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Volumetric properties of epoxy networks cured by cycloaliphatic mono- and diamines

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Several diglycidyl ether of bisphenol A epoxy systems cured by isophorone diamine with a monoamine, trimethylcyclohexylamine, used as chain extender were studied by density, dilatometry and viscoelasticity measurements. The crosslink density controls the free volume fraction at T_g, the coefficient of cubical expansion in the rubbery state and the extrapolated volume of the liquid at 0 K. The glassy state characteristics, essentially the packing density, are practically independent of the crosslink density, which could only influence the volume component linked to beta motions.

(Keywords: epoxide; network; packing; density; free volume)

INTRODUCTION

Despite the large amount of available literature on the volumetric properties of polymers[1–4], little is known in this area on densely crosslinked systems such as, for instance, amine crosslinked epoxies. One interesting question concerns the effect of the crosslink density n on the packing density in the glassy state. Many authors have observed an increase of the density with n, for instance in sample families where the structural variable is the cure extent[5,6], or the degree of polymerization of the (di)epoxide[7]. Other authors, however, have observed the opposite trends, essentially for samples differing in the epoxide/amine molar ratio[8–10], and in systems differing only in the cure extent[11], or by the presence of external plasticizers[12]. In these cases, it was suggested either that the free-volume fraction increases with n, due to the packing hindrance by the steric restrictions imposed by crosslinking[8,9], or that there is a volume contraction linked to the addition of a third component in the reactive mixture[12]. Although these theories seem to be supported by elastic modulus[8,9,12], gas diffusion[13] or water absorption[11] measurements, it remains to explain the above marked exceptions[5–7].

An alternative explanation can be proposed on the basis of packing density (ρ^* = van der Waals volume/total volume) determinations. When the chemical structure varies, which is the case of all the above sample families, the density variations are not necessarily representative of packing density variations. Van der Waals volume changes linked to epoxide ring opening during crosslinking could be involved for instance[14]. On the other hand, it appears that hydrogen bonding plays a considerably more important role in packing density than crosslinking[15]. Furthermore, it has recently been shown that modulus variations, in many structural series, affect essentially the viscoelastic component linked to local motions (relaxation times typically above 10^{-6} s), and cannot be interpreted in terms of packing density variations[16].

The aim of this work is to study the volumetric properties of binary or ternary, stoichiometric or non-stoichimetric networks based on one diepoxide, the diglycidyl ether of bisphenol A (DGEBA), one diamine, isophorone diamine (IPD), and one primary monoamine, trimethylcyclohexylamine (TMCA), used as chain extender. Particular attention will be paid to the eventual effects of the crosslink density on glassy state packing density and both glassy state and liquid state cubical dilatation coefficients.

EXPERIMENTAL

Materials

DER 332 (Dow Chemicals Ltd), pure diglycidyl ether of bisphenol A (DGEBA) epoxy resin, was used in this study. The curing agent was isophorone diamine (IPD), a cycloaliphatic compound having two different amine functions. A third monomer was used as a chain extender: it was trimethylcyclohexylamine (TMCA), which has only one amine function. Both amines were obtained from VEBA Chemie. Chemical structures of the epoxy resin and curing agents are shown in *Figure 1*. Seven different epoxy resin formulations were investigated. Their codes and compositions are reported in *Table 1*. The components were mixed with a low-pressure mixing machine (SECMER), then poured into polytetrafluoroethylene (PTFE) moulds. The curing cycle was 1 h at 140°C followed by 6 h at 190°C. No residual cure exotherm was observed, in these conditions, by d.s.c.

Density measurements

The density at room temperature was determined in a density gradient column and also by picnometry. The results of both methods were in good agreement.

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Dilatometric measurements

The coefficient of linear thermal expansion β was measured from room temperature (T_0) to 250°C at a heating rate of $10\,\mathrm{K\,min^{-1}}$ on a Mettler TA 3000 TMA 40 thermal mechanical analyser. Since β is very small and assuming that the sample is isotropic, the coefficient of cubical expansion α and the specific volume $v(T)$ at temperature T are given by:

$$\alpha = 3\beta$$

$$v(T) = \frac{1}{\rho(T)} = \frac{1+\alpha(T-T_0)}{\rho(T_0)}$$

Viscoelastic measurements

Dynamic mechanical properties were determined using a Rheometrics Dynamic Analyser (RDA 700), between 20 and 250°C, at 16 frequencies from $15.9\times10^{-3}\,\mathrm{Hz}$ ($0.1\,\mathrm{rad\,s^{-1}}$) to 15.9 Hz ($100\,\mathrm{rad\,s^{-1}}$). A detailed analysis of the results will be published shortly[17]. Here, only the C_1 and C_2 coefficients of the WLF equation[18] will be reported. According to the well known Doolittle equation[19], the free-volume fraction at T_g can be derived from C_2: $f_g = C_2\Delta\alpha$, where $\Delta\alpha = \alpha_l - \alpha_g$, α_l and α_g being the coefficients of cubical expansion in, respectively, the liquid and glassy state.

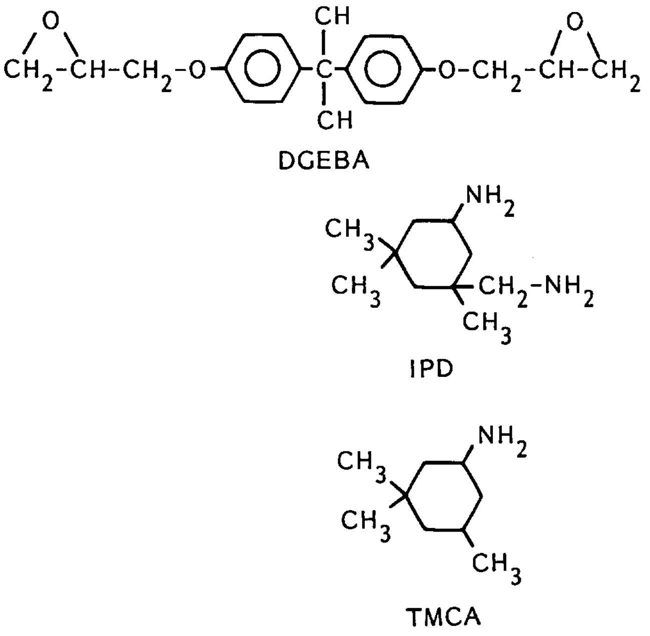


Figure 1 Structures of the epoxide and amines under study

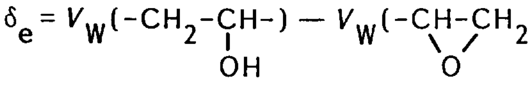
RESULTS

A constituent repeat unit (CRU) based on 2 moles of DGEBA units was chosen for the calculations. Its composition is given, for each sample under study, in *Table 1*. In samples 1 to 5, assuming no free chain ends, the crosslink density is the tertiary amine concentration. In samples having an epoxide excess (6 and 7), it was assumed that:

$$N = N_T - N_E$$

where N is the number of crosslink mers, N_T the total number of tertiary amines and N_E the number of tertiary amines directly linked to a free epoxide group in a 'monomer unit'. It is thus assumed that each free epoxide group is isolated from all the others by at least one network junction, which constitutes a good approximation in the case of low excess epoxide. The molar mass M of the CRU and the crosslink density $n = N/M$ are listed in *Table 1*.

For the determination of the van der Walls volume V_W, we used Bondi's data[2]. For IPD and TMCA cycles, it was considered, from model compound data, that the cycle increment is $\delta_c = -1.13\,\mathrm{cm^3\,mol^{-1}}$. Although estimations could be made[14], it will be considered that the contribution of the epoxide ring is not known, and that:



$$\delta_e = V_W(\text{-CH}_2\text{-}\underset{\text{OH}}{\text{CH}}\text{-}) - V_W(\text{-}\underbrace{\text{CH-CH}_2}_{\text{O}})$$

The measured densities ρ and the calculated van der Walls volumes V_W are listed in *Table 2*. From these data, the packing density ρ^* at 293 K can be determined:

$$\rho^*_{293} = \frac{V_W}{V} = \rho\frac{V_W}{M}$$

Table 2 Van der Waals volume of the 'monomer unit', experimental value of the specific weight and packing density of the systems under study

System	V_W ($\mathrm{cm^3\,mol^{-1}}$)	ρ_{293} ($\mathrm{g\,cm^{-3}}$)	ρ^*_{293}
1	493	1.1639	0.6746
2	519	1.1541	0.6785
3	537	1.1348	0.6730
4	516	1.1668	0.6813
5	548	1.1560	0.6858
6	$472-0.8\delta_e$	1.1748	0.6796[a]
7	$494-0.8\delta_e$	0.1607	0.6795[a]

[a] Calculated neglecting δ_e

Table 1 Sample code, amine/epoxide molar ratio, IPD/TMCA molar ratio, molar mass of the 'monomer unit', crosslink density, hydroxyl concentration, aromatic concentration and glass transition temperature of the samples under study

System	Z	f	M ($\mathrm{g\,mol^{-1}}$)	n ($\mathrm{mol\,kg^{-1}}$)	[OH] ($\mathrm{mol\,kg^{-1}}$)	[Ar] ($\mathrm{mol\,kg^{-1}}$)	T_g (K)
1	1	1	850	2.35	4.706	4.706	432
2	1	0.7	883.6	1.58	4.530	4.530	404
3	1	0.5	906	1.10	4.415	4.415	381
4	1.2	1	884	1.80	4.525	4.525	410
5	1.2	0.7	924.3	1.21	4.328	4.328	387
6	0.8	1	816	0.98	3.921	4.902	377
7	0.8	0.7	843	0.66	3.796	4.745	364

The corresponding values are also listed in *Table 2*. These results call for the following comments.

The hierarchies of packing density and density values are not the same. The most apparent structural effect is the increase of ρ^* with the amine excess:

$\rho^* > 0.68$ for samples 4 and 5

$\rho^* < 0.68$ for all the other samples

The systems having an epoxide excess (6 and 7) appear to be slightly more densely packed than the corresponding stoichiometric systems (1 and 2), because the negative increment of the epoxide ring (δ_e) has been neglected. The conditions to have the same packing density for systems 1 and 6 can be ascribed:

$$\frac{V_{W6} - 0.85\delta_e}{M_6} \rho_6 \simeq \rho_1^*$$

which leads to $\delta_e = 4.37\,\text{cm}^3\,\text{mol}^{-1}$, i.e. a physically reasonable value[14].

The dilatometric curves of the samples under study are presented in *Figure 2*. From these curves, the coefficient of expansion of the glass α_g and the rubber α_l were determined graphically and listed in *Table 3*. Both coefficients are almost monotonic decreasing functions of the crosslink density (*Figure 3*); $\Delta\alpha = \alpha_l - \alpha_g$ decreases with also n (*Figure 3*).

Using the experimentally determined values of ρ_{293}, T_g, α_g and α_l, we determined V_g, the specific volume at T_g, V_{10}, the extrapolated specific volume of the liquid at 0 K, and the product $\Delta\alpha T_g$. The results are listed in *Table 3*.

The whole results of viscoelastic measurements will be presented and discussed in a subsequent article[17]. The values of C_2 are reported here only because they give access to the free-volume fraction at T_g: $f_g/\Delta\alpha = C_2$ according to the classical free-volume theory. These data are to be considered as preliminary results in which the hierarchy of C_2 and f_g values (*Table 3*) can be discussed.

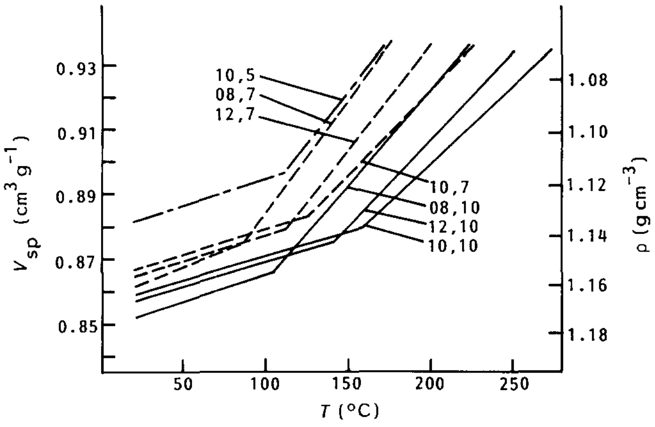


Figure 2 Dilatometric curves

DISCUSSION

Volumetric properties at ambient temperature

The trends of density variations with the crosslink density n depend on the chosen structural variable. When this latter is the amine/epoxide molar ratio r, the DGEBA/IPD/TMCA systems display 'abnormal' behaviour[8–10]: ρ is a decreasing function of n. When the structural variable is the diamine/monoamine molar ratio, the opposite behaviour is observed: ρ is an increasing function of n as for crosslinked polyesters[20] or certain stoichiometric epoxide–amine systems[7,25]. The same trends are observed at T_g (*Table 3*). It thus seems logical to suppose that there are factors other than the crosslink density that can play a determinant role in density variations. Among these factors, the atomic composition, segment stiffness and hydrogen bonding are especially important.

Atomic composition. It has recently been shown[21] that the density of polymers increases more or less regularly with their 'average atomic weight' M_a:

$$M_a = M \Big/ \sum n_i$$

where M is the molar mass of the CRU, which contains $\sum n_i$ atoms. For linear polymers:

$$0.1 < \Delta\rho/\Delta M_a < 0.2$$

The samples under study display the same trends:

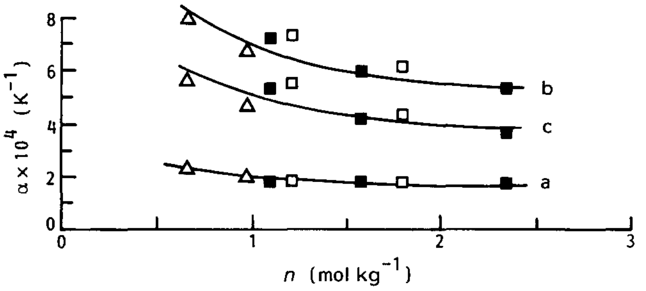


Figure 3 Cubical coefficients of expansion in glassy state and rubbery state and the free volume against crosslink density: (■) systems with $r=1$; (□) systems with $r=1.2$; (△) systems with $r=0.8$

Table 3 Cubical coefficients of expansion in glassy (α_g) and liquid (α_l) states, extrapolated specific volumes at $T_g(v_g)$ and 0 K (v_{l0}, liquid state) and Simha–Boyer free-volume fraction ($\Delta\alpha T_g$) of the samples under study

System	α_g $\times 10^4$ (K^{-1})	α_l $\times 10^4$ (K^{-1})	v_g (cm^3 g^{-1})	v_{l0} (cm^3 g^{-1})	$\Delta\alpha T_g$	C_2 (K)	$f_g \times 10^2$
1	1.71	5.36	0.879	0.714	0.1577	52.9	1.93
2	1.80	5.95	0.883	0.712	0.1677	47.5	1.97
3	1.88	7.21	0.895	0.701	0.2053	43.6	2.35
4	1.78	6.13	0.874	0.698	0.1788	52.6	2.29
5	1.83	7.34	0.879	0.685	0.2172	44.2	2.44
6	2.04	6.75	0.865	0.690	0.1776	53	2.50
7	2.33	7.98	0.875	0.678	0.2057	48.9	2.76

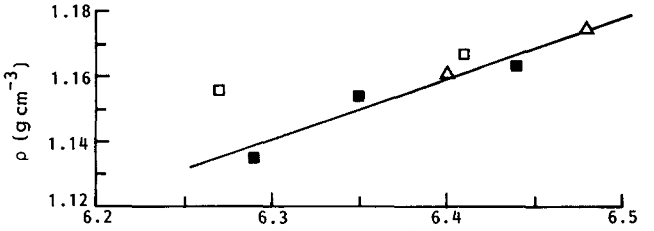


Figure 4 Density at 293 K against 'average atomic weight' (see text). Some symbols as in *Figure 3*

$\Delta\rho/\Delta M_a = 0.15$ (*Figure 3*). The lower (sample 3) and the higher (sample 6) densities correspond respectively to the lower ($M_a = 6.29$) and the higher ($M_a = 6.52$) weight fraction of 'heavy' heteroatoms (essentially oxygen). Thus, the density variations at the second decimal level can be mainly attributed to this factor.

Segment stiffness. It can be observed in *Figure 4* that the samples 4 and 5 having an amine excess, e.g. corresponding to the lowest aromatic group concentration, are more densely packed than all the others. The following explanation could be proposed. The aromatic groups increase the chain stiffness, which disfavours the packing of network segments. As a matter of fact, it is well known that the radius of gyration of linear polymer coils increases with their stiffness.

Hydrogen bonding. An amine excess leads to a density increase in many systems hardened by aromatic amines[10,21]. Factors other than the aromatic group concentration are thus involved. A consequence of the amine excess is the presence of secondary amine groups, able to participate in NH...X hydrogen bonds (X being an electronegative group). It has recently been found that hydrogen bonding causes a strong increase of ρ^*, especially when NH groups are involved as in the case of polyamides[15].

Expansion coefficients

The influence of the crosslink density appears in contrast clearly on both cubic expansion coefficients α_g and α_l (*Figure 3*). The amplitude of the variations is considerably higher for α_l than for α_g as in the case of polyesters[20]. It can be deduced that the thermal energy required to create a given amount of free volume is an increasing function of the crosslink density. As quoted by Shibayama and Suzuki[20], crosslinking reduces the number of possible lattice configurations so that entropy factors[22] are also probably involved. It can be remarked that $\Delta\alpha = \alpha_l - \alpha_g$ behaves as the heat capacity jump ΔC_p at T_g, which decreases when the crosslink density increases in DGEBA–IPD systems[23].

The values of $\Delta\alpha T_g$ (*Table 3*) reveal a considerable departure from the Simha–Boyer rule[24] ($\Delta\alpha T_g \simeq 0.11$). They decrease almost monotonically with the crosslink density.

A detailed study of the volume expansion in the glassy state would probably be interesting; unfortunately, low-temperature dilatometric data are not yet available. It has been shown, in the case of linear polymers, that there is some jump of the cubical expansion coefficient α_g at secondary transitions[25]:

$$\Delta\alpha(T_\beta) \leqslant 0.5 \times 10^{-4}\,\mathrm{K}^{-1}$$

By analogy, and since for the epoxies under study, $T_\beta \simeq 200\,\mathrm{K}$[23], it can be assumed that the volume excess linked to beta motions at ambient temperature is such that:

$$(\Delta v/v)_{293} = \Delta\alpha(T_\beta)(293 - T_\beta) \leqslant 5 \times 10^{-3}$$

In the case of poly(vinyl chloride) (PVC), it has been shown that external plasticization reduces $\Delta\alpha(T_\beta)$[25], whereas mechanical measurements reveal a partial suppression of the beta motions[27]. This latter behaviour was observed in various cases of 'internal plasticization' of epoxies[12,16,26], where the effects of structure modifications leading to a T_g decrease were examined. It appeared that, in these cases, the population of segments participating in beta motions is an increasing function of the crosslink density.

According to these observations, $(\Delta v/v)_{293}$ must be maximum for the most densely crosslinked system (sample 1) of the series under study.

Thus, the fact that a volume component linked to local motions increases with the crosslink density seems to support Morgan's theory[28]. However:

(i) It is too small to explain the density variations with structure at ambient temperature.

(ii) It is linked to beta motions rather than free volume.

Finally, the situation could be depicted by *Figure 5*, where it can be seen that the glassy phase is densely packed at 0 K, as the crosslink density is low.

Extrapolated volume of the liquid at 0 K

It is generally considered that the specific volume of the liquid at 0 K, v_{l0}, corresponds to the closest molecular packing[4]. The available, physically valid, extrapolation methods from liquid[29] or crystalline[30] state data cannot be used here. It can, however, be observed that α_l relative variations with the structure are noticeably larger than

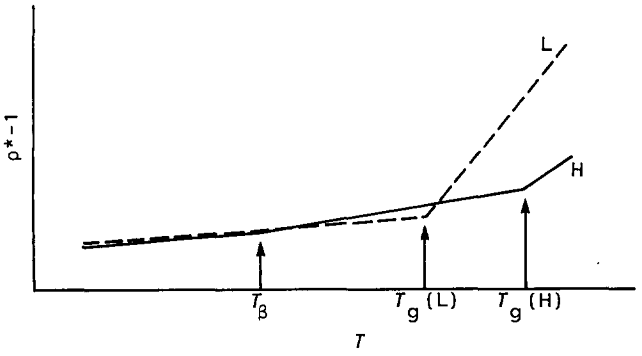


Figure 5 Hypothetical shape of the curves of reciprocal packing density against temperature for a stoichiometric (high crosslink density, H) and a non-stoichiometric (low crosslink density, L) network

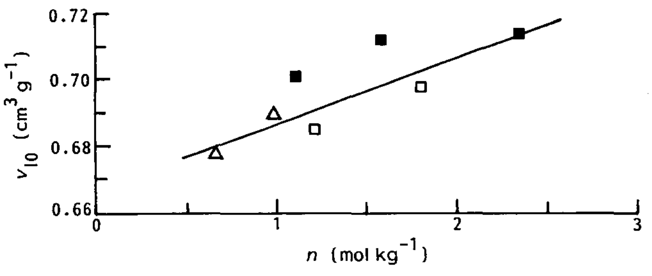


Figure 6 Extrapolated liquid specific volume at 0 K against crosslink density. Same symbols as in *Figure 3*

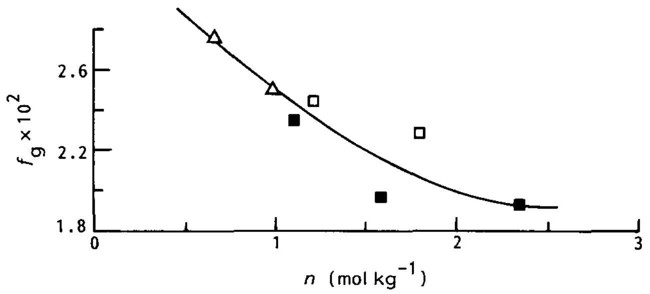


Figure 7 Free-volume fraction at T_g (from viscoelasticity measurements) against crosslink density. Same symbols as in *Figure 3*

the corresponding variations of v_g or T_g (*Table 3*). As a consequence, v_{l0} must be an increasing function of the crosslink density, as for the glassy phase, which can be easily interpreted in terms of network steric restrictions to packing. Although the model of linear expansion is questionable[31], the results of *Figure 6* seem to be at least qualitatively valid.

Free-volume fraction at T_g

As observed by Shibayama and Suzuki in the case of polyesters[20], the free-volume fraction at T_g is a decreasing function of the crosslink density (*Figure 7*), which contradicts the previously proposed theories[8–13] but seems to confirm a general tendency of chemical and physical (semicrystalline polymer[32]) networks. It remains to explain by which process the steric effects of three-dimensional junctions, which in principle must favour free-volume freeze-in during vitrification, are largely counterbalanced. This important question could be difficult to resolve on the basis of purely 'volumetric' theories and needs further research.

CONCLUSIONS

The above investigations on the volumetric properties of the DGEBA/IPD/TMCA binary or ternary systems leads to the following conclusions.

Although in a given structural series, the density is a minimum at the stoichiometric point, e.g. for the most crosslinked system, as observed for many other epoxy systems, the results show clearly that the packing density cannot be considered to be a decreasing function of the crosslink density. The network structure seems to play a minor role compared to other structural factors such as atomic composition, aromaticity and hydrogen bonding.

The cubical expansion coefficients in both glassy and rubbery states decrease regularly with the crosslink density. Consequently, network steric restrictions would have a limiting effect on the packing density at low temperature.

The only volume component that increases with the crosslink density is the one created by beta motions. However, its variations are too small to be easily observed.

The free-volume fraction at T_g as derived from the free-volume approach of viscoelasticity is a decreasing function of the crosslink density.

REFERENCES

1 Tobolsky, A. V. 'Properties and Structure of Polymers', Wiley, New York, 1960

2 Bondi, A. 'Physical Properties of Molecular Liquids, Crystals and Glasses', Wiley, New York, 1968

3 Van Krevelen, D. W. and Hoftyzer, P. 'Properties of Polymers, Their Estimation and Correlation with Structure', Elsevier, Amsterdam, 1976

4 Roberts, C. E. and White, E. F. T. 'The Physics of Glassy Polymers', Applied Science, London, 1973

5 Cizmecioglu, M., Gupta, A. and Fedors, R. F. *J. Appl. Polym. Sci.* 1986, **32**, 6177

6 Chang, T. D., Carr, S. H. and Brittain, J. O. *Polym. Eng. Sci.* 1982, **22**, 1213

7 Misra, S. C., Manson, J. A. and Sperling, L. H. *ACS Symp. Ser.* 1979, **114**, 37

8 Findley, W. N. and Reed, R. M. *Polym. Eng. Sci.* 1977, **17**, 837

9 Morgan, R. J., Kong, F. M. and Walkup, C. M. *Polymer* 1974, **25**, 375

10 Gupta, V. B., Drzal, L. T. and Lee, C. Y. C. *Polym. Eng. Sci.* 1985, **25**, 812

11 Enns, J. B. and Gilham, J. K. *J. Appl. Polym. Sci.* 1983, **28**, 2831

12 Daly, J., Britten, A., Garton, A. and McLean, P. D. *J. Appl. Polym. Sci.* 1984, **29**, 1403

13 Barton, J. M. *Polymer* 1979, **20**, 1019

14 Bellenger, V., Dhaoui, W. and Verdu, J. *J. Appl. Polym. Sci.* 1987, **33**, 2647

15 Bellenger, V., Dhaoui, W. and Verdu, J. *J. Appl. Polym. Sci.* 1988, **35**, 563

16 Morel, A., Bellenger, V., Bocquet, M. and Verdu, J. *J. Mater. Sci.* 1989, **24**, 69

17 Won, Y. G., Galy, J. and Gerard, J. F. to be published

18 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701

19 Doolittle, A. K. *J. Appl. Phys.* 1951, **22**, 1471

20 Shibayama, K. and Suzuki, Y. *J. Polym. Sci.* (*A*) 1965, **3**, 2637

21 Dhaoui, W., Ph.D. Thesis, ENSAM, Paris, 1988

22 Di Marzio, E. A. *J. Res. NBS* (*A*) 1964, **68**, 611

23 Sabra, A., Thesis, Univ. Lyon, France, 1985

24 Simha, R. and Boyer, R. F. *J. Chem. Phys.* 1962, **37**, 1003

25 Heydemann, P. and Gwicking, H. D. *Kolloid Sci. Polym.* 1963, **193**, 16

26 Williams, J. G. *J. Appl. Polym. Sci.* 1979, **23**, 3433

27 Bohn, L. *Kunststoffe* 1963, **51**, 826

28 Morgan, R. J. *Adv. Polym. Sci.* 1985, **72**, 1

29 Goldhammer, D. A. *Z. Phys. Chem.* 1910, **71**, 577

30 Biltz, W. 'Raunchemie der Festen Stoffe', B. Voss, Leipzig, 1934

31 Martin, G., Rogers, S. S. and Mandelkern, D. *J. Polym. Sci.* 1959, **20**, 579

32 Kunugi, T., Isobe, Y., Kimura, K., Asanuma, Y. and Hashimoto, M. *J. Appl. Polym. Sci.* 1979, **24**, 923