Acronal–polymethyl acrylate interpenetrating polymer networks

D. J. Hourston and J. A. McCluskey
Department of Chemistry, University of Lancaster, Bailrigg, Lancaster LA1 4YA, UK
(*Received* 21 *December* 1979; *revised* 16 *June* 1980)

Four interpenetrating polymer networks were prepared by swelling crosslinked Acronal (a copolymer of styrene and butyl acrylate) with methyl acrylate plus crosslinking agent and then polymerizing the methyl acrylate *in situ*. Certain properties of the constituent network materials, plus the interpenetrating polymer networks which contained 70, 50, 35 and 25% by weight of polymethyl acrylate, were investigated. Electron microscopy showed the interpenetrating polymer networks to be two-phase materials with the polymethyl acrylate domain size increasing with increasing polymethyl acrylate content. Longitudinal sonic velocity measurements indicate that at around 50% by weight of polymethyl acrylate both phases become continuous while dynamic mechanical spectroscopy leads to the view that the constituent networks were not extensively mixed.

INTRODUCTION

The term interpenetrating polymer network (IPN) was coined by Millar[1] in 1960 and is now taken to describe the situation where a three dimensional polymeric network is synthesized in the presence of another previously or simultaneously established network. This leads to varying degrees of intimacy of mixing depending on the mutual solubility of the pair of networks and represents a blending procedure which does not require mechanical mixing.

Synthesis of these materials may be achieved in a variety of ways. For example, the first network can be prepared separately and then it may be swollen with the monomer, crosslinking agent and initiator of the second network which is then polymerized *in situ*. This procedure leads to a sequential IPN[2]. Starting with a mixture of two monomers, and the necessary crosslinking agents, which polymerize by distinct mechanisms leads to simultaneous IPNs[3–5]. Interpenetrating elastomeric networks[6] are synthesized by taking a pair of latexes of linear polymers which are mixed, coagulated and then crosslinked simultaneously.

With IPNs complete interpenetration only exists when the two networks are completely miscible. Consequently the majority of IPNs reported so far show varying degrees of phase separation. It is likely that for many two-phase IPNs extensive network interpenetration only occurs at and near phase boundaries.

There are several recent reviews[7–9] of the syntheses and properties of IPNs.

In this work Acronal, which is a thermally crosslinkable copolymer of butyl acrylate and styrene, was crosslinked by heating and then swollen to varying extents with methyl acrylate containing divinylbenzene as crosslinking agent and the AIBN as initiator. The methyl acrylate was then polymerized. The resulting IPNs were investigated using electron microscopy, longitudinal sonic velocity measurements and dynamic mechanical spectroscopy.

EXPERIMENTAL

Materials

The Acronal used in this work (grade 230D) was donated by BASF as an aqueous, plasticizer-free dispersion with a solids contents of $50 \pm 1\%$. It had a minimum film-forming temperature of ~ 24 C and optimum crosslinking was developed at temperatures between 120 and 150 C. The methyl acrylate was supplied by BDH Ltd. and the divinylbenzene by Cambrian Chemicals.

IPN preparation

Acronal sheets were prepared by pouring the emulsion into glass casting trays and allowing the water to evaporate at ~ 25 C. The resulting sheets were subsequently hot pressed at 135 C for 30 min to effect crosslinking.

The molecular weight between crosslinks ($\bar{M}_c$) of the Acronal sheet was determined by swelling pieces ~ 1 cm^2 in nine solvents whose solubility parameters covered the range from 7.24 to 14.5 (cal cm^{-3})$^{1/2}$. By plotting the degree of swelling *versus* solubility parameter, maximum swelling was found to occur at 8.8 (cal cm^{-3})$^{1/2}$ which was taken[10] to be the solubility parameter of the polymer. Using this value the polymer–solvent interaction parameter (χ_1) was determined from the following approximate expression[11]:

$$\chi_1 = \beta_1 + \frac{V_s}{RT}(\delta_p - \delta_s)^2$$

Here V_s is the molar volume of the swelling agent, R and T have their usual significance while δ_p and δ_s are the solubility parameters of the polymer and the solvent, respectively. β_1 is the lattice constant.

Scott and Magat[12] used the above expression assuming a constant value for β_1 of 0.3 in all solvents. Yenwo *et al.*[13] have suggested a value of 0.35 ± 0.1. For this calculation a value of 0.3 was assumed and χ_1 calculated for the

0032-3861/81/030405-05$02.00

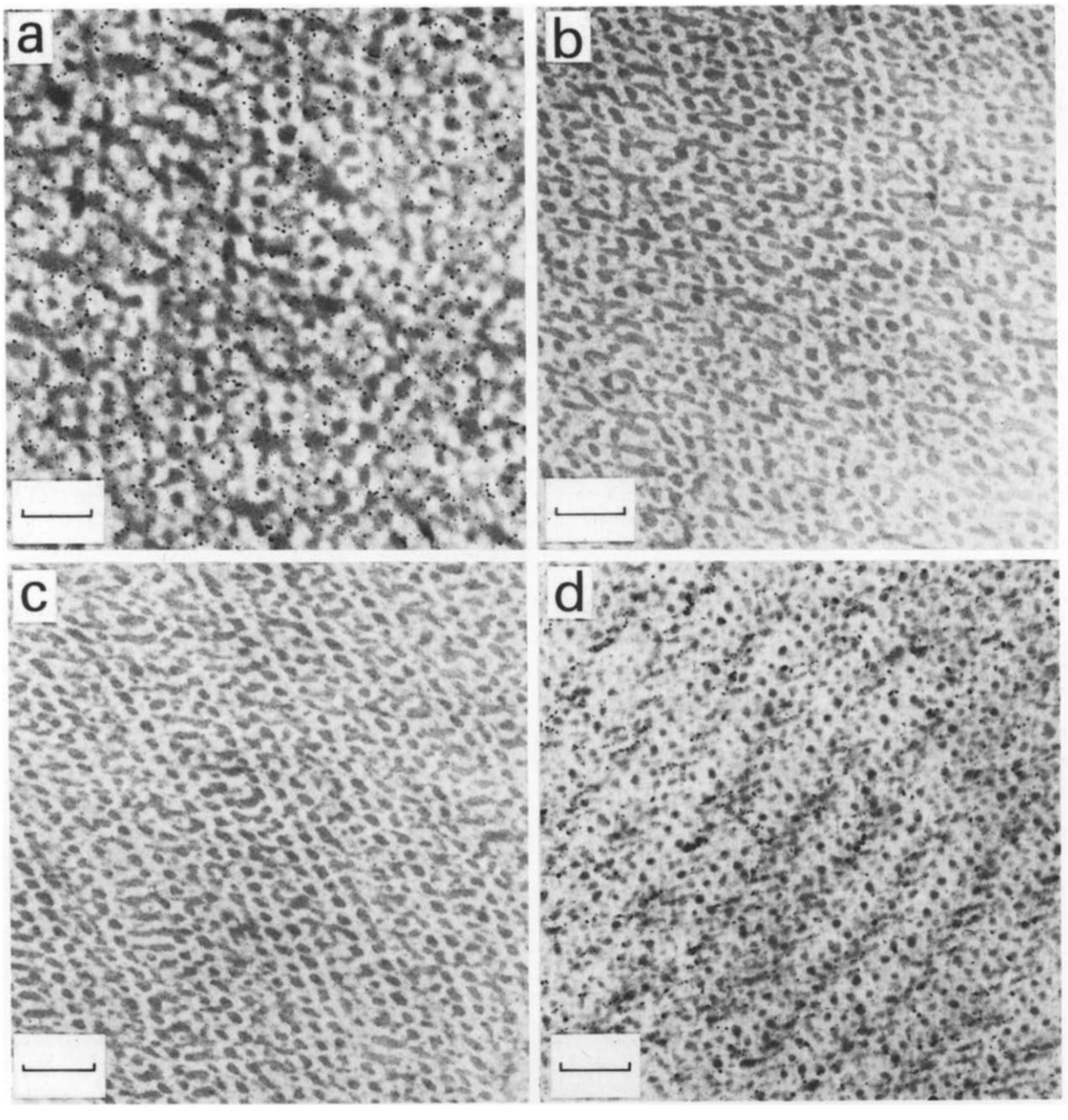

Figure 1 Electron micrographs of IPNs containing 70% (a), 50% (b and c) and 25% (d) by weight of polymethyl acrylate. The samples were stained using osmium tetroxide. The scale mark represents 500 nm

Acronal–chloroform, carbon tetrachloride and toluene systems.

Using the Flory–Rehner[13] equation it was found that the average value of $\bar{M}_c$ for the Acronal sheet swollen in these three solvents was ~8000.

Weighed sheets of the crosslinked Acronal were immersed in methyl acrylate containing divinylbenzene (1% by weight of monomer) and AIBN (0.2% by weight of monomer) in an air-tight vessel. To vary the eventual polymethyl acrylate content sheets were withdrawn after various times of swelling and placed in a metal mould sealed with a teflon-coated rubber gasket. The mould was then heated at 90°C for 8 h to form the second network. All samples were placed in a vacuum oven at around 20°C for at least a week to ensure the removal of all traces of residual monomer. The IPNs prepared contained 70, 50, 35 and 25% by weight of polymethyl acrylate, respectively.

Crosslinked polymethyl acrylate sheet was prepared in the metal moulds as in the second stage of the IPN synthesis.

Techniques

A Rheovibron Dynamic Viscoelastometer (model DDV-II-B) was used at frequencies of 3.5, 11, 35 and 110 Hz to obtain the dynamic mechanical data. The rate of temperature change was 1–2°C min^{-1}. The longitudinal sonic velocity measurements[14] were made at 20°C using a Morgan Pulse Propagation Meter (model PPM-5R) at a frequency of 15 kHz.

RESULTS AND DISCUSSION

Figures 1(a–d) show electron micrographs of the IPNs containing 70, 50 (*b* and *c*) and 25% by weight of polymethyl acrylate, respectively. The materials are phase separated with the second formed material, polymethyl

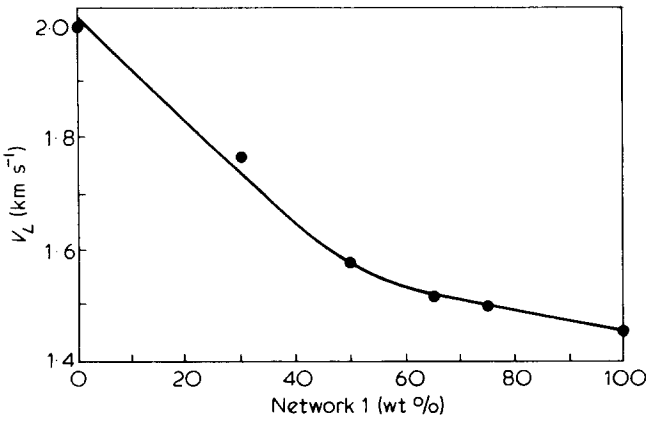

Figure 2 Plot of longitudinal sonic velocity (V_L) *versus* composition

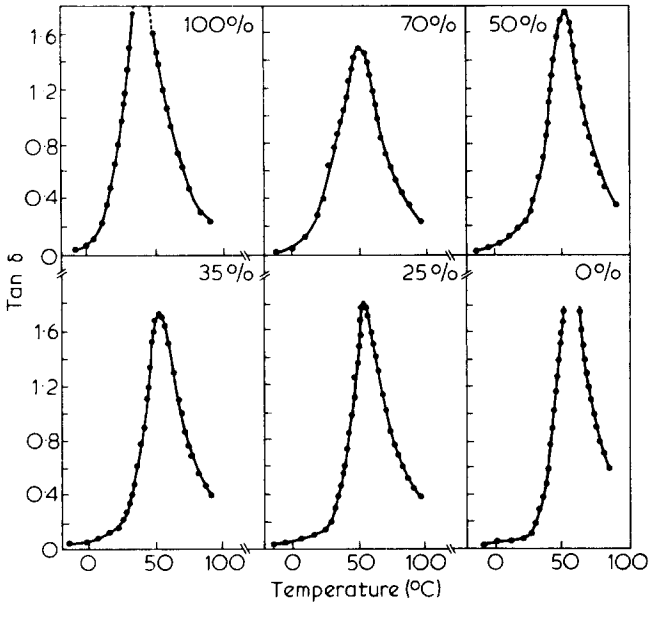

Figure 3 Plots of tan δ *versus* temperature for the parent networks and for the IPN's. The polymethyl acrylate content is indicated (wt %) on each Figure. Frequency, 35 Hz

acrylate, being the darker phase. It is also evident that the average size of the polymethyl acrylate domains decreases as the polymethyl acrylate content decreases. At 70% by weight of polymethyl acrylate the average domain size is ~126 nm while at 50 and 25% by weight of polymethyl acrylate the sizes are ~96 and 61 nm, respectively.

The sample containing 50% by weight of polymethyl acrylate showed regions where the polymethyl acrylate domains were randomly distributed (*Figure 1b*) and other areas where the domains occurred in approximately linear arrays (*Figure 1c*).

In *Figure 2* the longitudinal sonic velocity (V_L) is plotted against weight percent of the first formed network and exhibits two essentially linear regions. As V_L is equal to the square root of the sonic modulus divided by density, a plot of V_L^2 *versus* composition was constructed. It also had two distinctly linear regions, which interested at about the mid point of the composition scale. As the glass transition temperatures of both the parent networks, and, therefore, those of the IPNs are above the test temperature (20°C), their glassy moduli at 15 kHz should be similar (see *Figures 5–7*) meaning that the positions of the glass transition should not influence the magnitude of the V_L values appreciably. Consequently the change of slope in the V_L-composition plot at ~50% of the second network may be interpreted as the composition region at which this network becomes a continuous phase. It is not clear from the 50% by weight polymethyl acrylate electron micrographs (*Figure 1*) that the phases are co-continuous, but there can be little doubt that the polymethyl acrylate (70% by weight) phase is continuous in *Figure 1*.

Figure 3 shows the tan δ *versus* temperature dispersions (35 Hz) for both the polymethyl acrylate and the Acronal networks plus the four IPN systems. *Table 1* lists the glass transition temperatures, the maximum values of tan δ (tan δ_{max}) and the half-peak widths for all the materials.

With the glass transition temperatures of the parent networks differing by only 17°C at 35 Hz, it is inevitable that the dynamic mechanical technique will be unable to resolve the tan δ-temperature spectra for the IPNs into the two components, which from consideration of the morphology (*Figure 1*) should clearly exist. Only in the case of the IPN containing 70% by weight of polymethyl acrylate is there any evidence of broadening, from the half-peak widths, which would be expected to occur if there was any significant degree of interaction between the two networks. The same conclusion was reached for all four frequencies studied. By plotting log frequency *versus* the reciprocal of the absolute temperature[15] the activation energies (E_A) of the transitions may be obtained.

Linear relations were found for all six materials over the limited frequency range investigated. It has been assumed that it is correct to use this procedure for systems in which two distinct relaxation time distributions overlap. The error in the E_A values is estimated to be about ±20 kJ mol^{-1} indicating that only the samples with 70 and 25% by weight of polymethyl acrylate differ significantly from the parent networks (see *Table 2*). An increase in activation energy may indicate interaction between the parent networks.

Figure 4 shows plots of the glass transition temperature *versus* composition for the four frequencies. There is a

Table 1 Dynamic mechanical data at 35 Hz

Composition (wt % polymethyl acrylate)	T_g (°C)	Tan δ_{max}	Half-peak width (°C)
100	39	2.16*	30
70	50	1.50	37
50	51	1.74	30
35	51	1.74	30
25	53	~1.80	28
0	56	2.08*	29

* Estimated by extrapolation

Table 2 Activation energies (E_A) based on tan δ data

Composition (wt % polymethyl acrylate)	E_A (kJ mol^{-1})
100	170
70	240
50	215
35	220
25	250
0	200

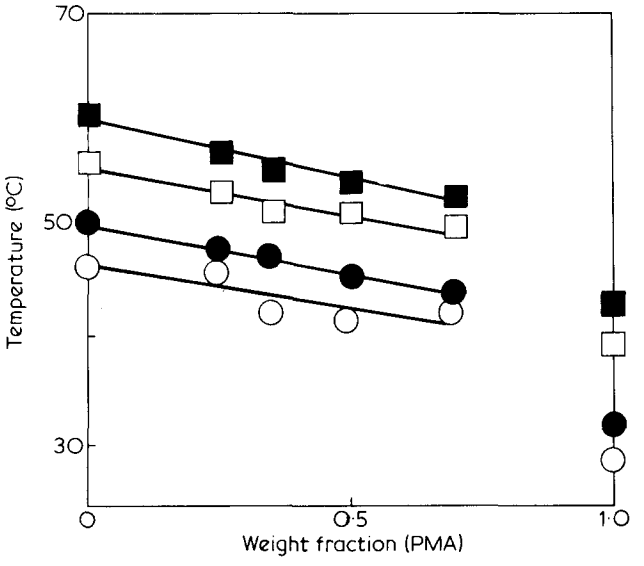

Figure 4 Plots of glass transition temperature *versus* composition for frequencies of 110 Hz (■), 35 Hz (□), 11 Hz (●) and 3.5 Hz (○), respectively

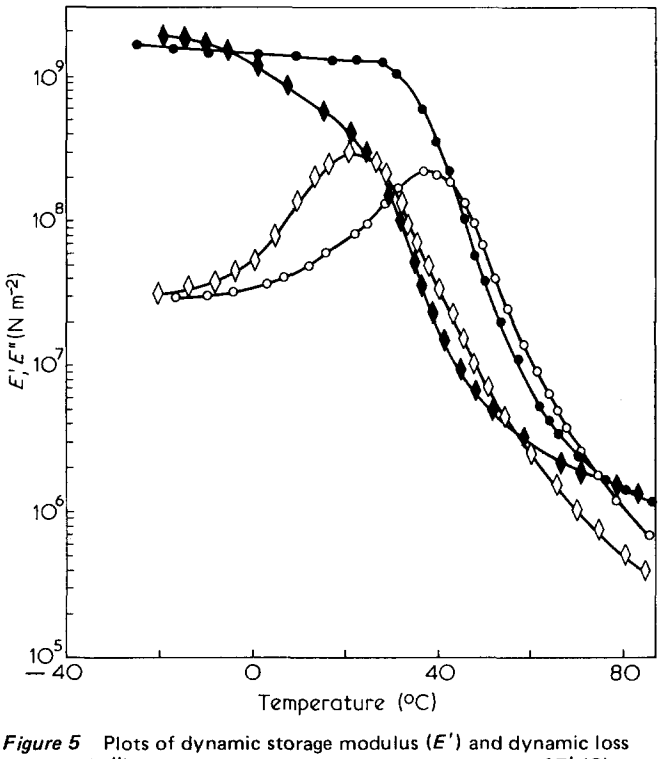

Figure 5 Plots of dynamic storage modulus (E') and dynamic loss modulus (E'') *versus* temperature for crosslinked Acronal [E' (●) and E'' (○)] and for crosslinked polymethyl acrylate [E' (♦) and E'' (◇)]. Frequency, 35 Hz

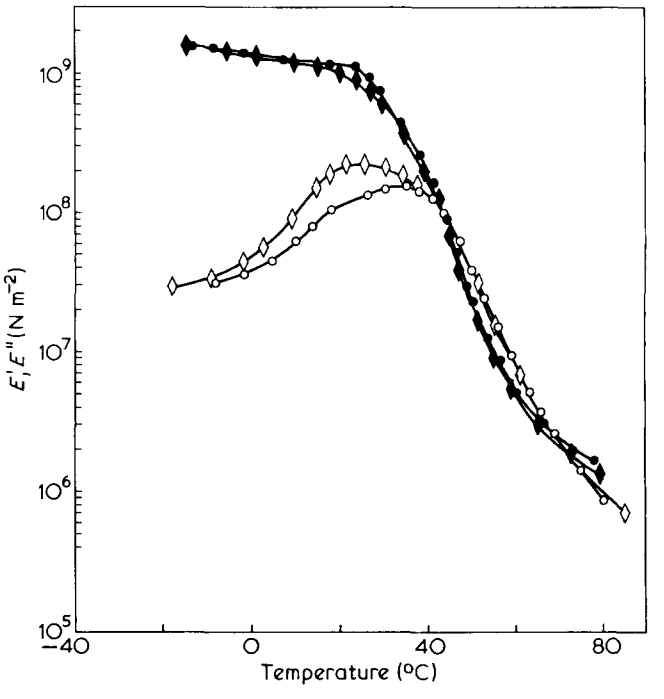

Figure 6 Plots of dynamic storage modulus (E') and dynamic loss modulus (E'') *versus* temperature for the IPN containing 25% by weight of polymethyl acrylate [E' (●) and E'' (○)] and for the IPN containing 35% by weight of acrylate polymethyl [E' (♦) and E'' (◇)]. Frequency, 35 Hz

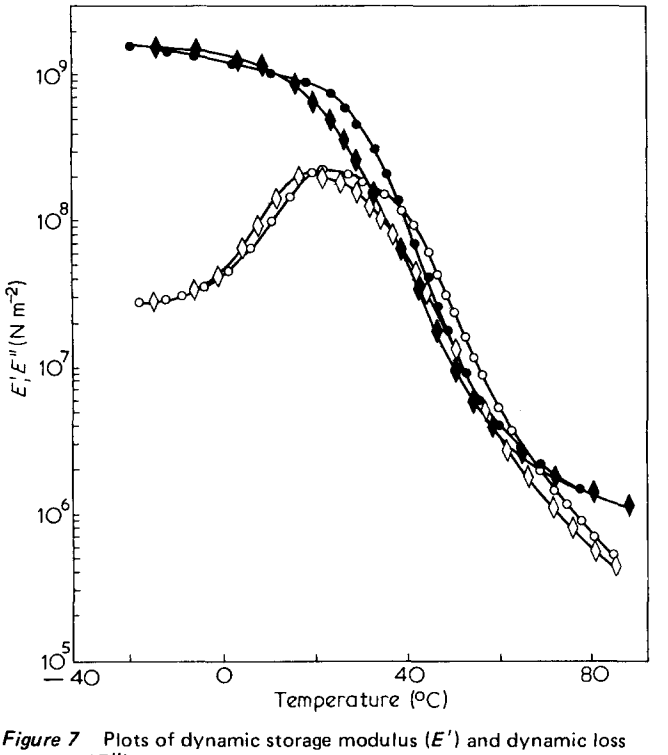

Figure 7 Plots of dynamic storage modulus (E') and dynamic loss modulus (E'') *versus* temperature for the IPN containing 50% by weight of polymethyl acrylate [E' (●) and E'' (○)] and for the IPN containing 70% by weight of polymethyl acrylate [E' (♦) and E'' (◇)]. Frequency, 35 Hz

linear decrease in the glass transition temperature for the IPNs as the polymethyl acrylate content is raised. However, above 70% by weight of polymethyl acrylate the trend is no longer linear.

Figures 5–7 show the dynamic storage modulus (E') and the dynamic loss modulus (E'') *versus* temperature plots. From the E'' curves in *Figure 5* the glass transition temperatures are at 37 and 22°C, respectively, for the Acronal and polymethyl acrylate networks. For the four IPNs the E'' curves show a broadened relaxation region with, in all four cases, evidence for both the parent network transitions, confirming the highly incompatible nature of these materials.

ACKNOWLEDGEMENTS

J. McCluskey wishes to thank the Science Research

Council for a CASE award held in collaboration with the Rubber & Plastics Research Association.

REFERENCES

1 Millar, J. R. *J. Chem. Soc.* 1960, **263**, 1311
2 Huelck, V., Thomas, D. A. and Sperling, L. H. *Macromolecules* 1972, **5**, 340, 348
3 Touhsaent, R. E., Thomas, D. A. and Sperling, L. H. *J. Polym. Sci. (C)* 1974, **46**, 175
4 Kim, S. C., Klempner, D., Frisch, K. C., Radigan, W. and Frisch, H. L. *Macromolecules* 1976, **9**, 258
5 Touhsaent, R. E., Thomas, D. A. and Sperling, L. H. 'Toughness and Brittleness of Plastics' (Eds R. D. Deanin and A. M. Crugnola) Adv. Chem. Ser. 154 Am. Chem. Soc., Washington, 1976
6 Frisch, H. L., Klempner, D. and Frisch, K. C. *J. Polym. Sci. (B)* 1969, **7**, 775
7 Klempner, D. and Frisch, K. C. 'Polymer Alloys', Plenum Press, New York, 1977
8 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites', Plenum Press, New York, 1976
9 Thomas, D. A. and Sperling, L. H. 'Polymer Blends', (Eds D. R. Paul and S. Newman) Academic Press, New York, 1978, Vol 2
10 Gee, G. *Trans. Inst. Rubber Ind.* 1943, **18**, 266
11 Huggins, M. L. *J. Chem. Phys.* 1941, **9**, 440
12 Scott, R. L. and Magat, M. *J. Polym. Sci.* 1949, **4**, 555
13 Yenwo, G. M., Sperling, L. H. and Manson, J. A. 'Chemistry and Properties of Crosslinked Polymers' (Ed S. S. Labana) Academic Press, New York, 1977
14 Beamish, A. and Hourston, D. J. *Polymer* 1976, **17**, 577
15 Muruyama, T. 'Dynamic Mechanical Analysis of Polymeric Material.' Elsevier, 1978