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