PII: S0032-3861(96)01004-X

Polymer Vol. 38 No. 16, pp. 4175–4184, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00 + 0.00

Interactions of solvents with poly(methyl methacrylate)

V. Bellenger*, J. Kaltenecker-Commerçon and J. Verdu
ENSAM, 151 Bd de l'Hôpital, 75013 Paris, France

and P. Tordjeman
ELF ATOCHEM GR de Lacq, BP 34, 64170 Artix, France

(Revised 4 October 1996)

A slightly crosslinked sample of atactic poly(methyl methacrylate) was used to determine the solubility parameters from gravimetric sorption tests made at 40°C with about 30 solvents of solubility parameter ranging from 17.2 to 47.4 MPa$^{1/2}$. It was shown that solubility spectra of this sample and a linear homopolymer do not differ significantly. Classical methods of unidimensional or bidimensional mapping failed to determine precisely and unambiguously the solubility parameters of the polymer. The best approach consisted of distinguishing between three solvent families, respectively, poorly, moderately and strongly hydrogen bonded, as proposed by Burrell. The maximum capacity of solvent absorption varies in the order poorly > moderately > strongly hydrogen bonded solvent, which was tentatively explained by the importance of the plasticizing efficiency of the solvents. This provides an explanation of the difference between the solubility parameter value determined from solvent sorption tests (19–21.5 MPa$^{1/2}$) and from ultrasonic measurement of the bulk modulus (23 MPa$^{1/2}$). © 1997 Elsevier Science Ltd.

(Keywords: poly(methyl methacrylate); interactions with solvents; solubility parameter)

INTRODUCTION

Polymer glasses are especially sensitive to damage (crazing, cracking) in the presence of solvents in liquid or vapour state. It is generally recognized that the mutual solubility is a good criterion of the degree of interaction between a polymer and a solvent. The solubility of a solvent in a given polymer is usually determined from its equilibrium concentration in sorption tests. In the case of glassy polymers, the solvent induces a plasticizing effect expressed by

$$T_g = f(s)$$

where T_g is the glass transition temperature of the polymer–solvent mixture, s is the solvent weight fraction, and f is a function derived from empirical or physical (free volume, entropy, etc.) considerations. If T_a is the temperature of sorption tests, there is in principle a critical concentration s_a such that

$$s_a = f^{-1}(T_g)$$

where f^{-1} is the reciprocal function of f. Let s_∞ be the equilibrium concentration: if $s_\infty > s_a$, the polymer–solvent mixture becomes rubbery, and if $s_\infty < s_a$ the polymer–solvent mixture remains glassy.

The nature of this equilibrium is less understood in the second case than in the first one where it results from the balance between the osmotic force linked to the entering solvent and the entropic force linked to chain extension induced by swelling. However, there is no doubt about the existence of an 'equilibrium' in the glassy state: in sorption tests on water for instance, the concentration of the diffusing species tends effectively towards an asymptotic value. Furthermore, mixtures of glassy polymers with small molecules such as residual monomers or additives are monophasic and stable for very long times. Indeed, the term 'equilibrium' carries in this case some ambiguity since it is well known that the glassy state is, by definition, out of equilibrium. It would be more rigorous to use the term 'pseudo-equilibrium', indicating a state where the rate of structural relaxation is so low that the polymer–solvent mixture can be considered stable over periods many orders of magnitude higher than the time scale of the experiments.

If it is considered as licit to establish structure–property relationships for glassy polymers, then it must be licit too to discuss the relationships between the 'equilibrium' properties of a polymer–solvent mixture in the glassy state and the characteristics of its components. Indeed, entering solvent induces swelling and this latter induces stresses. There is some analogy between sorption tests and mechanical tests: below a critical strain, the phenomenon is fully reversible and no heterogeneity appears. Above this critical point, damage occurs and may influence further solvent sorption.

There are more or less complex methods to predict the solubility of a solvent in a polymer. The simplest one is based on the use of Hildebrand's solubility parameter δ, which is the square root of cohesive energy density. The solvent–polymer miscibility would be a decreasing function of $(\delta_p - \delta_s)^2$ where δ_p and δ_s are the respective solubility parameters of the polymer and the solvent. In

---

* To whom correspondence should be addressed

their pioneering work, Bernier and Kambour[1] found that the efficiency of a solvent to promote damage in a polymer, which is well represented by a critical strain ε_c determined from creep experiments, is directly related to the solubility parameters, ε_c being an increasing function of $(\delta_p - \delta_s)^2$. Solvents having the same δ_s value, but different molecular size, have, however, different efficiencies. This last effect, together with the effect of the solubility parameter, is taken into account in the Flory–Huggins interaction parameter χ[2]. χ can be decomposed into two components:

$$\chi = \chi_S + \chi_H$$

where χ_S is the entropic component, usually considered independent of structure, and χ_H is the enthalpic component given, in its simplest form, by

$$\chi_H = \frac{V_s}{RT}(\delta_p - \delta_s)^2$$

where V_s, the molar volume of the solvent, expresses the effect of molecular size. The miscibility of a given polymer–solvent pair is a decreasing function of χ_H.

These considerations can be effectively applied to systems in which the cohesion is dominated by dispersion (London) forces. Complications are systematically found when polar (Debye, Keesom) and hydrogen bonding interactions play a significant role in cohesion. Neither δ nor χ values display good correlations with polymer–solvent miscibility or critical strain. Many distinct approaches to this problem have been proposed in the literature of the past 30 years, the most popular one being an empirical extension of Hildebrand's theory based on the hypothesis of trivariance of miscibility[3–6] and which we summarize briefly as follows: one partial solubility parameter is defined per type of interaction: δ_d for dispersion forces, δ_p for dipole–dipole interactions and δ_h for hydrogen bonding, and the conditions for maximum miscibility can be ascribed:

$$\delta_{dp} = \delta_{ds}$$

$$\delta_{pp} = \delta_{ps}$$

$$\delta_{hp} = \delta_{hs}$$

Indeed, a trivariant interaction coefficient can be defined on the same basis. More detailed studies can take into account the fact that polar (δ_h and δ_p) components are temperature dependent whereas the dispersive component is temperature independent[7].

More refined theoretical developments take into account the key role of the finite compressibility of the mixture and the existence of specific interactions with the associated entropy effects. In these theories also, the solubility characteristics, for instance, the interaction parameter χ, are temperature dependent[8,9]. In practice, however, the above 'trivariant' theory is the most widely used to predict polymer–solvent interactions. In many cases, it appeared sufficient to distinguish between non-polar (δ_d) and polar $[\delta_a = (\delta_p^2 + \delta_h^2)^{1/2}]$ components or between hydrogen bonding (δ_h) and non-hydrogen bonding $[\delta_v = (\delta_d^2 + \delta_p^2)^{1/2}]$ components.

All these approaches have been applied to poly(methyl methacrylate) (PMMA)[5,10,11], but the results display a considerable scatter. For instance, Hildebrand's solubility parameters ranging from 19.9[11] to 23.1[3,4] have been reported. Similar discrepancies have been found for partial solubility parameters, for instance for non-polar (δ_d) and polar (δ_a) values: $\delta_d = 18.8\,\mathrm{MPa}^{1/2}$ and $\delta_a = 13.3\,\mathrm{MPa}^{1/2}$ [3,4] against $\delta_d = 17.6\,\mathrm{MPa}^{1/2}$ and $\delta_a = 5.9\,\mathrm{MPa}^{1/2}$ [11]. Considerations of critical strain and interaction parameter gave no better results[12], but this is not surprising since χ_H depends on δ values and these latter involve strong uncertainties.

Indeed, a general explanation for this scatter can be found in the fact that the theoretical background of these predictions is far from being firmly established. However, there are also uncertainties due to the mode of determination of solubility parameters, usually by monodimensional (Hildebrand's parameter), bidimensional ($\delta_d - \delta_a$ and/or $\delta_h - \delta_v$) or tridimensional (δ_d, δ_p and δ_h) mapping[3,6,7,10–13]. These methods obviously lack precision and depend more or less on the solvent choice.

Finally, another possible cause of this scatter could be more fundamental: δ_d, δ_p and δ_h (and the molar volume V_s) could not be the only factors influencing the polymer–solvent interaction. The aim of this paper is to propose a new method for the determination of solubility parameters, essentially based on the use of a slight crosslinked PMMA sample and about 30 solvents in the following range of solubility parameters: $15.6 \leq \delta \leq 47.4$, $15.1 \leq \delta_d \leq 20.0$, $0 \leq \delta_p \leq 26.2$ and $0 \leq \delta_h \leq 42.3$.

EXPERIMENTAL

Materials

Both materials under study were bulk polymerized, radical initiated, atactic PMMAs. The first one (A) was a linear homopolymer of molecular weight $\bar{M}_w = 220\,\mathrm{kg\,mol^{-1}}$ with a polydispersity index of 2.2. The second one (B) was a methyl methacrylate–ethylene-glycol dimethacrylate (EGDMA) in which the weight fraction of EGDMA was 500 ppm. It is insoluble in the solvents under study (see below). Its molar weight between crosslinks $\bar{M}_c$ was calculated assuming a negligible dangling chain concentration: $\bar{M}_c = 200\,\mathrm{kg\,mol^{-1}}$. Its glass transition was 112°C as against 105°C for A. We cannot exclude the cases where the asymptotic solvent concentration is linked to the swelling equilibrium of the entanglement network—the disentanglement rate being negligible in the time scale of experiments. In such cases, eventual differences in the 'crosslink' density between the studied samples could involve differences in solvent 'absorption spectra'.

However, it can be recalled that the average molar weight between entanglements ($\bar{M}_e$) is less than $10\,\mathrm{kg\,mol^{-1}}$ in linear PMMA[14]. In other words, despite the fact that it is completely gelled, sample B must be very close to sample A owing to the low incidence of chemical crosslinking compared to the physical one (entanglement), and to the presumably low 'copolymer effect' of EGDMA due to its low concentration and its structural similarity to PMMA. Plaques of 2 mm thickness were used for solvent interaction experimental studies. The physical characteristics are summarized in *Table 1*.

Solvents

About 30 solvents (analytical grade) were used in this study. Some of their important characteristics are listed in *Table 2*.

Sorption testing

Both samples were previously dried to constant weight in a vacuum oven at 50°C and then treated at 105°C for 3 h in a forced air oven, in an attempt to relax stresses associated with their thermal and mechanical (machining) history. Exposure of rectangular samples of 20 x 30 mm was made in saturated solvent vapour at 40°C. The samples were periodically weighed using a laboratory balance of relative precision 10^{-4}. The equilibrium concentration was arbitrarily expressed in terms of solvent volume v (in cm^3) per 100 g of polymer. For certain solvents, no equilibrium was reached after 35 days of exposure. The equilibrium concentration of some of these solvents was then determined using solution-cast films of sample A of 200–300 μm thickness.

Table 1 Initial characteristics of samples

Sample	$\bar{M}_w$ (kg mol^{-1})	$\bar{M}_w/\bar{M}_n$	$\bar{M}_e$ exp. (kg mol^{-1})	T_g (°C)
A	220	2.2	6	105
B	—	—	6	112

$\bar{M}_w$ = average molar weight; $\bar{M}_e$ = average molar weight between entanglements; T_g = glass transition temperature

Ultrasonic elastic constants

The propagation rate of ultrasonic waves was determined for transverse (v_T) and longitudinal (v_L) vibrations, using a Sofranel 5055 PR pulsar/receiver wave generator with 5 MHz probes for longitudinal (M110) and transversal (V150) waves, with mineral oil or grease as coupling agent. The bulk modulus B_u and Poisson's ratio ν_u were determined from the following relationships:

$$R = v_L/v_T; \quad \nu_u = \frac{2 - R^2}{2(1 - R^2)}; \quad B_u = v_L^2 \rho \frac{1 + \nu_u}{3(1 - \nu_u)}$$

where ρ is the density. These measurements were made only on unswollen sample A for which we had available plaques of sufficient thickness (6 mm).

RESULTS

Cohesive energy density from ultrasonic measurements

Ultrasonic measurements at 5 MHz gave $\nu_u = 0.331 \pm 0.011$ and $B_u = 5.74 \pm 0.27$ GPa. These data are not unreasonable, compared to static or low frequency

Table 2 Equilibrium concentration of solvents (v expressed in cm^3 per 100 g of polymer)

Solvent	v (cm^3/100 g)		δ_h (J$^{1/2}$ cm$^{-3/2}$)	δ_p (J$^{1/2}$ cm$^{-3/2}$)	δ_d (J$^{1/2}$ cm$^{-3/2}$)	δ (J$^{1/2}$ cm$^{-3/2}$)	δ_v (J$^{1/2}$ cm$^{-3/2}$)	δ_a (J$^{1/2}$ cm$^{-3/2}$)
Methyl isobutyl ketone	83	M	4.1	6.1	15.3	17.2	16.5	8.5
Toluene	108	P	2.0	1.4	18.0	18.2	18.0	2.5
Ethyl acetate	—	M	7.2	5.3	15.8	18.6	16.7	10.6
Chloroform	250	P	5.7	3.1	17.8	19.0	18.1	6.6
Methyl acetate	115	M	7.6	7.2	15.5	19.6	17.1	11.7
Dioxane	127	M	7.4	5.9	17.5	20.2	18.5	7.6
Nitrobenzene	109	P	4.1	8.6	20.0	20.5	21.8	13.0
Aniline	—	M	10.2	5.1	19.4	21.0	20.1	11.4
Acrylonitrile	106	M	6.8	17.4	16.4	21.5	23.9	18.7
Pyridine	142	M	5.9	8.8	19.0	21.9	20.9	10.6
Dimethylphthalate	—	M	4.9	10.8	18.6	21.9	21.5	11.9
N,*N*′-Dimethylacetamide	—	M	10.2	11.5	16.8	22.1	20.4	15.4
n-Pentanol	0.16	S	13.9	4.5	16.0	22.3	16.6	14.7
Nitroethane	161	P	4.5	15.5	16.0	22.7	22.3	16.2
N-Methylpyrrolidone	—	M	7.2	12.3	17.9	22.9	21.7	14.2
Isopropanol	7	S	16.4	6.1	15.8	23.5	16.0	17.5
Acetonitrile	112	M	6.1	18.0	15.3	24.1	23.6	19.0
n-Propanol	22	S	17.4	6.8	16.0	24.3	17.4	18.6
Methoxyethanol	120	S	16.4	9.2	16.2	24.7	18.6	17.0
Dimethylformamide	123	M	11.3	13.7	17.4	24.9	22.1	17.8
Ethanol	30	S	19.4	8.8	15.8	26.0	18.1	18.1
Nitromethane	90	P	5.1	18.8	15.8	26.0	24.6	19.5
2-Pyrrolidone	0.06	M	11.3	17.4	19.5	28.4	26.1	20.7
Methanol	27	S	22.3	12.3	15.1	29.6	19.5	25.4
Formamide	0.1	S	19.0	26.2	17.2	39.3	31.3	32.4
Water	2	S	42.3	16.0	13.3	47.4	22.3	45.2
Dimethyl sulphide	130	P	—	—	18.0	18.4	—	5.9
Dichloroethane	211	P	4.1	5.1	18.1	20.1	19.0	8.4
Acetone	143	M	7.0	10.4	15.5	20.3	18.7	12.6
Butyrolactone	—	M	7.4	16.6	19.6	29.0	25.7	17.5
Propanediol	0.4	S	23.3	9.4	16.9	30.3	19.3	25.1
Octane	0.3	P	0.0	0.0	15.6	15.6	15.6	0.0

P = poorly hydrogen bonded solvents; M = moderately hydrogen bonded solvents; S = strongly hydrogen bonded solvents; Hildebrand's solubility parameter δ; partial solubility parameter, δ_h for hydrogen bonding, δ_d for dispersion interactions, δ_p for dipole–dipole interactions; $\delta_a = (\delta_p^2 + \delta_h^2)^{1/2}$ and $\delta_v = (\delta_d^2 + \delta_p^2)^{1/2}$ values dynamic data[5,15]. The bulk modulus, as derived from a Lennard–Jones potential, is expected to be proportional to the cohesive energy density e_c. On the other hand, e_c is the square of the Hildebrand's solubility parameter δ, so that

$$B = b\delta^2$$

The theoretical value of the constant of proportionality b is 8.04 according to Tobolsky[16]; thus, for PMMA, we would have $\delta \sim 27\,\mathrm{MPa}^{1/2}$, e.g. a value significantly higher than the values determined from solvent–polymer interaction studies (19–23 $\mathrm{MPa}^{1/2}$ as seen in the Introduction). For a relatively large series of epoxies[17] and vinyl esters[18], it was, however, observed that, at 5 MHz frequency and ambient temperature, the constant b was somewhat higher than its theoretical value: $b = 11 \pm 1$. Using this value, we obtained a δ value of 23 $\mathrm{MPa}^{1/2}$, e.g. in good agreement with the highest limit of the range of literature values.

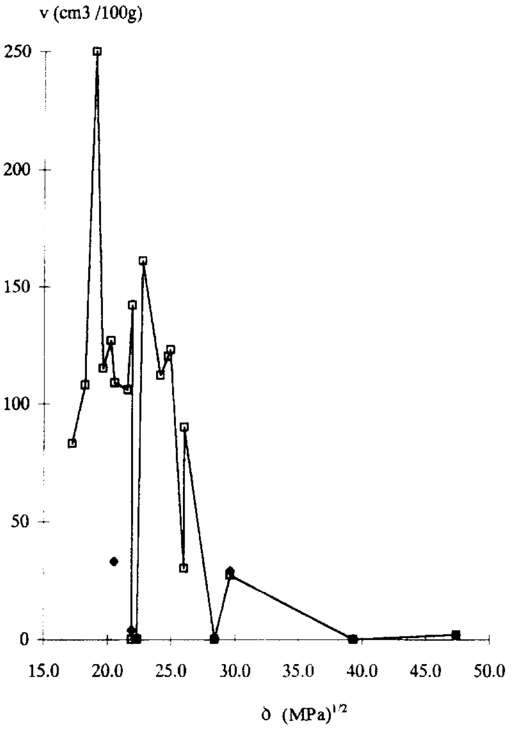


Figure 1 Solvent equilibrium concentration expressed in cm^3 per 100 g of polymer as a function of the solubility parameter δ of the solvent: (◆) for the uncrosslinked PMMA sample A and (□) for the crosslinked PMMA sample B; the line joining the experimental points is representative of a 'solubility spectrum' (see ref. 5)

General characteristics of the solvent sorption behaviour

Uncrosslinked PMMA is soluble in a wide variety of solvents whose interaction characteristics cannot be easily differentiated using our experimental method. In contrast, a crosslinked sample, just above the gel point, is expected to reach a swelling equilibrium, even in the case of strongly interactive solvents. As mentioned above, sample B is insoluble in good solvents of A, so that it is well adapted to solubility parameter determinations from sorption tests. The fact that it is well representative of the linear homopolymer is attested by the comparison of 'solubility spectra' (v *versus* δ) in *Figure 1*. For the non-solvents of A, the equilibrium concentrations in A and B are very close.

Some sorption kinetic curves are shown in *Figure 2*. They reveal the existence of many distinct mechanisms characterized by:

(a) A single plateau and a continuously decreasing sorption rate (apparently Fickian processes).
(b) An autoaccelerated character in the early period of exposure and, eventually, the existence of an intermediary pseudo-equilibrium followed by an increase of sorption rate before the final equilibrium (the case of dimethylformamide or methoxyethanol for instance).

This 'anomalous' character has been often attributed to the existence of a relaxation process induced by the polymer plasticization (case II)[19,20]. In certain cases, for instance isopropanol, the sharp autoacceleration of solvent sorption occurring just before equilibrium has been attributed to swelling stresses. They would induce cavitational damage in the sample core, increasing thus further solvent penetration. At equilibrium, however, plasticization can favour healing processes restoring the material's homogeneity[21,22]. Generally, sorption anomalies are found for the most strongly interactive solvents[19], but this is not obvious here: solvents of low polarity such as chloroform, display a pseudo-Fickian behaviour

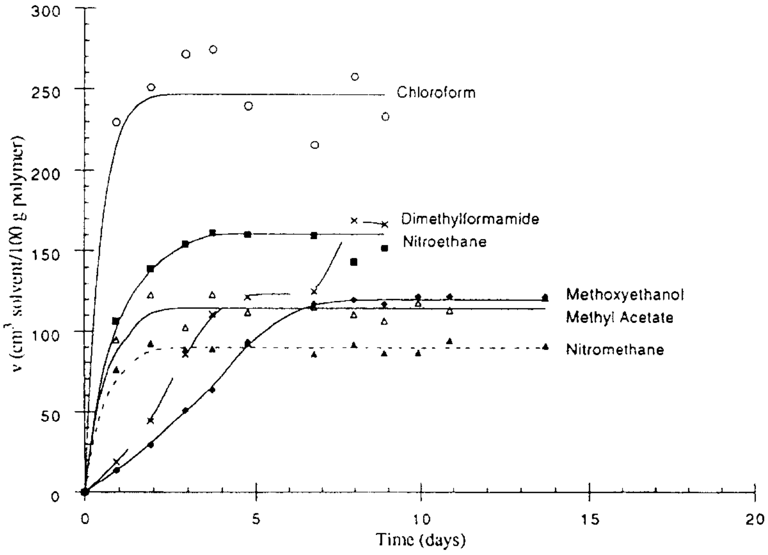


Figure 2 Sorption kinetic curves of sample B: solvent concentration expressed in cm^3 per 100 g of polymer *versus* the sorption time expressed in days

despite their high equilibrium concentration. In contrast, highly polar solvents having a medium or low equilibrium concentration, such as isopropanol, display sorption 'anomalies'. This somewhat paradoxical situation could be explained from consideration of Deborah number (Deb) defined as follows:

$$\mathrm{Deb} = \tau_D/\tau_R$$

where τ_D is a characteristic time of diffusion (typically τ_D is of the order of L^2/D, L being the sample thickness and D the solvent coefficient of diffusion in the polymer matrix) and τ_R the relaxation time.

If Deb $\ll 1$, we are in the case of 'elastic' diffusion.

If Deb $\gg 1$, we are in the case of 'viscous' diffusion.

In both cases, sorption curves are expected to be Fickian or pseudo-Fickian. It could be reasonably supposed that the diffusion is 'viscous' for strongly interactive solvents such as chloroform, and 'elastic' for poorly interactive solvents such as water. However, in an intermediary state where Deb ~ 1, complicated situations, involving non-monotonic variations of the sorption rate (or even the solvent concentration) can be found. This could be the case, for instance, with isopropanol.

Hildebrand's solubility spectrum

In *Figure 1*, the equilibrium concentration is plotted against Hildebrand's solubility parameter δ. It appears clear that this curve cannot be considered as a mononodal distribution allowing a determination of a value of the polymer solubility parameter δ_p such that v would be a continuously decreasing function of $|\delta_p - \delta_s|$. The solvents having solubility parameters out of the 16–28 MPa$^{1/2}$ range have a very low interactivity towards PMMA, but within this range, no clear trend can be observed. If we consider for instance a more restricted interval such as 20–24 MPa$^{1/2}$, we can distinguish at least two very different families: alcohols, for which $v \leq 30$, and poorly or moderately hydrogen bonded solvents for which $v \geq 100$. In the same way, in the range 19–21 MPa$^{1/2}$ we could distinguish between poorly hydrogen bonded solvents, for which $v \geq 200$, and moderately hydrogen bonded solvents for which $v \leq 150$.

The definition of a single solubility parameter δ_p thus seems to be useless. As proposed by Burrell[23], it should be convenient to define three solubility parameters for the three above defined solvent families, which would lead to:

P → poorly hydrogen bonded solvents:

$$\delta_{p(PH)} \sim 19.0\,\mathrm{MPa}^{1/2}$$

M → moderately hydrogen bonded solvents:

$$\delta_{p(MH)} \sim 22 \pm 2\,\mathrm{MPa}^{1/2}$$

S → strongly hydrogen bonded solvents:

$$\delta_{p(SH)} \sim 27 \pm 1\,\mathrm{MPa}^{1/2}$$

The maximum absorption capacity would differ from one family to another (P > M > S). To take into account molar volume effects, we have defined three interaction parameters as follows:

$$\chi_P = \frac{V_s}{RT}(\delta_s - 19.0)^2$$

$$\chi_M = \frac{V_s}{RT}(\delta_s - 22.0)^2$$

and

$$\chi_S = \frac{V_s}{RT}(\delta_s - 27.0)^2$$

where V_s and δ_s are, respectively, the solvent molar volume and solubility parameter. The values are listed in *Table 3*. Attempts were made to correlate χ with v (or better v^{-1}), but the results were deceiving. It can be concluded from these results that:

- The sorption mechanism is presumably dominated by one type of interaction: dispersion for solvents of low polarity (P), polar interactions for polar solvents which are non-hydrogen donors (in hydrogen bonding), but polar solvents (M), and hydrogen bonding for solvents having a hydrogen capable of establishing hydrogen bonds (S).

The differences between the behaviour of these three families strongly suggest that the process of solvent absorption cannot be described as a 'cooperation' between the three types of interactions. On the contrary, the predominant interaction seems to 'inhibit' the two other ones. It can be seen for instance that δ_v has the same value: 18.1 for chloroform and ethanol. In the case of chloroform, δ_v (non-hydrogen bonding solubility parameter) corresponds to the major component of the interaction, and this latter is the strongest one. In the case of ethanol, despite the same value of δ_v, the equilibrium concentration is eight times lower than for chloroform. In other words, hydrogen bonding by the hydroxyl group seems to 'inhibit' the dispersion and dipole–dipole interactions.

In the same way, the comparison of *N*-methylpyrrolidone (NMP) with chloroform ($\delta_h = 5.7$, $\delta_d = 17.8$) suggests that in NMP, dipole–dipole interactions ($\delta_p = 12.3$ as against $\delta_p = 3.4$ for chloroform) could 'inhibit' dispersion interactions.

- Among the three interaction mechanisms, dispersion and hydrogen bonding are, respectively, responsible for the highest and the lowest capacity of solvent absorption.
- No reliable predictions can be made from the experimental data, even by differentiating the three solvent families.
- Diffusion 'anomalies' are not necessarily associated with the highest equilibrium concentrations.

Bidimensional solubility maps

Since monodimensional spectra of solubility parameters displayed a low predictive value, the study of bidimensional solubility maps as proposed by many authors[3,13] seemed interesting to us. Four groups of solvents were defined from their v values: group (a): $v \geq 200$; group (b): $200 > v \geq 125$; group (c): $125 > v \geq 80$; group (d): $v < 80$.

The corresponding contours in $(\delta_d - \delta_a)$ and $(\delta_v - \delta_h)$ maps are presented in, respectively, ***Figures** 3* and *4*. In the $(\delta_d - \delta_a)$ map, the contours of the above defined solvent groups tend to be closed, concentric curves, the degree of interactions increasing, as expected, from the outer to the inner region. There is, however, a domain, around the point of coordinates $\delta_a = 17.0$, $\delta_d = 16.0$ ($\delta = 23$–24), where all the groups, except (a), 'interfere'.

Table 3 Interaction parameter χ_P for poorly hydrogen bonded solvents, χ_M for moderately hydrogen bonded solvents, and χ_S for strongly hydrogen bonded solvents

Solvent		V (cm^3 mol^{-1})	δ (J$^{1/2}$ cm$^{-3/2}$)	χ_P	χ_M	χ_S
Toluene	P	106.8	18.2	0.026		
Chloroform	P	80.7	19.0	0.000		
Nitrobenzene	P	102.7	20.5	0.089		
Nitroethane	P	71.5	22.7	0.376		
Nitromethane	P	54.3	26.0	1.022		
Dimethyl sulphide	P	73.3	18.4	0.010		
Dichloroethane	P	78.7	20.1	0.037		
Octane	P	162.6	15.6	0.722		
Methyl isobutyl ketone	M	125.8	17.2		1.113	
Ethyl acetate	M	98.5	18.6		0.437	
Methyl acetate	M	79.7	19.6		0.176	
Dioxane	M	85.7	20.2		0.107	
Aniline	M	91.5	21.0		0.035	
Acrylonitrile	M	67.1	21.5		0.006	
Pyridine	M	80.9	21.9		0.000	
Dimethylphthalate	M	163.0	21.9		0.001	
N,*N*′-Dimethylacetamide	M	92.5	22.1		0.000	
N-Methylpyrrolidone	M	96.4	22.9		0.030	
Acetonitrile	M	52.6	24.1		0.089	
Dimethylformamide	M	77.0	24.9		0.249	
2-Pyrrolidone	M	76.3	28.4		1.200	
Acetone	M	73.3	20.3		0.081	
Butyrolactone	M	76.3	29.0		1.436	
n-Pentanol	S	108.2	22.3			0.918
Isopropanol	S	76.8	23.5			0.361
n-Propanol	S	75.2	24.3			0.211
Methoxyethanol	S	78.8	24.7			0.160
Ethanol	S	58.5	26.0			0.022
Methanol	S	40.7	29.6			0.106
Propanediol	S	73.2	30.3			0.306
Formamide	S	39.8	39.3			2.312
Water	S	18.0	47.4			2.877

The points representative of the most strongly interactive solvents (chloroform and dichloroethane), are in the bottom part of the 'core' zone. Points are lacking in a relatively large zone just above these points (typically $\delta_d = 18 \pm 1.5$; $\delta_a = 12 \pm 3$) and we cannot exclude the hypothesis that the polymer coordinates could be in this zone. In the ($\delta_h - \delta_v$) map (*Figure 4*), group (a) appears to be intermediary between groups (b) and (c), which seems to indicate that the separation between (b) and (c) was not pertinent. The region of maximum interaction appears relatively sharp and almost triangular, its boundaries being delimited by the points:

$$\mathrm{I}(\delta_h = 7.0, \delta_v = 17.5);\ \mathrm{J}(\delta_h = 4.0, \delta_v = 21.5)$$
$$\text{and } \mathrm{K}(\delta_h = 3.0, \delta_v = 18.0)$$

We see first that the Hildebrand parameter cannot be higher than δ_J, e.g. $\delta \leq 21.5$. This condition eliminates all the top part of the core (void) zone in the ($\delta_d - \delta_a$) map (*Figure 3*). Let us now consider some extreme cases of solvents having their representative points in the core zone of both maps:

(a) Solvents having their representative point close to I in the ($\delta_h - \delta_v$) map (*Figure 4*): $\delta_h \sim 7.0; \delta_v \sim 17.5$. From this latter value, we deduce that $\delta_d \leq 17.5$, whereas from the ($\delta_a - \delta_d$) map in *Figure 3*, we see that $\delta_d \geq 16.0$. The extreme values could be thus:

$$\mathrm{I}_1\!: \delta_h = 7.0;\ \delta_d = 16.0;\ \delta_p = 7.1$$
$$\mathrm{I}_2\!: \delta_h = 7.0;\ \delta_d = 17.5;\ \delta_p = 0$$

(b) Solvents having their representative point close to J in the ($\delta_h - \delta_v$) map (*Figure 4*): $\delta_h = 4.0; \delta_v = 21.5$. Here, the value of δ_d is limited by the core zone of ($\delta_a - \delta_d$) map: $16.0 \leq \delta_d \leq 19.0$. These values lead to

$$\mathrm{J}_1\!: \delta_h = 4.0;\ \delta_d = 16.0;\ \delta_p = 14.4$$
$$\mathrm{J}_2\!: \delta_h = 4.0;\ \delta_d = 19.0;\ \delta_p = 10.1$$

(c) Solvents having their representative point close to K in the ($\delta_h - \delta_v$) map (*Figure 4*): $\delta_h = 3.0; \delta_v = 18.0$. Indeed, δ_d cannot be higher than 18.0 whereas its lower limit is 16.0 as indicated by the ($\delta_d - \delta_a$) map. The extreme values of the coordinates of such points are thus:

$$\mathrm{K}_1\!: \delta_h = 3.0;\ \delta_d = 16.0 \text{ and } \delta_p = 8.2$$
$$\mathrm{K}_2\!: \delta_h = 3.0;\ \delta_d = 18.0 \text{ and } \delta_p = 0$$

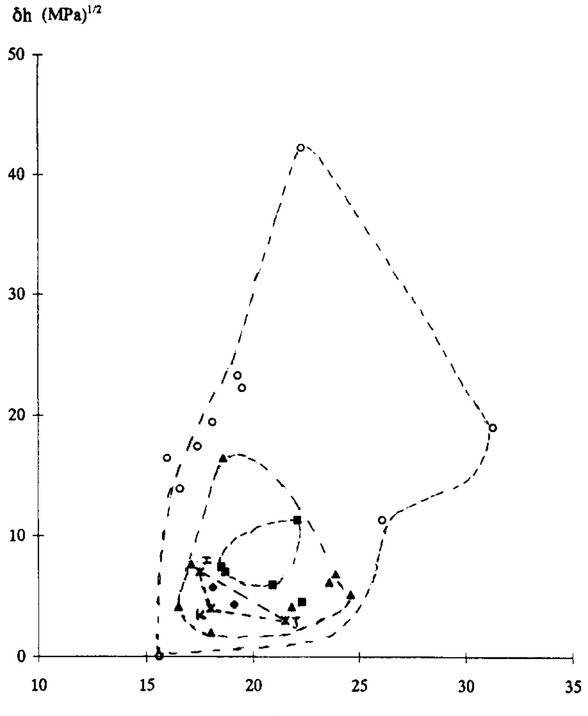


Figure 3 Bidimensional solubility map, δ_a *versus* δ_d: (◆) group a, $v \geq 200$; (■) group b, $200 > v \geq 125$; (▲) group c, $125 > v \geq 80$; (O) group d, $v < 80$

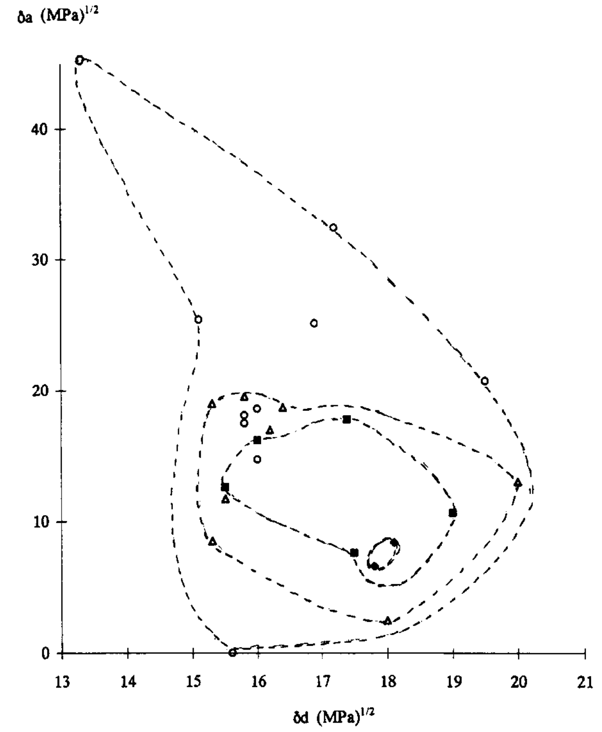


Figure 4 Bidimensional solubility map, δ_h *versus* δ_v: (◆) group a, $v \geq 200$; (■) group b, $200 > v \geq 125$; (▲) group c, $125 > v \geq 80$; (O) group d, $v < 80$

It must be first remarked that points $J_1(\delta_a = 14.9)$ and $K_2(\delta_a = 3.0)$ can be rejected because they are out of the core zone.

(d) Solvents having their representative point in the centre of the triangle I J K, for instance close to the clorinated solvents used here:

$$C: \delta_h \sim 5–6;\ \delta_d \sim 18 \pm 0.2;\ \delta_p \sim 3–4$$

All these points delimit a relatively large domain in a tridimensional map:

$$16.0 \leq \delta_d \leq 19.0$$

$$0 \leq \delta_p \leq 10.1$$

$$3.0 \leq \delta_h \leq 7.0$$

It can be reasonably supposed that the representative point of PMMA lies in this zone. We see thus that, despite the relatively high number of solvents used for this study, the method of bidimensional mapping does not allow a precise determination of the polymer coordinates. It displays an especially high imprecision on the δ_p value since this latter could vary between zero and more than 10.

The case of alcohols

We may use seven results corresponding to seven different alcohols, among which are five alkyl monoalcohols (from methanol to pentanol). The value δ_h has been plotted against δ_p for all the alcohols under study in *Figure 5*. Alkyl monoalcohols form an homogeneous family in which δ_h increases regularly with δ_p, but the representative points of propanediol and methoxyethanol are, respectively, above and below the curve for alkylmonoalcohols.

In *Figure 6*, v is plotted against δ for all the alcohols.

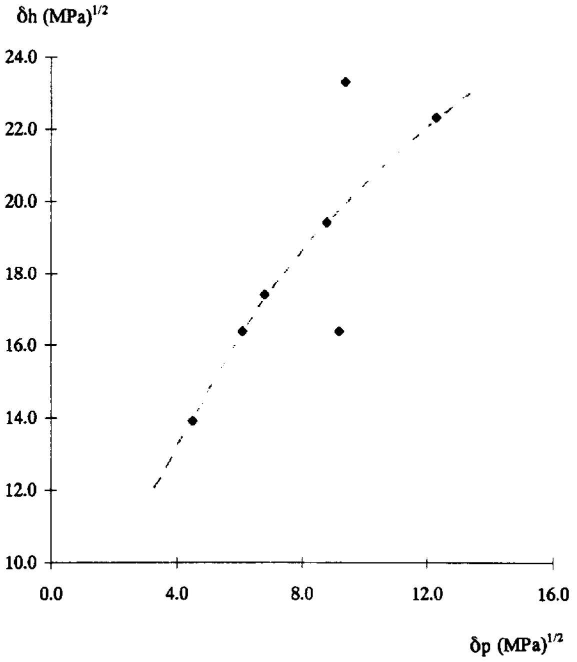


Figure 5 Bidimensional solubility map of alcohols, δ_h *versus* δ_p; the representative points for propanediol and methoxyethanol are above and below, respectively, the curve for alkylmonoalcohols

Ignoring first methoxyethanol, we obtain a Gauss shaped curve with a maximum close to $\delta \sim 26\,\mathrm{MPa}^{1/2}$, corresponding to $\delta_h \sim 20\,\mathrm{MPa}^{1/2}$, in accordance with Burrell's approach[23] and the (reasonable) hypothesis that, for this solvent family, interactions are dominated by hydrogen bonding and that the δ_h value for PMMA is close to $20\,\mathrm{MPa}^{1/2}$. In this case, methoxyethanol, which is close to isopropanol ($\delta_h = 16.4$ for both solvents), and n-propanol ($\delta_p = 9.2$ as against 6.8), would be expected

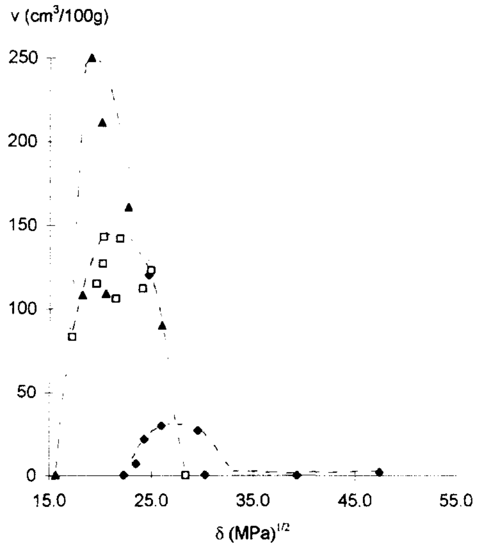


Figure 6 Solvent equilibrium concentration v expressed in cm^3 per 100 g of polymer *versus* the solubility parameter δ: (△) poorly hydrogen bonded solvents; (□) moderately hydrogen bonded solvents; (◆) strongly hydrogen bonded solvents

to give v values of the same order ($v \leq 22$) instead of the 120 experimental values. No rule linking v to the distance between the polymer and solvent representative points in the ($\delta_d, \delta_p, \delta_h$) space, or even in the (χ_P, χ_M, χ_S) space seems to be able to predict such a discrepancy.

DISCUSSION

If P and S are the respective representative points of the polymer and a solvent in a mono-, bi- or tri-dimensional solubility parameter or interaction coefficient map, the simplest approach for the determination of polymer characteristics consists of searching for the P coordinates which satisfy the following condition in the whole studied range:

$$d\nu / d(\overrightarrow{PS})^2 < 0 \qquad (1)$$

In other words, the solvent equilibrium concentration is a decreasing function of the distance between P and S. As a consequence of this rule: if the space under study, for instance (δ_d, δ_h) is homogeneously filled by the representative points $S_1, S_2 \ldots S_N$ of the N solvents under study, and if the maximum absorption corresponds to S_i, then the polymer coordinates must be close to those of S_i, for instance $\delta_{dp} = \delta_{dsi}$; $\delta_{pp} = \delta_{psi}$ and $\delta_{hp} = \delta_{hsi}$, the uncertainty being in the order of magnitude of the distance between one point S and its closest neighbours.

The above experimental results clearly show the low predictive value of this rule: The monodimensional spectra, using Hildebrand's solubility parameter as well as the corresponding interaction coefficient, display many maxima. Moreover, for a given value range of the chosen variable, for instance $\delta = 20$–$24\,MPa^{1/2}$, at least three solvent families, having, respectively, high ($v > 150$), medium ($100 < v < 140$) and low ($v < 10$) equilibrium concentrations can be easily distinguished.

Bidimensional maps ($\delta_v - \delta_h$) and ($\delta_d - \delta_a$) give also a fuzzy image of the polymer properties, since they display zones of overlapping of the contours of the solvent families (for instance close to $\delta_d = 16\,MPa^{1/2}$) in the ($\delta_d - \delta_a$) map, and zones where S points are lacking. Despite this latter remark, applying the above rule leads to the conclusion that the polymer coordinates must be not so far from the chlorinated solvent ones, e.g. $\delta_d \sim 18.5 \pm 0.5$; $\delta_p \sim 4 \pm 1$ and $\delta_h \sim 5 \pm 1$.

This hypothesis seems to be reasonable; however, it involves the fact that cohesion would be largely dominated by dispersion forces in PMMA, whereas data relative to electrical properties (dipole moments, dielectric constants, etc.), as well as empirical prediction from molar group additive laws[5,6], suggest that the ester group plays an important role through dipole–dipole interactions. The gap between Hildebrand solubility parameter as determined from these mapping methods ($\delta \sim 19$–$20\,MPa^{1/2}$) and the value determined from ultrasonic measurements (23 MPa) is impressive and would need an explanation. The heterogeneity of space filling by the representative points of solvents, is, however, obvious in bidimensional maps; this opens the way to the hypothesis that the polymer coordinates could significantly differ from the chlorinated solvent ones. If one agrees with the idea that the polar component δ_p of the solubility parameter of PMMA must be higher than in the chlorinated solvents, but that the PMMA representative point must be in the 'core' zone of the bidimensional maps, one could admit the possibility for polymer coordinates to be close to the point J, for instance:

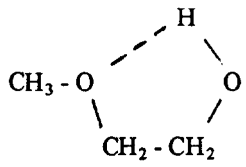
$$J_2(\delta_d = 19.0;\ \delta_p = 10.1;\ \delta_h = 7.0)$$

or

$$J_3(\delta_d = 18.0;\ \delta_p = 11.8;\ \delta_h = 7.0)$$

However, it is noteworthy that the representative points of solvents such as acetone, pyridine or dioxane would be closer to the polymer one than those of chlorinated solvents so that we must imagine the existence of zones of non-monotonic (or at least quasi-discontinuous) change of v with the solvent coordinates. In other words, the problem of the low polarity of PMMA would have been solved, but it would have been replaced by another problem. It appears thus that equation (1) applied to mono-, bi- or tri-variant solubility parameters is only capable of rough estimations of the PMMA solvent interaction. Some uncertainties can be attributed to a non-optimal solvent choice, but it is clear that many 'anomalies' linked to non-monotonic variations of v with $(\overrightarrow{PS})^2$ would not be suppressed by a so-called ideal choice. It can be thus concluded that three or even four (including molar volume) parameters are insufficient to predict the solvent–PMMA interaction from a unique rule.

It seems better to consider separately three mechanisms for, respectively, poorly, moderately and strongly hydrogen bonded solvents as proposed by Burrell[23]. This approach suppresses the most important anomalies, but some of them remain, indicating that, even in restricted solvent families, the solubility parameters are insufficient to describe precisely the polymer–solvent behaviour. The most suggestive example of such anomalies is the case of methoxyethanol: Despite its partial solubility parameter values and its structure, confirming that it belongs to the alcohol family (strongly hydrogen bonded solvents), its v value ($1.2\,cm^3\,g^{-1}$) is rather characteristic of moderately hydrogen bonded solvents. A possible explanation could be found in the existence of an intramolecular hydrogen bond:



In this form, methoxyethanol must behave as a noticeably less polar solvent. Anyhow, it is not unreasonable to suppose that subtle effects such as intramolecular interactions, isomerisms, etc., not taken into account in solubility parameters, can effect the polymer–solvent behaviour. Burrell's method seems to be the better approach for a prediction of PMMA–solvent interaction; however, it needs to explain why the maximum capacities of absorption are in the order poorly > moderately > strongly hydrogen bonded solvents. A tentative explanation could involve the plasticizing efficiency of the solvents in PMMA. As a matter of fact, for the temperature T_a of sorption tests, two regimes could be distinguished, depending on the glass transition temperature T_g of the polymer–solvent mixture:

1. For $T_g < T_a$ (e.g. in the rubbery state), the equilibrium concentration is expected to depend only on the interaction coefficient and solvent molar volume (for a given polymer crosslink density[24]). This situation must correspond to the highest solvent 'reactivities'.
2. For $T_g \geq T_a$; then, the behaviour of the system is expected to depend sharply on the plasticizing efficiency, which can be, for instance, derived from the free volume theory[25].

$$T_g = \frac{\alpha_p T_{gp}(1-\varphi) + \varphi\alpha_s T_{gs}}{\alpha_p(1-\varphi) + \varphi\alpha_s} \qquad (2)$$

where the subscripts 's' and 'p' refer, respectively, to the solvent and the polymer, α is the expansivity coefficient of the free volume, T_g the glass transition temperature, and φ the solvent volume fraction in the mixture. If the Simha–Boyer rule is obeyed[26] (αT_g = constant), which can be considered valid to estimate the overall trend of variation, equation (2) can be simplified as follows:

$$\frac{1}{T_g} = \frac{1}{T_{gp}} + A\varphi$$

where A can be considered as a coefficient expressing the plasticizing efficiency given by

$$A = \frac{1}{T_{gs}} - \frac{1}{T_{gp}}$$

It appears that the plasticizing efficiency depends essentially on the solvent glass transition temperature T_{gs}. This latter depends on many molecular factors among which:

- Its cohesive energy density (T_{gs} increases with e_c), so that T_{gs} is expected to increase in the order

  poorly < moderately
  < strongly hydrogen bonded solvents

  Thus, the higher capacity of solvent absorption of the solvents of low polarity would be explained by their highest plasticizing efficiency.
- Its molecular size (T_{gs}) increases with the molar weight of the solvent M_s and thus, also, with the molar volume V_s whose importance would be higher than expressed in the interaction coefficient.

The solvent equilibrium concentration would thus depend on at least four factors:

- The nature of the solvent (poorly, moderately or strongly hydrogen bonded).
- Its solubility parameter.
- Its molar volume.
- Its glass transition temperature.

The importance of this latter would be such that polymer–solvent interaction characteristics would not depend only on cohesion parameters. This can explain the paradoxical fact that PMMA cohesion appears to be dominated by dispersion forces even though there is much evidence that polar interactions play a key role. This could also explain the difference between the δ values determined from ultrasonic measurements and from solvent sorption. The former would correspond to cohesion, whereas the latter is shifted towards low values owing to the stronger plasticizing effect of low polarity solvents.

CONCLUSIONS

In the case under study, conventional methods of uni- (δ), bi- ($\delta_v - \delta_h$ or $\delta_d - \delta_a$) and tri-dimensional ($\delta_d, \delta_p, \delta_h$) mapping fail to predict unambiguously the polymer solubility parameters. It is clearly shown that whatever the chosen system of coordinates, there are non-monotonic variations of the equilibrium solvent concentration of the polymer, which disagrees with the current theories or empirical approaches.

It appears in contrast that Burrell's method[23], which consists of considering separately three solvent families, respectively, poorly, moderately, and strongly hydrogen bonded, could give relatively accurate predictions. As a matter of fact, the equilibrium solvent concentration varies in a pseudo-parabolic way with the solvent solubility parameter in each family, which allows an unambiguous determination of the corresponding polymer coordinate. This result, which could be useful in practice, remains to be explained theoretically. Each solvent family differs from the others by its maximum capacity of absorption, which has been tentatively explained by the important role of the solvent plasticizing effect. This effect could explain the noticeable discrepancy between δ values determined on the one hand from the cohesive energy density derived from ultrasonic modulus measurements ($\delta = 23\,\mathrm{MPa}^{1/2}$) and the most probable values derived on the other from classical solubility parameter mapping techniques ($19\text{–}21.5\,\mathrm{MPa}^{1/2}$). In other words, the plasticizing effect would lead to an overestimation of the dispersive component relative to the polar and hydrogen bonding ones.

REFERENCES

1. Bernier, G. A. and Kambour, R. P., *Macromolecules*, 1968, **1**, 393.
2. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, NY, 1953.
3. Hansen, C. M., *J. Paint Technol.*, 1967, **39**, 104, 511.
4. Hansen, C. M., *Ind. Eng. Chem. Prod. Res. Dev.*, 1969, **8**, 2.
5. Van Krevelen, D. W., *Properties of Polymers. Their Correlation with Chemical Structure*, 3rd edn. Elsevier, Amsterdam, 1990, Ch. 7, p. 189.
6. Barton, A. F. M., *Handbook of Solubility and Other Cohesion Parameters*. CRC Press, Boca Raton, FL, 1983.
7. Blanks, R. F. and Pravsnitz, J. M., *Ind. Eng. Chem. Fund.*, 1964, **3**, 1.
8. Sanchez, I. C., in *Polymer Compatibility and Incompatibility, Principles and Practices*, MMI Press Symposium Series 2, ed. K. Solc and N. Y. Harwood, 1982, p. 59.
9. Flory, P. J., Orwoll, R. A. and Vrij, A., *J. Amer. Chem. Soc.*, 1964, **86**, 3515.
10. Brandrup, J. and Immergut, E. H., *Polymer Handbook*. John Wiley, London, 1975, p. IV-349.
11. Mai, H. W., *J. Mater. Sci.*, 1986, **21**, 904.
12. Bagley, E. B., Nelson, T. P. and Scigliano, J. M., *J. Paint. Technol.*, 1971, **43**, 35.
13. Henry, L. F., *Polym. Eng. Sci.*, 1974, **14**, 167.
14. Wu, S., *J. Polym. Sci., Polym. Phys. Ed.*, 1989, **27**, 723.
15. Gilbert, D. G., Ashby, M. F. and Beaumont, P. W. R., *J. Mater. Sci.*, 1986, **21**, 3194.
16. Tobolsky, A. V., *Properties and Structure of Polymers*. John Wiley, New York, 1960.
17. Morel, E., Bellenger, V., Bocquet, M. and Verdu, J., *J. Mater. Sci.*, 1989, **24**, 69.
18. Bellenger, V., Verdu, J., Ganem, M. and Mortaigne, B., *Polym. and Polym. Composites*, 1994, **2**, 9.
19. Hopfenberg, H. B. and Frisch, H. L., *Polym. Letters*, 1969, **7**, 405.
20. Alfrey, T., *Chem. Eng. News*, 1965, **43**, 64.
21. Peterlin, A., *Makromol. Chem.*, 1969, **124**, 136.
22. Thomas, N. L. and Windle, A. H., *Polymer*, 1978, **19**, 225.
23. Burrell, H., *Official Digest*, 1995, **27**, 726.
24. Flory, P. J. and Rehner, J., *J. Chem. Phys.*, 1944, **11**, 52.
25. Keilley, F. N. and Bueche, F. J., *J. Polym. Sci.*, 1961, **50**, 549.
26. Simha, R. and Boyer, R. F., *J. Chem. Phys.*, 1962, **37**, 1003.