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Correlation of photophysical parameters with conformational structure of crystalline isotactic polystyrene and comparison with data of atactic polystyrene

B. Wandelt
Institute of Polymers, Technical University, Zwirki 36, Lodz, Poland
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Analysis of the excimer fluorescence emission decay for a wide range of wavelengths is reported for crystalline isotactic polystyrene (iPS) and for atactic polystyrene (aPS) film. A two-exponential function was used to fit the fluorescence decays of crystalline iPS. The decay time (lifetime) of the main component (88%) was estimated to be 21 ns and was also observed as one of three decay parameters of aPS. It is suggested that the 21 ns lifetime parameter corresponds to an excimer structure associated with the amorphous lamellar border region of the crystalline material.

(Keywords: excimer fluorescence; fluorescence decay; lifetime; isotactic polystyrene gel)

INTRODUCTION

Many reports concerning intramolecular excimer formation in polymer systems have been published since the development of nanosecond time-resolved transient techniques. Particularly, interpretation of the photophysical parameters resulting from mathematical analysis of the fluorescence emission decays of polymeric systems has become of major interest[1–5]. Although there should be two decay constants in a dual monomer–excimer fluorescence system, the decays of some polymers have been fitted better by a three-exponential equation[2,3].

The complexity of the photophysical processes in polymers, related to excimer formation and energy migration[6], and additionally to the inherent complexity of polymer systems like tacticity[7] and molecular weight[8], make these problems difficult to elucidate. The freely rotating chain of a polymer in dilute solution is represented by a statistical distribution of conformational structures of the chain. The resultant excimer fluorescence emission is a broad Gaussian band.

In spite of many studies, it is still not clear how these factors influence the excimer emission band and the fluorescence decay parameters and how they correspond to the polymer structure.

The aim of this paper is to study the photophysical parameters, i.e. the decay constants, of isotactic polystyrene in selected, well defined conformations of the chain to obtain some correlation with the conformational structure. It was also interesting to compare these results with the data from atactic polystyrene.

Isotactic polystyrene (iPS) in the gel state was used to obtain a selected, homogeneous conformation of the polymer chain. The iPS chain of the fresh gel is in the extended conformation, which can be easily transformed to the three-helix conformation by annealing at a temperature higher than the glass transition temperature (T_g)[9]. The three-helix conformation of the iPS chain was identified using d.s.c. analysis of the melting behaviour and microscopy studies of the corresponding supermolecular structure.

EXPERIMENTAL

Materials

Isotactic polystyrene (iPS) of molecular weight $M_w = 9.1 \times 10^5$ was obtained from Shell Chemicals (batch 439/12). It was purified in decane for 3 h under nitrogen, and then rinsed with methanol and dried in a vacuum for 10 h. This procedure removes low-molecular-weight additives. The tacticity of the polymer was investigated using ^{1}H n.m.r. analysis[10], and the structure was found to be 95% isotactic. Gel preparative grade benzyl alcohol was used as solvent and was obtained from Aldrich Chemical Company. The purity of the solvent was checked using fluorescence spectroscopy.

Atactic polystyrene (aPS) of molecular weight $M_w = 1.3 \times 10^5$ was purified by precipitation with methanol three times from a 3% solution in chloroform and dried in a vacuum. Films were cast from chloroform solution on a glass plate at room temperature and dried in a vacuum.

The gel (10% iPS with benzyl alcohol) was prepared by heating the mixture to 170°C under nitrogen (boiling temperature of solvent is 205°C). Then the solution was transferred onto precooled quartz plates and quenched to 0°C. The clear gel film 40 μm thick (after 24 h storage in a refrigerator) was annealed (under nitrogen) at 120°C for 3 h, and then the solvent was evaporated to residual 17%.

The melting behaviour was studied using a DuPont Differential Scanning Calorimeter equipped with TA 2000.

Fluorescence measurements

Benzyl alcohol was chosen as the solvent for these studies, because it produces good and clear gel films and because it is not photoactive in the region of polystyrene

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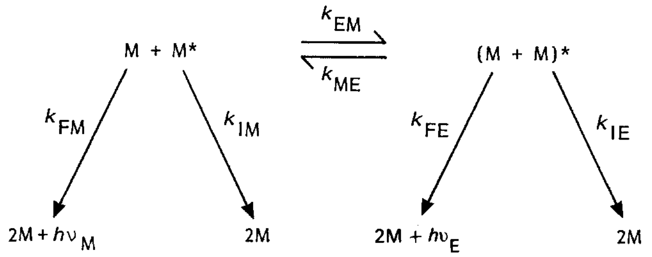

Scheme 1

excimer emission. There is spectral overlap of the polystyrene monomer emission and the benzyl alcohol emission and absorption spectra. No influence of solvent concentration in the iPS gel on the excimer emission band has been observed.

Steady-state fluorescence emission spectra were recorded using a Perkin–Elmer LS-50 spectrofluorophotometer with 2.5 nm slit width and 257 nm excitation wavelength. No changes in the emission spectrum were observed with change of the excitation wavelength. The films were mounted at 45° to the exciting beam. To separate the scattered light, a polarizer in the emission beam at the magic angle was used.

Fluorescence decay measurements were performed using a time-correlated single-photon-counting fluorometer incorporating a metal flashlamp[11]. Measurements were made on decay data obtained with 10^4 counts in the peak channel using 10 nm slit width.

Lifetimes and intensities were obtained by reconvolution analysis, which includes the rising edge of the decays, using an Edinburgh Instruments model 199N data analyser and a non-linear least-squares method with χ^2 as the criterion for goodness of fit[11]. All the fluorescence decay parameters were obtained with $\chi^2 \leqslant 1.3$.

RESULTS AND DISCUSSION

Both excited species, monomer M* and excimer (M + M)*, may undergo photophysical processes for deactivation of excited states, as is described in *Scheme 1*, where k_{FM}, k_{FE} and k_{IM}, k_{IE} are the rate constants of radiative and non-radiative decay of monomer and excimer, respectively. The rate constant k_{EM} contains all the effects of intramolecular excimer fluorescence resulting from internal rotation and energy migration. In the solid state the first process is restricted and only energy migration is possible. The rate constant k_{ME} contains all the effects of excimer fluorescence decrease resulting from dissociation of excimer (negligible in the solid) and/or energy migration).

Under transient decay conditions, the intensity of emission in the excimer region, in agreement with *Scheme 1*, can be described as follows[5]:

$$I_E(t) = [k_{FE}k_{EM}\tau_M\tau_E M_0/(\tau_E - \tau_M)] \times [\exp(-t/\tau_E) - \exp(-t/\tau_M)] \qquad (1)$$

where

$$\tau_M = (k_{FM} + k_{IM} + k_{EM})^{-1}$$

$$\tau_E = (k_{FE} + k_{IE})^{-1}$$

The second exponential factor is negligible in the long-lived excimer emission condition. So, only excimer emission is responsible for the intensity of fluorescence decay in the excimer region.

Figure 1 presents steady-state fluorescence spectra of atactic polystyrene film and crystalline isotactic polystyrene prepared as described earlier.

The fluorescence decays at different wavelengths of the excimer spectrum are shown in *Figure 2* for crystalline isotactic polystyrene and in *Figure 3* for atactic polystyrene film. The results of the analysis of the fluorescence decays are gathered in *Table 1* for iPS and in *Table 2* for aPS film.

The recorded decay curves of emission intensity $I(t)$ have been synthesized by means of a reconvolution function of the type:

$$I(t) = \sum_n B_n \exp(-t/\tau_n) \qquad \text{with } n = 1, 2, 3, \ldots \qquad (2)$$

where τ_n and B_n are the lifetime parameter and pre-exponential function of the nth component. The B_n values in *Tables 1* and *2* are the relative contributions of the components to the fluorescence at the emission wavelength. The fluorescence decays of crystalline iPS shown in *Figure 2* have been fitted by a two-exponential function. The results of the analysis are reported in *Table 1*.

The presence of some short-lived component in the lifetime data of crystalline isotactic polystyrene corresponding to monomer emission is due to the overlap between monomer and excimer emission bands. The long-lived component of 21 ns lifetime is in the majority (more than 80%) and the lifetime parameter does not change with wavelength. This suggests that there is only one excimeric component. The lifetime parameter increases negligibly (in comparison with deviation) at higher emission wavelength and/or decreases at lower wavelength. A negligible amount of a different excimer

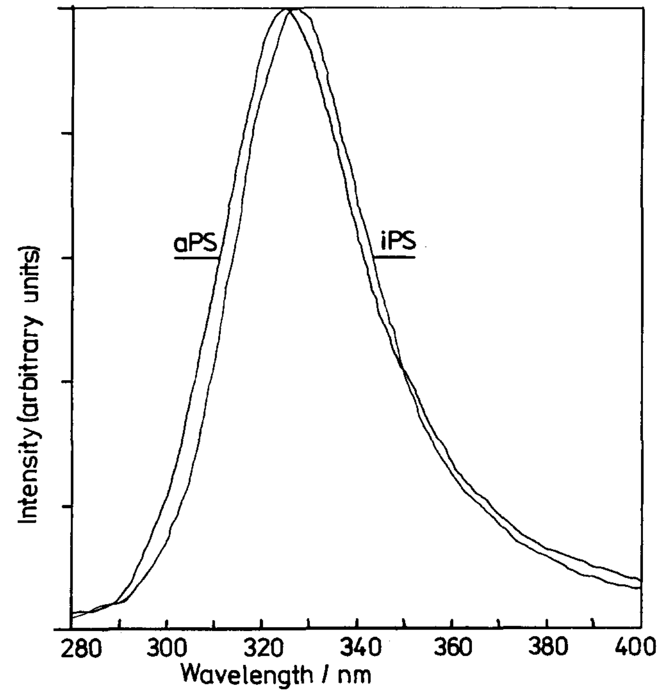

Figure 1 Steady-state fluorescence emission spectra of crystalline isotactic polystyrene and of atactic polystyrene film (obtained from chloroform at room temperature)

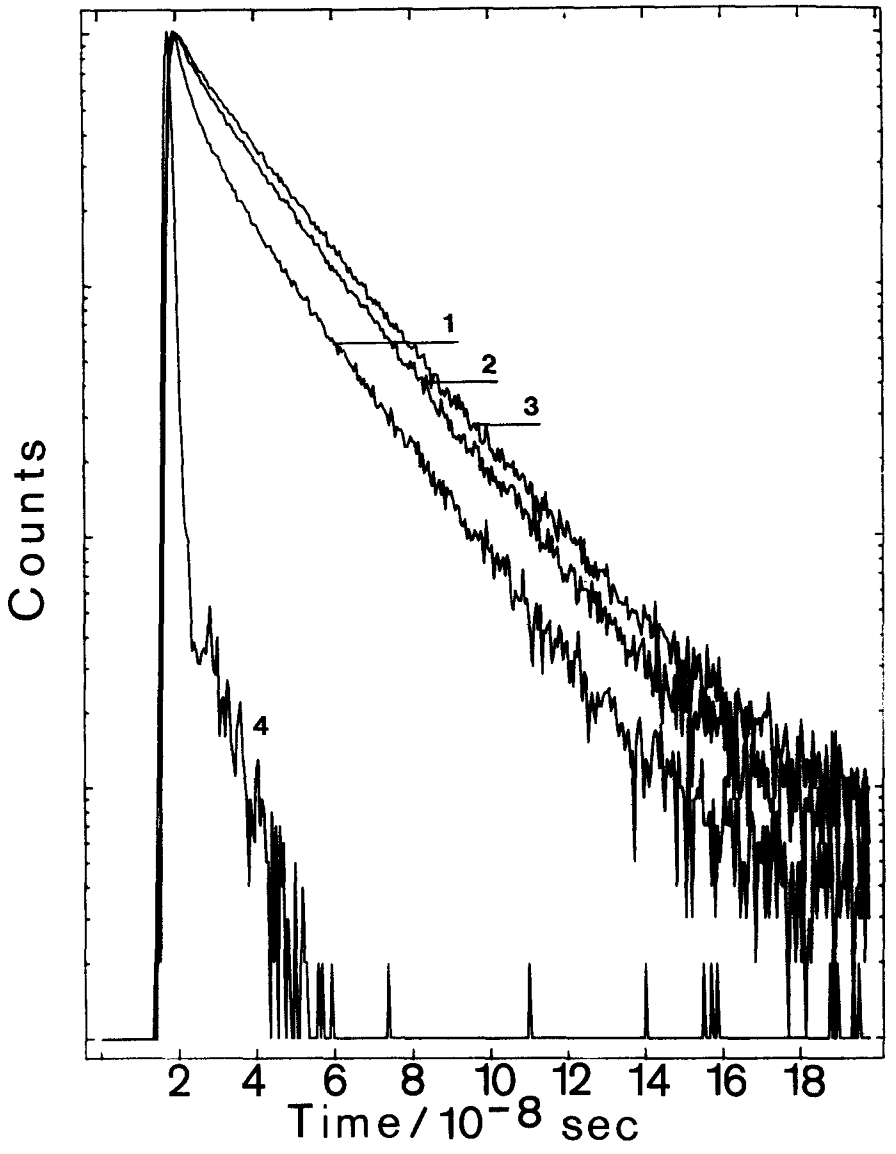

Figure 2 Fluorescence emission decays of crystalline isotactic polystyrene at (1) 310 nm, (2) 330 nm and (3) 350 nm and (4) the excitation pulse

component is possible. No dependence on the residual solvent concentration was observed.

The d.s.c. thermograms of the crystalline iPS and the fresh gel are shown in *Figure 4*. There is one melting peak in the thermogram of crystalline iPS with melting temperature 222°C. It corresponds to the melting temperature of the three-helix crystalline form of iPS, reported recently in the literature[9,12,13]. The fresh gel thermogram in *Figure 4* (curve 2) presents only a solvent evaporation peak at 191°C. The spherulitic morphological forms of iPS observed in the crystalline material shown in *Figure 5* are similar to recently reported[14] spherulites due to the three-helix conformation of the iPS chain. The value for the heat of fusion $\Delta H = 80.4$ J g^{-1} (ref. 12) was used to determine the percentage crystallinity. The value of crystallinity obtained from the endotherm of crystalline iPS in *Figure 4* (68%) corresponds to the recently reported value[13] (63%) of crystallinity for solution-grown crystals.

Basically, in the three-helix conformation of the iPS chain, the phenyls do not form excimer states. The distance between parallel phenyls in this conformation, reported by Sundararajan *et al.*[14,15], was 6.65 Å. This distance is too large for excimer formation because the distance between the associated phenyls in the excimer state is 3.0–3.5 Å. In this situation excimers can be formed only outside the crystalline regions, e.g. in the region of lamellar borders, where deformation of the helical form of the polystyrene chain is most probable. The excitation energy would migrate along the helix (built into the lamellae) to the lamellar border, where pre-excimer sites are much more probable.

The effectiveness of energy migration would be responsible for the strong increase of the excimer fluorescence emission of the crystalline iPS in comparison with amorphous polymer, reported by David *et al.*[7], and the observed 10 times increase in comparison with fresh gel during these studies. If we take the 68% crystalline material (with lamellae 50 Å thick[13]) and the 88% component in *Table 1*, each of the chromophores involved in the lamellae is responsible for excimer emission in comparison with 20% of chromophores in the amorphous part. That would be possible with high effectiveness of the energy migration process.

The fluorescence decay curves of atactic polystyrene were fitted by a three-exponential function. The photo-

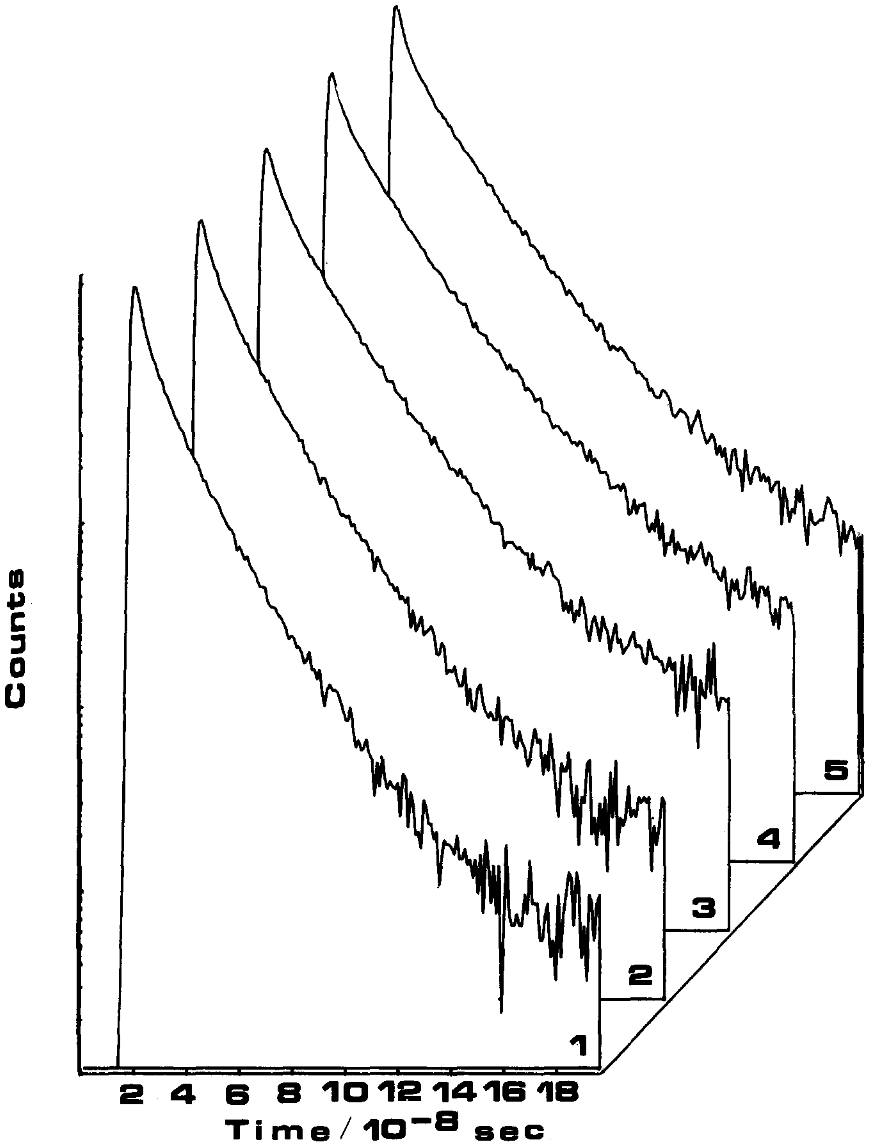

Figure 3 Fluorescence emission decays of atactic polystyrene film at (1) 310 nm, (2) 320 nm, (3) 330 nm, (4) 340 nm and (5) 350 nm

Table 1 Fluorescence decay data for crystalline isotactic polystyrene

λ_{EM} (nm)	τ_1 (ns)	τ_2 (ns)	B_1 (%)	B_2 (%)	χ^2
310	3.7±0.4	19.6±0.2	27.2	72.8	1.27
320	4.3±0.3	20.5±0.3	16.7	83.3	1.16
330	5.2±0.3	21.0±0.3	11.9	88.1	0.99
340	5.1±0.9	21.3±0.4	9.9	90.0	1.11
350	4.7±0.6	21.6±0.2	6.9	93.1	1.09

physical parameters are recorded in *Table 2*. A noticeable amount of the short-lived component corresponding to monomer emission in the whole region of excimer emission, similarly to iPS, is observed. The noticeable emission of monomer in solid polystyrene may be due to an energy migration process equal to excimer dissociation, which is absent in the solid, with rate constant k_{ME} in *Scheme 1*.

Considerable changes of the excimer lifetime with change of the emission wavelength suggest more than one excimer structure. The component with lifetime parameter of 21 ns is observed at emission wavelength 320 nm (49%). A noticeable amount of the long-lived component, very close to the other, increases the lifetime parameters in the process of mathematical analysis of the fluorescence decays obtained at higher emission wavelength. The steady-state fluorescence emission spectrum of aPS film from chloroform in *Figure 1* is broader than that of iPS and there is a noticeable red side tail. Comparison of the decay parameters of excimer emission from crystalline iPS and aPS suggests that the excimer emission spectrum of aPS results from many different excimer structures. Red-shifted excimer emission has been observed in the fluorescence emission spectrum of iPS gel after annealing at temperatures lower than T_g of the gel[16]. That would correspond to emission of deformed excimer structures.

CONCLUSIONS

For crystalline iPS, a two-exponential analysis was found to be satisfactory, with the lifetime parameter 21 ns of excimer (88% component).

Table 2 Fluorescence decay data for atactic polystyrene film

λ_{EM} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	B_1 (%)	B_2 (%)	B_3 (%)	χ^2
310	1.6 ± 0.4	7.4 ± 0.6	19.4 ± 0.4	15.4	41.5	43.1	1.18
320	1.8 ± 0.6	8.5 ± 0.9	21.3 ± 0.4	12.2	39.1	48.7	1.22
330	2.6 ± 0.3	13.4 ± 0.9	29.2 ± 0.9	14.2	54.5	31.3	1.27
340	2.1 ± 0.3	13.8 ± 0.9	30.0 ± 0.9	12.7	51.8	35.5	1.19
350	2.1 ± 0.3	15.0 ± 1.2	32.8 ± 1.2	16.2	53.0	30.8	1.23

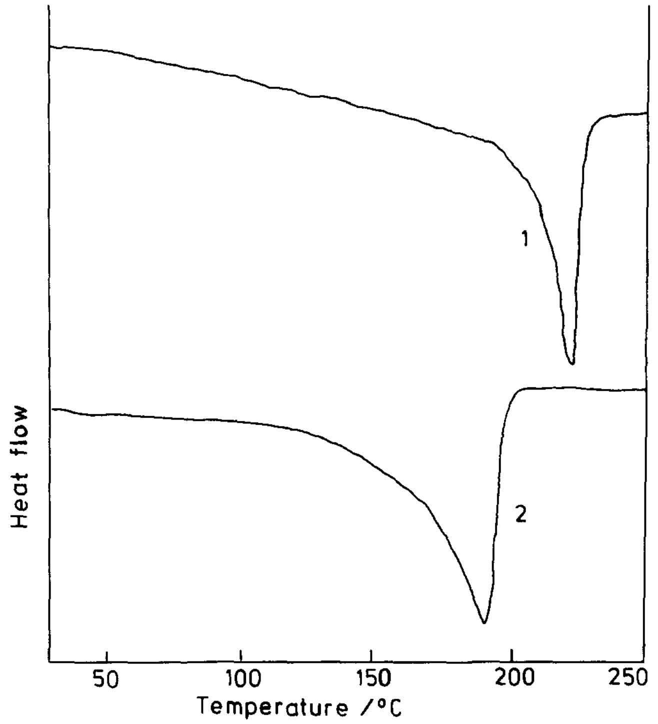

Figure 4 D.s.c. thermograms for (1) crystalline iPS and (2) fresh gel of iPS with benzyl alcohol

For atactic PS, a three-exponential function was found to be necessary to fit the fluorescence decays.

The fluorescence decay parameters of aPS change with wavelength. This suggests that more than one excimer species is involved.

It is suggested that the excimers in crystalline iPS are associated with the amorphous lamellar border region.

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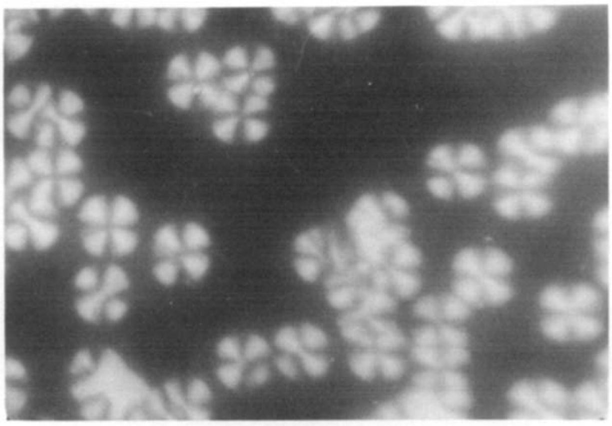

Figure 5 Spherulitic structures observed in crystalline iPS

REFERENCES

1 Phillips, D., Roberts, A. J. and Soutar, I. *Eur. Polym. J.* 1981, **17**, 101
2 Soutar, I., Phillips, D., Roberts, A. J. and Rumbles, G. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 1759
3 Phillips, D., Roberts, A. J. and Soutar, I. *Macromolecules* 1983, **16**, 1593
4 Holden, D. A., Wang, P. Y. K. and Guillet, J. E. *Macromolecules* 1980, **13**, 295
5 Itagaki, H., Horie, K. and Mita, I. *Macromolecules* 1983, **16**, 1395
6 MacCallum, J. R. *Polymer* 1982, **23**, 175
7 David, C., Putman de Lavareille, N. and Geuskens, G. *Eur. Polym. J.* 1974, **10**, 617
8 Itagaki, H., Guillet, J. E., Sienicki, K. and Winnik, M. A. *J. Polym. Sci., Polym. Lett. Edn.* 1989, **27**, 21
9 Atkins, E. D. T., Hill, M. J., Jarvis, D. A., Keller, A., Sarhene, E. and Shapiro, J. S. *Colloid Polym. Sci.* 1984, **262**, 22
10 Shepherd, L., Chen, T. K. and Harwood, H. J. *Polym. Bull.* 1979, **1**, 445
11 Birch, D. J. S. and Imhof, R. E. *Rev. Sci. Instrum.* 1981, **52**, 1206
12 Dedeurwaerder, R. and Oth, J. F. M. *J. Chim. Phys.* 1959, **56**, 940
13 Guenet, J. M., Sadler, D. M. and Spells, S. J. *Polymer* 1990, **31**, 195
14 Tyrer, N. J. and Sundararajan, P. R. *Macromolecules* 1985, **18**, 511
15 Tyrer, N. J., Bluhm, T. L. and Sundararajan, P. R. *Macromolecules* 1982, **15**, 286
16 Wandelt, B., Birch, D. J. S., Imhof, R. E. and Pethrick, R. A. *Macromolecules* in press