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Modulated differential scanning calorimetry: 2. Studies of physical ageing in polystyrene

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Physical ageing in polystyrene (PS) has been studied by means of modulated differential scanning calorimetry (m.d.s.c.). The results show that there exists a characteristic annealing temperature at which relaxation enthalpy has a maximum value. When annealing below 65°C, another relaxation peak has been found. The position of this relaxation peak, which changes with annealing temperature, lies approximately between 54 and 64°C. It has been postulated previously in the literature that the relaxation behaviour involves phenyl ring relaxation. As measured from heat capacity curves, this transition is evident as a shoulder on the glass transition. With increasing annealing temperature, the glass transition of PS increased slightly.

(Keywords: modulated differential scanning calorimetry; polystyrene; physical ageing)

INTRODUCTION

In all non-equilibrium systems, relaxation phenomena can be observed involving a time-dependent return to equilibrium after a disturbance. Relaxation behaviour, for example mechanical or dielectric relaxation, is universal. In fact, the process of physical ageing is also a typical relaxation phenomenon. During controlled cooling of a polymer in the equilibrium melt state from a high temperature, a moment is reached when the rate of structure rearrangement in the melt state, which depends on the thermal mobility of chain segments, starts to lag behind the cooling rate. The molecules in the sample will then show a progressive deviation in conformation from the equilibrium one. At low temperature, the sample will possess a frozen-in structure. With time, the frozen-in structure will relax towards the equilibrium state.

A growing body of data has been published[1–13] about the physical ageing of polymer materials. The results show (a) a decrease in the relaxation enthalpy, ΔH, during annealing; and (b) that ΔH is a linear function of $\ln t$ (where t is the ageing time).

Recently, a new thermal analysis technique[14,15], modulated differential scanning calorimetry (m.d.s.c.), has become available. It enables the reversible response of the sample at a given frequency to be deconvoluted from the total enthalpy change; the difference between these two quantities, the so-called non-reversing heat flow, is then a measure of the relaxation enthalpy. This non-reversing signal contains contributions from processes that are reversible at frequencies lower than that chosen for the modulation, but, to a first approximation, this simply represents a small constant correction term that does not fundamentally change any of the arguments and observations presented here. This makes the method very suitable for the study of physical ageing in polymer materials. In this paper, the physical ageing of a polystyrene (PS) sample with a controlled thermal history was investigated by m.d.s.c.

EXPERIMENTAL

Sample

The PS sample was obtained from BP Chemicals. The M_n value was 9.3×10^4 and the M_w value was 2.1×10^5, as determined by g.p.c. (Waters Instrument, model 510) calibrated using PS standards.

Sample preparation

The sample was heated to 180°C and held at this temperature for 5 min. It was then cooled slowly to 150°C and held there for 5 min to ensure that it was in the equilibrium state and to eliminate the effect of any previous thermal history. The sample was then rapidly immersed into liquid nitrogen, and held at liquid nitrogen temperature for 10 min before being removed

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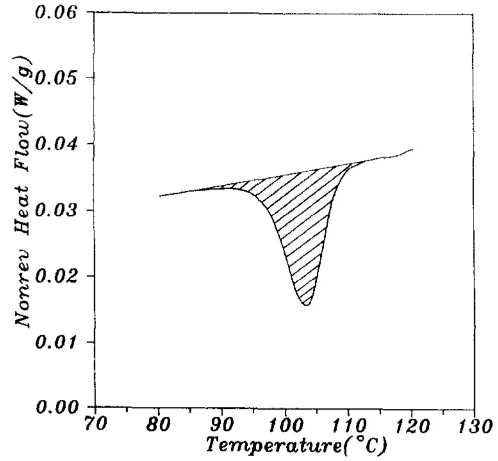

Figure 1 Schematic diagram of the calculation of relaxation enthalpy from a non-reversing heat flow signal

and allowed to warm to room temperature. It was stored at room temperature prior to use.

Instrumentation

A m.d.s.c. instrument manufactured by TA Instruments was used. Only a brief review of the m.d.s.c. technique is given here. The temperature programme consists of the conventional linear temperature rise with time ramp, which in the case of m.d.s.c. is modulated by a small sinusoidal perturbation. The modulated heat flow signal is averaged to obtain the total heat flow signal which is equivalent to a normal d.s.c. experiment. The amplitude of the cyclic response is measured by a Fourier transform technique and from this a value for the heat capacity, called the cyclic heat capacity, is obtained. By multiplying this by the underlying heating rate the reversing signal is obtained. By subtracting this reversing signal from the total heat flow the non-reversing signal is calculated. It has been observed[16] that the cyclic heat capacity contains contributions from irreversible kinetic processes that can be removed by use of the phase lag between the perturbation and the heat flow response. This correction has not been applied here as it is very minor for the types of transition discussed in this paper.

Calorimetry conditions

The sample was heated at 5°C min^{-1} to the ageing temperature, T_a, kept at that temperature for the required time, and then cooled at 10°C min^{-1} to 30°C, the temperature selected for the start of the measuring scan, which involved heating at 4°C min^{-1} to 150°C. An oscillation amplitude of 0.8°C and an oscillation period of 60 s were used throughout this investigation.

In addition, to obtain the necessary accuracy, a calibration of heat capacity was carried out by running a standard sapphire sample. The melting peak temperature and cell constant were calibrated using indium, and the baseline was established by running an empty pan. The relaxation enthalpy was calculated using the non-reversing heat flow signal (see *Figure 1*). In all the thermograms presented, endothermic signals are downward pointing.

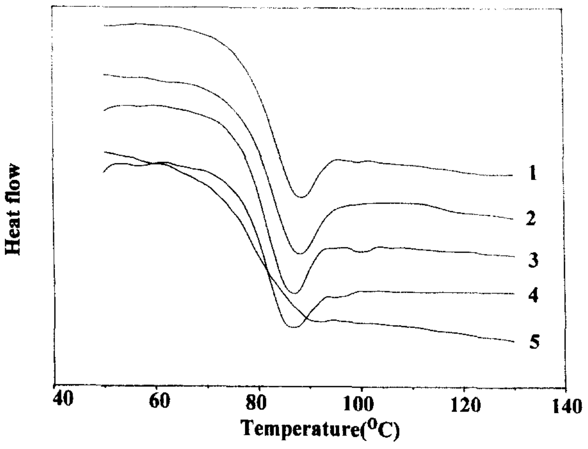

Figure 2 M.d.s.c. curves obtained at a heating rate of 4°C min^{-1} for aged PS. The ageing time was 1 h. (Curve 1: 80.5°C; curve 2: 79.0°C; curve 3: 74.0°C; curve 4: 72.0°C; curve 5: unaged sample). The data are shifted vertically for clarity

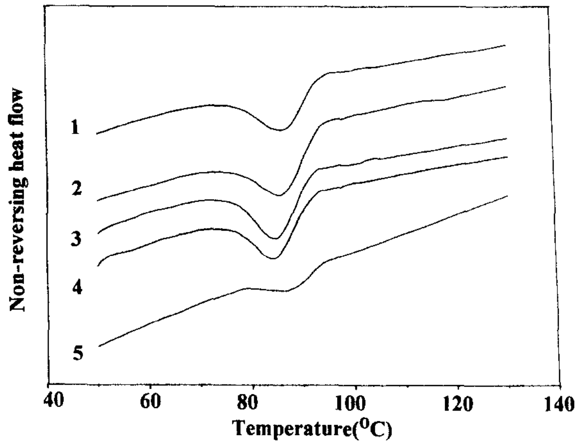

Figure 3 Non-reversing heat flow curves from the samples listed in *Figure 1*. The data are shifted vertically for clarity

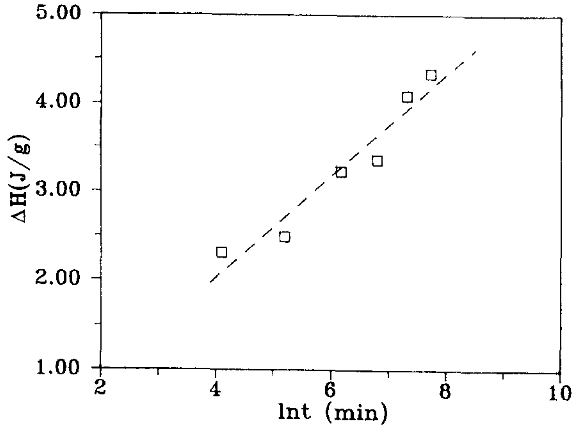

Figure 4 The variation of the experimentally determined relaxation enthalpy with ageing time. The ageing temperature was 72°C

RESULTS AND DISCUSSION

Figures 2 and *3* show the relaxation data from both the total heat flow and non-reversing heat flow signals, respectively, for samples annealed at different temperatures. The ageing time was 1 h. The results show clearly that the relaxation behaviour is different for different annealing temperatures at the same fixed annealing time. *Figure 4* shows that the relaxation enthalpy increases as a linear function of ln t. *Figure 5* shows the changes of total relaxation enthalpy with T_a. The results indicate that

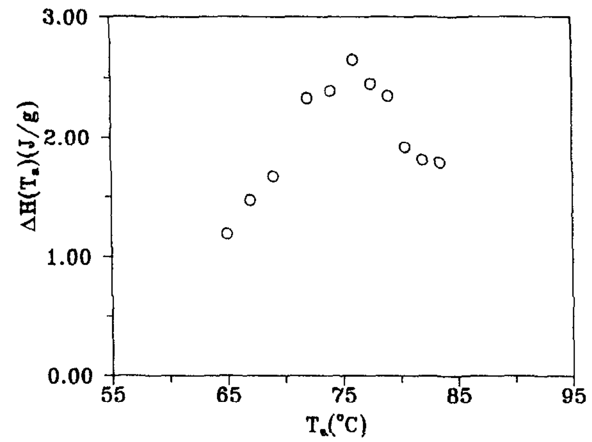

Figure 5 The variation of relaxation enthalpy with ageing temperature, T_a. The ageing time was 1 h

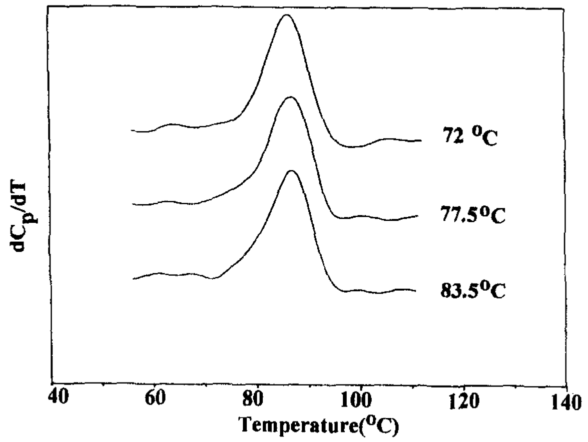

Figure 6 Variation of the differential of heat capacity of polystyrene with temperature for samples aged at different temperatures

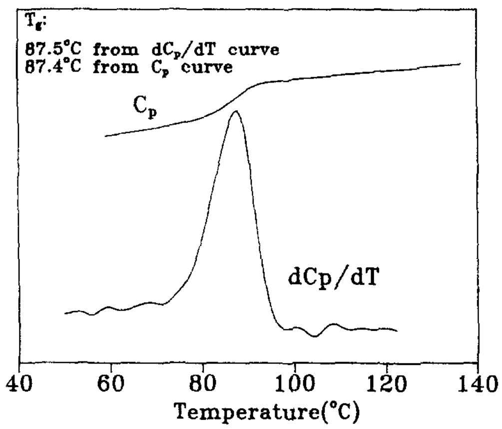

Figure 7 The relationship between the peak position of the differential of heat capacity and heat capacity with temperature

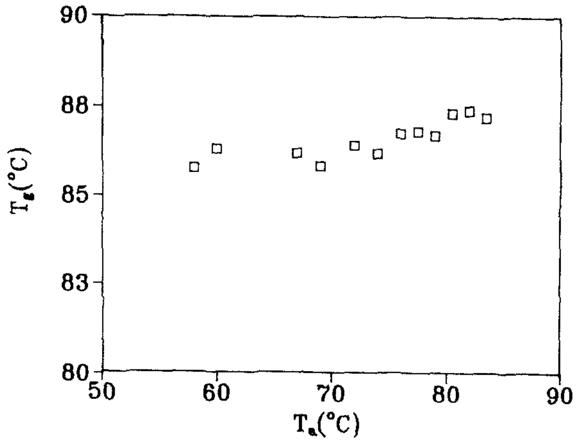

Figure 8 Variation of the glass transition with ageing temperature, T_a

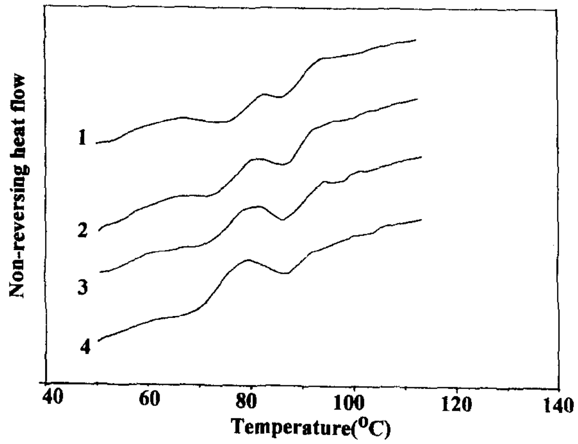

Figure 9 Non-reversing heat flow curves of aged PS at different ageing temperatures. The ageing time was 1 h (curve 1: 60.0°C; curve 2: 58.0°C; curve 3: 56.0°C; curve 4: 52.0°C)

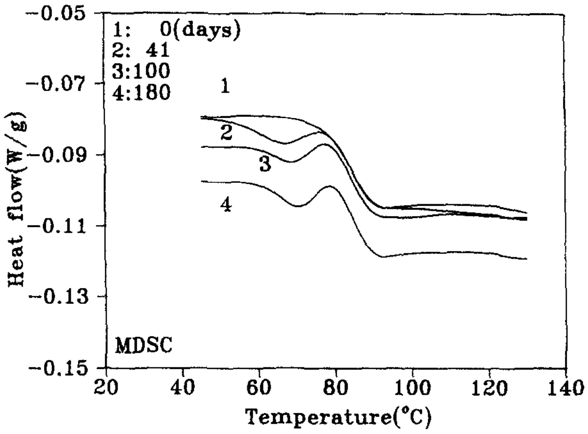

Figure 10 Variation of heat flow with temperature for samples aged at room temperature for different times

there exists a characteristic annealing temperature at which the physical ageing rate[17] reaches a maximum.

In fact, the glass transition is not a true phase transition. The different segmental motions result in a glass transition spectrum. For polymers, the heat capacity does not change suddenly at the glass transition temperature: its differential may be a continuous function of temperature.

The differential of heat capacity signal can be used to discuss the process of physical ageing. *Figure 6* shows the changes of the differential of heat capacity with temperature at different T_a values. The peak position of the differential of heat capacity with respect to temperature corresponds to the point of inflection of the heat capacity curve for the glass and the liquid states (see *Figure 7*).

At this point, the rate of change of heat capacity is at its maximum. This point can be taken as the glass

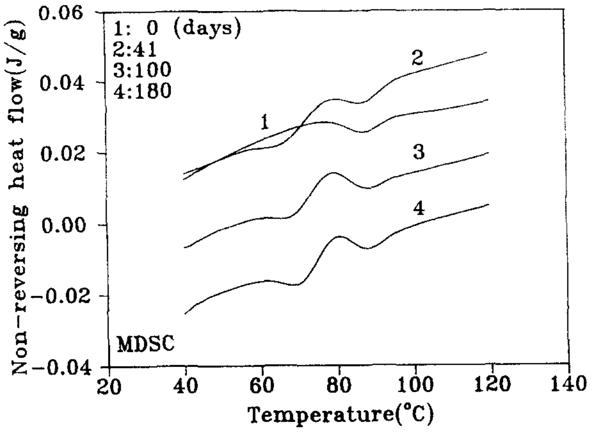

Figure 11 Variation of non-reversing heat flow with temperature for samples aged at room temperature for different times

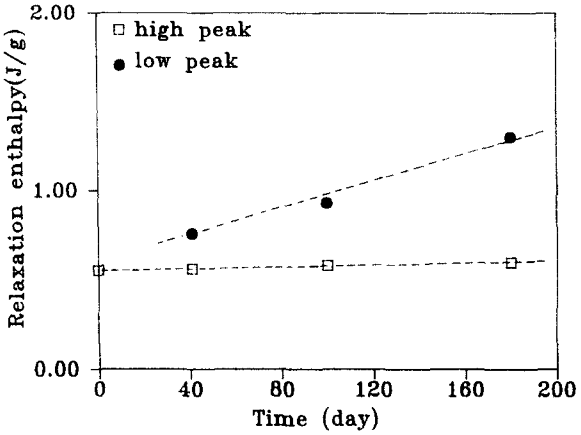

Figure 12 Variation of relaxation enthalpies with ageing time for samples aged at room temperature

transition temperature of average-length segments. Thus, the differential signal of heat capacity is clearly sensitive to the glass transition process. With increasing T_a, the peak position of the differential of heat capacity shifts slightly to higher temperatures. These small changes are shown in *Figure 8*. The glassy state will be different for different T_a values. At higher values of T_a, the rate at which the equilibrium state is reached will be faster.

When the annealing temperature was below 65°C, the non-reversing heat flow signal showed two relaxation peaks (see *Figure 9*). This two-peak behaviour has been found in other systems[18,19]. *Figures 10* and *11* show the changes of heat flow and non-reversing heat flow with temperature for samples that have been aged at room temperature for different times. The sample at zero time was used immediately it reached room temperature after being removed from the liquid nitrogen (see Experimental section). *Figure 12* shows the changes of relaxation enthalpy with ageing time for both the lower and higher temperature relaxation peaks. The variation of relaxation enthalpy of the lower relaxation peak is larger than for the higher relaxation peak, where the relaxation enthalpy changes very little.

Lindenmeyer[19] analysed thermodynamically the relaxation process of glassy polymers and suggested

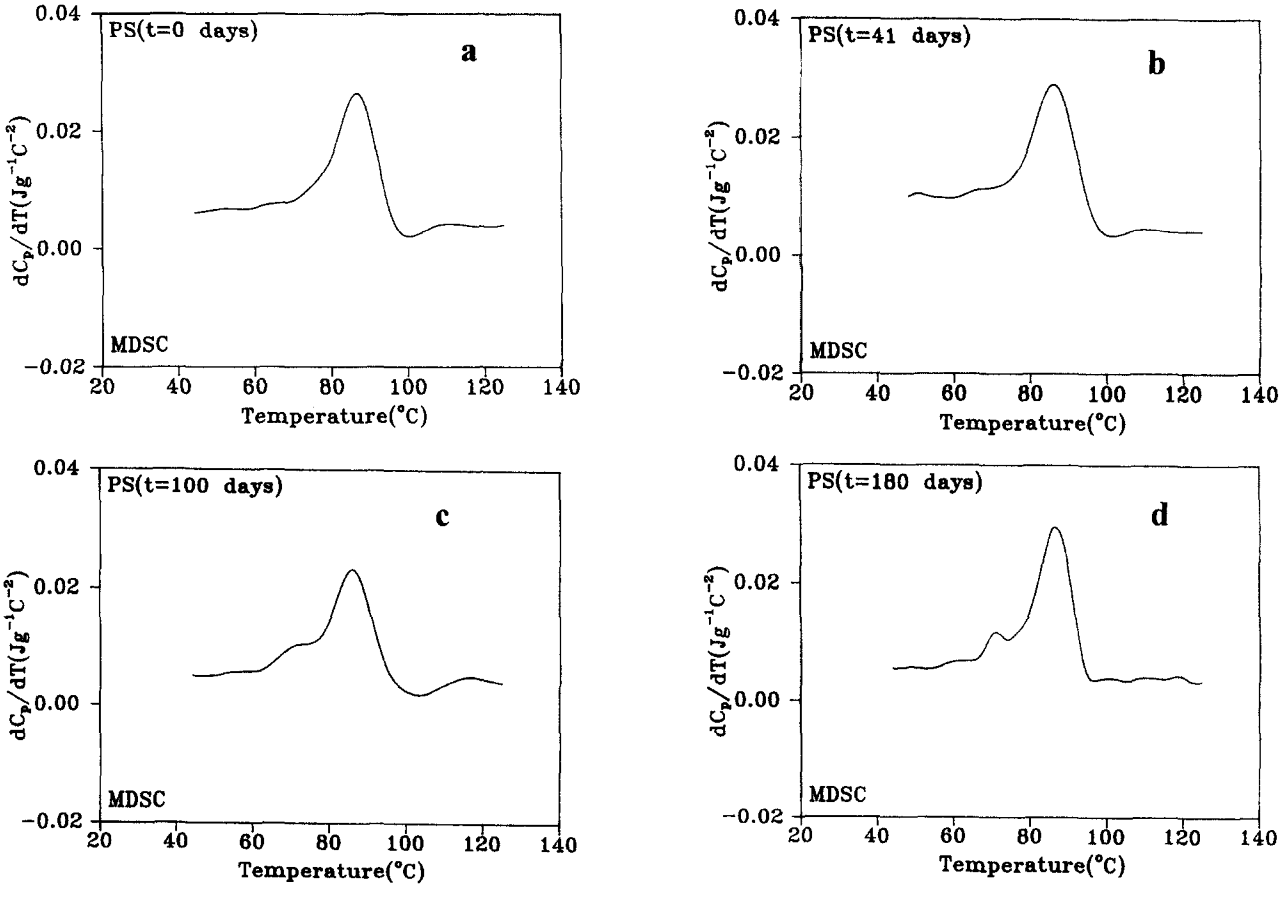

Figure 13 Differential of heat capacity with temperature at different ageing times for samples aged at room temperature

that glass formation may occur by a dissipative process that results from an inhomogeneous structure. For the PS used in this study, if the glassy state is inhomogeneous, it will change with annealing time. As the annealing time is increased, the glassy state will approach its equilibrium state. The increment of relaxation enthalpy of inhomogeneous structures may be similar. However, the difference is large.

Figures 13a–d show the changes of the differential of heat capacity with temperature at different ageing times for samples aged at room temperature. With increasing ageing time, a second relaxation peak appears in the signal. It is believed that the lower temperature relaxation peak may be the β-relaxation[20] found in the dynamic mechanical spectrum, rather than resulting from an inhomogeneous structure. If the temperature of the lower relaxation peak is defined as the β-relaxation temperature, T_β, its onset occurs approximately between 54 and 64°C (see *Figures 9* and *11*). The β-relaxation is experimentally much more difficult to locate accurately than the glass transition, as it appears as a shoulder on the relaxation curve rather than as a resolved peak. Wetton[20] concluded that it occurred in the dynamic mechanical spectrum between $T_g-100°C$ and T_g, but using m.d.s.c. and our experimental method, it can be located more accurately. Illers[21], in an early paper, assigned it to motions in parts of the polymer chains in which phenyl groups experience less steric hindrance. The amount of heat capacity arising from the β-relaxation is very small. The value is approximately $0.02\,J\,g^{-1}\,°C^{-1}$.

For PS, the energy difference between the higher energy *gauche* and lower energy *trans* states is $7.1\,kJ\,mol^{-1}$ (ref. 22). This can lead to a change in heat capacity at constant volume[20]. During physical ageing, the conformation changes are related to localized molecular rearrangements. Robertson[23] predicted that the volume available for segment relaxation for all glassy polymers is $4.32\,nm^3$. The value is small, but is believed to be the basis of the localized molecular rearrangments that occur during physical ageing.

CONCLUSIONS

The non-reversing heat flow signal from m.d.s.c. contains important information on irreversible processes. These results show that there exists a characteristic annealing temperature at which the physical ageing rate is at a maximum. At annealing temperatures below 65°C, it is believed that a secondary relaxation occurs between 54 and 64°C.

REFERENCES

1 Petrie, S. E. *J. Polym. Sci. Part A-2* 1972, **10**, 1255
2 Tant, M. R. *J. Appl. Polym. Sci.* 1981, **26**, 2813
3 Menczed, J. *J. Polym. Sci., Polym. Lett. Edn* 1981, **19**, 261
4 Kobayshi, Y., Zheng, W., Meyer, E. F., McGervey, J. D., Jamieson, A. M. and Simha, R. *Macromolecules* 1989, **22**, 2302
5 Cowie, J. M. G. and Ferguson, R. *Macromolecules* 1980, **22**, 2303 2312
6 Victo, J. G. and Torkelson, J. M. *Macromolecules* 1988, **21**, 3490
7 Hodge, I. M. *Macromolecules* 1987, **20**, 2897
8 Lindsay, G. A., Henry, R. A., Hoover, J. M., Knoesen, A. and Morlazavi, M. A. *Macromolecules* 1992, **23**, 4888
9 McGowan, C. B., Kim, D. Y. and Blumstein, R. B. *Macromolecules* 1992, **25**, 4658
10 Grenet, J., Saiter, J. M. C. and Bayard, J. *J. Thermal Anal.* 1992, **38**, 557
11 Montserrat, R. S. *Progr. Colloid Polym. Sci* 1992, **87**, 78
12 Hay, J. N. *Progr. Colloid Polym. Sci* 1992, **87**, 74
13 Hodge, I. M. *Macromolecules* 1986, **19**, 936
14 Gill, P. S., Sanerbrunn, S. R. and Reading, M. *J. Therm. Anal.* 1993, **40**, 931
15 Reading, M. *Trends Polym. Sci.* 1993, **1**, 24
16 Reading, M., Luget, A. and Wilson, R. *Thermochim. Acta* 1994, **238**, 295
17 Chaw, T. S. *Macromolecules* 1992, **25**, 440
18 Lee, S., Miyaji, H. and Geil, P. H. *J. Macromol. Sci.-Phys. (B)* 1983, **23**, 489
19 Lindenmeyer, P. H. *Polym. Eng. Sci.* 1981, **21**, 958
20 Wetton, R. E. in 'Dielectric Properties of Polymers' (Ed. F. E. Karasz), Plenum Press, New York, 1972
21 Illers, K. H. *Z. Electrochem.* 1961, **65**, 679
22 O'Reilly, J. M. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 165
23 Robertson, R. E. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 173