COHESIVE ENERGY DENSITIES OF POLYMERS

PART 2.—COHESIVE ENERGY DENSITIES FROM VISCOSITY MEASUREMENTS

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Values are deduced for the interaction parameter χ for polymethyl methacrylate, polystyrene, and polyvinyl chloride systems by an application of the Fox-Flory theory to the viscosities of a polymer fraction in a suitable range of solvents. Analysis of these values as in part 1 leads to the assignment of cohesive energy densities for the polymers. For natural and butyl rubbers it is shown that the analysis of viscosity and swelling measurements lead to identical values of cohesive energy density.

Assignment of c.e.d. to natural and synthetic rubber networks has been described in the preceding paper.[1] The c.e.d. of rubbers were deduced from the Flory-Huggins interaction parameters χ, obtained for the various rubber + liquid systems from the equilibrium degree of swelling and the application of rubber elasticity theory.[2-6] The method is therefore limited to polymer networks which show rubber-like elasticity and is applicable only with difficulty to polymers which are not rubbers at ordinary temperatures.

An alternative approach of wider applicability is to evaluate χ from viscosity measurements on polymer solutions. In particular, values of χ may be deduced from limiting viscosity numbers $[\eta]$ by means of the Fox-Flory theoretical treatment [7, 8]. Thereafter the method of assigning solubility parameters to the polymers follows that described.[1]

Solubility parameters for natural and butyl rubbers are derived in this paper using the published viscosity data in different solvents [6, 7] A comparison of these with solubility parameters deduced from swelling measurements indicates the consistency of the two approaches. Viscosity measurements on polystyrene, polymethylmethacrylate, and polyvinyl chloride fractions are then reported and solubility parameters derived.

EXPERIMENTAL AND RESULTS

MATERIALS

POLYSTYRENE.—Redistilled styrene with an equal volume of benzene was polymerized to 10% by heating to 60°C *in vacuo* with 0·25% benzoyl peroxide for 12 h. The polystyrene was then fractionated by adding the requisite volume of methanol to a 2% solution in methyl ethyl ketone, warming to complete dissolution, and cooling overnight to 25°C. A middle 28% fraction thus obtained was similarly refractionated to give an 8·5% fraction on which the viscosity measurements were made. This second-stage middle fraction had an osmotic molecular weight in benzene using Zimm-Myerson osometers fitted with *Allerfeinst* membranes of 247,000.[9]

POLYMETHYLMETHACRYLATE.—Redistilled monomer with an equal volume of benzene was polymerized *in vacuo* by 0·05% benzoyl peroxide to 15% conversion in 200 min at 50°C. Fractionation was carried out as for polystyrene to give a 6% second-stage middle fraction having an osmotic molecular weight in toluene of 1,360,000.

POLYVINYL CHLORIDE.—Commercial powdered polymer, Corvic D/65 of I.C.I. Ltd., was extracted with a boiling 3 : 2 benzene + acetone mixture to leach out about one third of the polymer of a relatively low viscosity. Fractionation of the extracted material by the addition of water to a 2% solution in tetrahydrofuran gave an 8% middle fraction of $[\eta] = 0{\cdot}719$ in tetrahydrofuran at 25°C. A published calibration [10] gives a molecular weight of 45,600.

VISCOSITY PROCEDURE

Viscosities at 25°C were measured using Ubbelohde viscometers. Kinetic energy corrections amounting to 0·5-5% were applied. Viscosity numbers at four concentrations plotted against concentration gave straight lines from which the limiting viscosity numbers $[\eta]$ and Huggin's constants [11] k' of

$$\eta_{sp}/c = [\eta] + k' c [\eta]^2$$

recorded in tables 4, 5, and 6 were obtained.

Theta viscosities $[\eta]_\theta$, that is, viscosities when polymer of infinite molecular weight is just soluble, were determined approximately for polystyrene, polymethylmethacrylate, and polyvinyl chloride in methyl ethyl ketone + methanol, benzene + methanol, and tetrahydrofuran + water mixtures respectively. Precipitation points at 25°C for the polymers of finite molecular weight which were used were determined. Three or four viscosity measurements with amounts of precipitant slightly less than that for precipitation gave, by a short extrapolation, viscosities of 0·396, 0·760, and 0·436 for polystyrene, polymethylmethacrylate, and polyvinyl chloride, respectively. These viscosities were taken as the *theta* viscosities. This is a good approximation for the higher molecular weight polymers, but the degree of approximation for the polyvinyl chloride is less certain.

DISCUSSION

The χ values for the various polymer + solvent systems can be derived according to the Fox-Flory treatment [7] with introduction of the Flory-Huggins [8] lattice approximation, from the expression;

$$0{\cdot}5 + x^{-\frac{1}{2}} - \chi = \frac{V_1}{2C'_M KM}\left\{\frac{[\eta]^{\frac{5}{3}}}{[\eta]_\theta^{\frac{2}{3}}} - [\eta]\right\},$$

where $[\eta]$ and $[\eta]_\theta$ are the limiting viscosities in the solvent and *theta* solvent respectively of a homogenous fraction of molecular weight M and chain length x in a solvent of molar volume V_1. $C'_M K$ is a constant dependent only on the specific volume of the polymer. There is also a further relation, $[\eta]_\theta = KM^{\frac{1}{2}}$. The calculated χ are recorded in tables 1, 2, 4, 5, and 6.

TABLE 1.—VISCOSITIES AND CALCULATED χ FOR NATURAL RUBBER IN DIFFERENT SOLVENTS.[6]

solvent	$[\eta]$	χ
2 : 2 : 4-trimethylpentane	$2{\cdot}05_2$	0·438
n-hexane	$2{\cdot}41_6$	0·426
n-heptane	$2{\cdot}40_4$	0·416
n-octane	$2{\cdot}23_1$	0·422
n-decane	$2{\cdot}14_8$	0·413
methyl cyclohexane	$3{\cdot}17_2$	0·356
*iso*butyl *n*-butyrate	$1{\cdot}97_0$	0·445
cyclohexane	$3{\cdot}27_5$	0·371
n-butyl acetate	$1{\cdot}56_8$	0·486
1 : 1 : 1-trichloroethane	$3{\cdot}19_6$	0·389
carbon tetrachloride	$3{\cdot}94_9$	0·326
toluene	$3{\cdot}22_6$	0·378
ethyl propionate	$1{\cdot}25_5$	0·504
1 : 1-dichloroethane	$2{\cdot}69_2$	0·442
benzene	$3{\cdot}00_5$	0·417
chloroform	$3{\cdot}54_0$	0·390
tetrahydrofuran	$2{\cdot}74_9$	0·442
methyl *iso*butyl ketone	$0{\cdot}90_1$	0·515
methylene chloride	$2{\cdot}66_5$	0·462
methyl *n*-propyl ketone	$0{\cdot}66_8$	0·518

TABLE 2.—VISCOSITIES AND χ FOR POLY*ISO*BUTYLENE + SOLVENT SYSTEMS [7]

$M = 1{,}460{,}000$, $2C'_{\mathrm{M}}K = 7{\cdot}06 \times 10^{-3}$,
$x = 26{,}100$, $K = 1{\cdot}08 \times 10^{-3}$,
$x^{-\frac{1}{2}} = 0{\cdot}006$, $[\eta]_\theta = 1{\cdot}28$ (calc.).

solvent	$[\eta]$	χ
2 : 2 : 3-trimethylbutane	3·53	0·458
n-heptane	3·18	0·468
n-hexadecane	2·52	0·474
cyclohexane	5·15	0·423
toluene	2·69	0·488
benzene	1·37	0·505

TABLE 3.—VALUES FOR THE SOLUBILITY PARAMETER OF NATURAL AND BUTYL RUBBERS OBTAINED BY SWELLING AND VISCOSITY MEASUREMENTS.

rubber	method	δ_2 from slope	δ_2 from intercept
natural	swelling	8·08	8·12-8·06
natural	viscosity	8·03	8·05-7·98
butyl	swelling	7·81	$7{\cdot}84_5$-7·77
butyl	viscosity	7·83	7·83-7·78

TABLE 4.—VISCOSITIES AND χ FOR POLYSTYRENE + SOLVENT SYSTEMS

$M = 247{,}000$, $[\eta]_\theta = 0{\cdot}396$ (expt.).
$x = 2370$, $2C'_{\mathrm{M}}K = 4{\cdot}8 \times 10^{-3}$,
$x^{-\frac{1}{2}} = 0{\cdot}021$, $K = 8 \times 10^{-4}$.
$[\eta]_\theta = 0{\cdot}398$ (calc.),

solvent	$[\eta]$	k'	χ
*iso*butyl *n*-butyrate	0·704	0·62	0·475
n-butyl acetate	0·678	0·44	0·489
carbon tetrachloride	1·324	0·32	0·396
toluene	1·061	0·31	0·432
methyl ethyl ketone	0·607	0·51	0·506
benzene	1·113	0·39	0·438
chloroform	1·215	0·31	0·429
methyl *iso*butyl ketone	0·497	0·53	0·513
cis-1 : 2-dichloroethylene	1·112	0·29	0·451
methylene chloride	1·403	0·31	0·420
1 : 2-dichloroethane	1·133	0·36	0·444

TABLE 5.—VISCOSITIES AND χ FOR POLYMETHYL METHACRYLATE + SOLVENT SYSTEMS

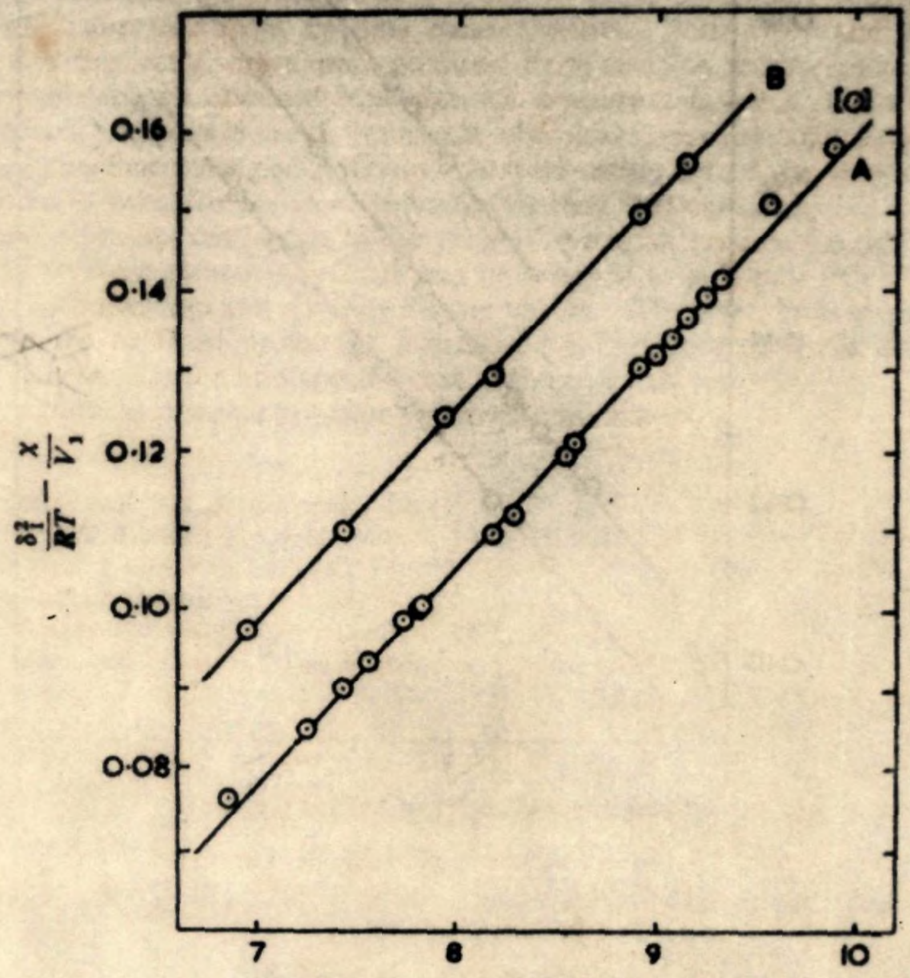
$M = 1{,}360{,}000$ $2C'_{\mathrm{M}}K = 4{\cdot}12 \times 10^{-3}$,
$x = 13{,}600$, $K = 6{\cdot}5 \times 10^{-4}$,
$x^{-\frac{1}{2}} = 0{\cdot}009$, $[\eta]_\theta = 0{\cdot}760$ (calc.).

solvent	$[\eta]$	k'	χ
n-butyl acetate	1·150	0·65	0·500
1 : 1 : 1-trichloroethane	2·998	0·34	0·429
n-propyl acetate	1·613	0·47	0·487
toluene	2·555	0·26	0·448
ethyl acetate	2·056	0·37	0·475
benzene	3·541	0·29	0·408
chloroform	4·903	0·32	0·335
methyl *iso*butyl ketone	1·303	0·64	0·496
cis-1 : 2-dichloroethylene	5·858	0·06	0·278
methyl *n*-propyl ketone	1·988	0·37	0·478

TABLE 6.—VISCOSITIES AND χ FOR POLYVINYL CHLORIDE + SOLVENT SYSTEMS

$M = 45{,}600$, $2C'_MK = 2.94 \times 10^{-3}$,
$x = 730$, $[\eta]_0 = 0{\cdot}436$ (expt.).
$x^{-\frac{1}{2}} = 0{\cdot}037$.

solvent	$[\eta]$	k'	χ
methyl ethyl ketone	0·565	0·49	0·465
mesityl oxide	0·585	0·51	0·428
tetrahydrofuran	0·719	0·29	0·364
chlorobenzene	0·478	0·58	0·514
1 : 2-dibromoethane	0·565	0·24	0·468
dioxane	0·506	0·58	0·503
1 : 2-dichloroethane	0·638	0·52	0·428
methyl *iso*propyl ketone	0·599	0·43	0·426
methyl *n*-propyl ketone	0·609	0·41	0·415



Solubility parameter of solvent (cal/cm³)½.

FIG. 1.—Determination of the solubility parameter.
A, natural rubber; B, butyl rubber (ordinate displaced by + 0·02).

There was very good agreement for polystyrene between the value of $[\eta]_0$ calculated from the published value [12] of K and that derived experimentally. The agreement was less satisfactory for the polymethylmethacrylate sample; since the published value [13] of K is derived from more extensive data than is our $[\eta]_0$, a value of $[\eta]_0$ calculated from the published K has been used. No value of K for polyvinyl chloride is available and so the experimental $[\eta]_0$ has had to be used without further check.

As in the preceding paper χ has been related to the solubility parameters for the liquid δ_1 and the polymer δ_2 by

$$\chi = \beta + \frac{V_1}{RT}(\delta_1 - \delta_2)^2,$$

where β is a further polymer + solvent interaction parameter. Fig. 1-2 show the satisfactory nature of the graphical determination of δ_2 as in part 1 by plotting $(\delta_1^2/RT - \chi/V_1)$ against δ_1, and the consistent δ_2 values obtained from the slopes and intercepts are given in tables 3 and 7.

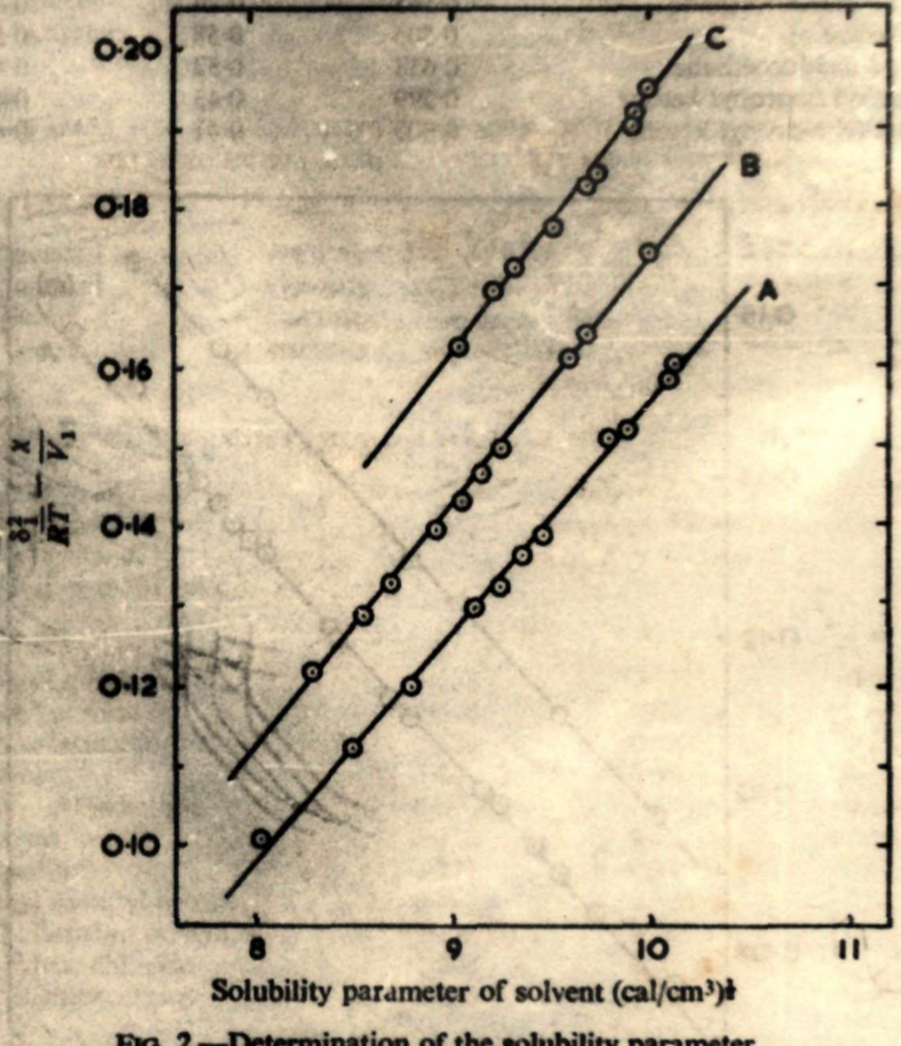


FIG. 2.—Determination of the solubility parameter.
A, polystyrene; B, polymethyl methacrylate (ordinate displaced by + 0·01); C, polyvinyl chloride (ordinate displaced by + 0·03).

TABLE 7.—VALUES OF THE SOLUBILITY PARAMETER δ_2

polymer	δ_2 from slope	δ_2 from intercep
polystyrene	8·56	8·59-8·52
polymethyl methacrylate	9·08	9·12-9·05
polyvinyl chloride	9·53	9·45-9·38

At this stage it is pertinent to enquire into any variations introduced into the δ_2 value determined from viscosity measurements by concentration-dependence of χ. Flory and Daoust [14] have given experimental support for a concentration dependence of χ of the form,

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 \ldots$$

The χ values obtained from swellings are therefore greater than those obtained from viscosity data by an amount depending on the relative magnitudes of χ_2, χ_3 etc. Viscosity measurements are restricted to solvent systems, and for these, Flory has shown that $\chi_2 < 0{\cdot}33$, $\chi_3 < 0{\cdot}25$ etc., and we have found that χ values from swelling exceed those of χ_1 from viscosity measurements by $\sim 0{\cdot}05 \pm 0{\cdot}03$.[6] The changes introduced into $\delta_1{}^2/RT - \chi/V_1$ are therefore small, and have no significant effect on the value of δ_2.

Table 3 shows the close correspondence between the values of δ_2 obtained from the swelling of natural and butyl rubber networks and the viscosities of rubber fractions. The viscosity treatment for other polymers is therefore considered to give comparative values of solubility parameters, the values obtained are given in table 7.

The value of $\delta_2 = 8{\cdot}56$ for polystyrene is distinctly lower than the approximately 9·1 estimated by Scott and Magat [15] and by Boyer and Spencer.[16] Some inadequacies of the former's treatment have been discussed previously.[1] For polyvinyl chloride, the value of $\delta_2 = 9{\cdot}4$ is in good agreement with Doty and Zable's [17] estimation from swelling measurements. Both Doty and Zable and Boyer and Spencer's values were obtained from swelling measurements, a value of χ for one solvent obtained from osmotic pressure data being used to calibrate the method. Small's [18] c.e.d. terms for chemical groups predict δ_2 values for polymethylmethacrylate and polyvinyl chloride within 0·1 of the values obtained here and a δ_2 value for polystyrene 0·5 higher than that obtained.

The conclusions reached as to the value of the c.e.d. concept for rubbers apply similarly to these polymers. C.e.d. can be assigned to polymers from interpretations of both swellings and viscosity measurements. There are, however, important contributions to these properties from non-c.e.d. factors of which there is no *a priori* knowledge for any specific case. Hence c.e.d. serve only as a very preliminary guide to possible polymer + solvent interaction.

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