Synthesis and characterization of T_g for pyrene end-labelled polystyrene having no ester linkages

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A series of pyrene end-labelled polystyrene (PS) samples having molecular weights ranging from 2000 to 40 000 have been synthesized anionically. Complete characterization data are provided. The end-labelling reaction is performed by coupling the living polystyryl anion with 1-bromobutylpyrene, with coupling efficiencies ranging from 72 to 90%. The resulting pyrene end-labelled PS has no ester linkage in the backbone, a common structure resulting from alternative end-labelling reactions proceeding via terminal hydroxyl units. This leads to a potential enhancement in thermal and hydrolytic stability; in fact, the samples have the same thermal stability as unlabelled PS. The glass transition temperatures (T_g) of our samples vary linearly with $\bar{M}_n^{-1}$, consistent with the Fox–Flory equation. However, the T_g values of the labelled PS samples are higher than the unlabelled ones with the difference widening as $\bar{M}_n$ decreases. This difference is explained by a decrease of chain end mobility and hence of free volume caused by bulky end groups.

(Keywords: polystyrene; glass transition; pyrene label; end effect)

INTRODUCTION

A powerful approach that has been used to study the dynamics and equilibrium properties of macromolecules is the fluorescence probe method[1]. This spectroscopic technique, which encompasses a relatively large ensemble of photostationary or transient measurement methods, has been used extensively in biochemistry[2,3], and relatively recently has become popular in polymer science[4–6]. The major advantage of this method is its sensitivity[1,2]. Three classes of fluorescent materials are possible: (1) the polymer could contain a fluorescent chromophore either in the backbone or pendant to the chain in every repeat unit; (2) the polymer could lack inherent fluorescence in the excitation range of interest but could have a small number of fluorescent chromophores incorporated into the chain by a copolymerization or modification procedure; (3) an extrinsic fluorescent dopant could be physically dispersed in the polymer matrix.

The latter two methods are of particular interest since a large number of fluorescent probes with different spectroscopic properties are known[7,8]. Ideally, however, the probe molecule should be covalently attached to the macromolecule in such a manner that the behaviour of the probe will directly reflect some dynamic or structural property of the macromolecule. A critical concern of all fluorescence probe experiments in which aromatic chromophores have been incorporated in otherwise non-fluorescent polymers is the possibility that the presence of the chromophore may significantly perturb the aspect of polymer physics under consideration. We explore several elements of this in this paper.

Previous work in the Stanford laboratory emphasized the first class of materials with extensive examination of poly(2-vinylnaphthalene) and polystyrene. These studies emphasized the application of intermolecular and intramolecular excimer fluorescence to interrogate the thermodynamics and kinetics of phase separation in blends of amorphous polymers[9–11]. Recently we have turned attention towards pyrene covalently attached to the polymer via chemical means as a tracer. Pyrene has many desirable properties, including high fluorescence quantum efficiency (0.4 in benzene solution), long fluorescence lifetime (~200 ns), ability to form stable excimers and thermal stability[8].

In the present work, we describe the synthesis of a series of pyrene end-labelled polystyrenes (PS). One of the primary motivations for making these fluorescent end-labelled materials is to explore the use of transient fluorescence depolarization to elucidate polymer chain equilibrium configurations[12]. In addition to having high labelling efficiencies, the samples are required to be thermally stable because they must be annealed above their glass transition temperature (T_g) to allow the chains to attain their equilibrium configurations. The results of this study will be reported separately[13].

Pyrene end-labelled PS was first synthesized and studied by Winnik[14]. His method of synthesis involved two steps. The first step was the anionic polymerization of styrene by a difunctional initiator, end capping the living polystyryl anions with ethylene oxide followed by termination with methanol. The second step was an esterification reaction between the hydroxyl end-capped

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PS and the acid chloride derivative of 1-pyrenebutyric acid.

Although a very high labelling efficiency (higher than 95%) can be achieved with this method[14], the major disadvantage is the presence of an ester linkage in the labelled product. Since PS is non-polar, the presence of a polar functional group in the probe may be undesirable in some cases. Moreover, the ester linkage is susceptible to hydrolytic cleavage, especially in the presence of water[15], thus rendering the labelled polymer less stable. Finally, it is prudent experimentally to avoid the use of ethylene oxide because it is highly toxic and explosive[16]. Based on these considerations alternative methods were attempted to obtain pyrene end-labelled PS.

EXPERIMENTAL

Synthesis of pyrene end-labelled PS

Polymerization of styrene was done anionically under highly purified argon in an apparatus recently designed for this purpose. The complete description of the apparatus for anionic polymerization under argon is given in the PhD thesis of Tang[17]. The procedures of the synthesis are briefly described below.

Solvent. Reagent grade tetrahydrofuran (THF) (Baker) was dried by Na/benzophenone under argon. It was refluxed until a deep purple colour was obtained indicating dryness. Then the solvent was collected under argon.

α-Methylstyrene and styrene purification. Monomer grade α-methylstyrene and styrene were purchased from Aldrich. They were distilled over CaH_2 twice. Then they were further purified by distillation from dibutylmagnesium.

Preparation of initiator (tetramer of α-methylstyryl potassium). About 2.5 g of potassium metal was put into 350 ml of dry THF. Purified α-methylstyrene (7 ml) was then added dropwise at room temperature. The deep red solution was stirred under argon overnight. This gave a concentration of carbanions of about 0.1 M; the exact concentration was determined by titration with acetanilide immediately before use.

Preparation of end-capping agent. 1-Bromobutylpyrene (BBPy) was synthesized by Molecular Probes Inc. It was done by reducing the more readily available 1-pyrenebutyric acid to alcohol and then bromination was carried out by using phosphorus tribromide and hydrogen bromide in CCl_4. The crude product was purified by column chromatography followed by recrystallization from methanol, yielding an extremely pure white product. The compound was dissolved in THF in an addition funnel.

Anionic polymerization of styrene. The reaction was done in a 1 litre multineck round-bottom flask under argon. A sufficient amount of the initiator solution was added to 500 ml THF in the reactor to maintain a pink colour while the solvent was cooled down to −70°C by a dry ice/isopropanol bath. This 'zero point' technique ensured the complete deactivation of impurities in the solvent that could potentially cause premature termination of the living chains. When a stable temperature was achieved, a known amount of initiator was added all at once. Then a known amount of styrene was added dropwise. (At the end of the styrene polymerization reaction, the solution should still be red.)

End-capping reaction. To achieve high labelling efficiency, a large excess (3–13 times the stoichiometric amount) of 1-bromobutylpyrene THF solution was added quickly at the end of the polymerization reaction. The dry ice/isopropanol bath was removed and replaced with a room temperature water bath. The red colour of the living polystyryl anion solution faded slowly and after about 1.5 h the reaction was complete. (The higher the BBPy/carbanion ratio, the shorter is the time for completion.)

Isolation and purification. The polymer products were isolated by precipitation in methanol. The samples were further purified by dissolving in THF and precipitating in methanol three more times. Since 1-bromobutylpyrene is soluble in methanol, this repeated precipitation method is effective in removing all the free dye molecules from the sample.

Characterization

The molecular weight and molecular weight distribution of the labelled PS samples were determined by a Waters 150C gel permeation chromatography (g.p.c.) system with five ultragel columns (ASI Co.) in THF. The solvent flow rate was 1 ml min^{-1} and the columns were calibrated with 17 PS standards purchased from Polymer Laboratories, having molecular weights ranging from 480 to 8×10^6. The system was equipped with a single refractometer detector. A Waters 244 GPC system (an HPLC system equipped with Styragel columns) with dual detectors (refractometer and u.v. absorbance at 313 nm) was used to ensure that the samples were free of small molecular weight dye impurities. The T_g and thermal degradation temperature (T_d) were determined by a DuPont DSC/TGA system. The heating rate for differential scanning calorimetry (d.s.c.) was 10°C min^{-1} and for thermal gravimetric analysis (t.g.a.) was 5°C min^{-1}. For the d.s.c. measurement, the sample was first heated past the T_g to about 200°C, cooled back down to room temperature and then the T_g measurement was performed. The temperature at the midpoint of the glass transition was taken as the T_g. The labelling efficiency was determined spectrophotometrically by a Beckman DU-8 spectrophotometer. Fluorescence measurements of the labelled samples and the model compound were made on an SLM spectrofluorometer.

RESULTS

The most obvious alternative to the Winnik approach to synthesize pyrene end-labelled PS is to use chloromethylpyrene or bromomethylpyrene to deactivate the living polystyryl anion, analogous to the use of 9-(chloromethyl) anthracene, which has been done very successfully[19]. However, we found that these compounds are too unstable, and difficult to purify. As a result, this precludes a high labelling efficiency. We have also tried pyrenecarboxaldehyde but found that it is polymerizable under our reaction conditions (THF, −70°C, potassium as counter ion). Evidence for polymerization is that the 130×10^3 molecular weight product shows a sizeable

Table 1 Characterization data of pyrene doubly end-labelled polystyrene

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_g (°C)[a]	T_d (°C)[b]	BBPy added Carbanions	% Tagging[c]
PS-1	2270	3190	1.405	81	~360	3.0	90
PS-2	3570	4768	1.335	91	~360	3.0	88
PS-3	6022	6894	1.145	100	~360	3.3	72
PS-4	21 898	24 928	1.138	104	~360	6.5	77
PS-5	38 580	40 743	1.056	104	~360	13.0	79

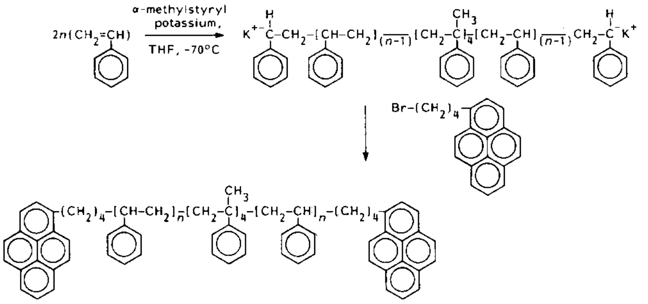
[a] Measured by d.s.c., heating rate = 10°C min^{-1}

[b] Measured by t.g.a., heating rate = 5°C min^{-1}. (No weight loss lower than 360°C, 50% weight loss at 440°C for all five samples)

[c] The $\bar{M}_n$ values were used to calculate these values. The percentage tagging is with respect to each polymer chain end

excimer peak in THF. Since the cyclization rate is very low for such a high molecular weight polystyrene sample, the excimer peak could not be caused by intramolecular end-to-end cyclization. We conclude that more than one pyrene molecule must have been attached to the chain ends. This is not surprising, as aldehydes are indeed known to be polymerizable[20].

A successful method was finally obtained by using 1-bromobutylpyrene as a coupling agent. The rationale is that more methylene units between the bromine atom and pyrene should make the compound more stable. Indeed, we found that 1-bromobutylpyrene is a very stable compound that can be easily purified to a very high purity level (99+ %). The four methylene units also separate the pyrene from the PS chain to minimize the possibility that excimer formation between the two chain ends would be inhibited by steric interactions with phenyl groups in the PS chain[14]. This is an advantage when the samples are studied in solution and the pyrene excimer formation is used to determine the cyclization rate of PS[14]. The polymerization and pyrene-labelling reactions of PS are shown below:



The initiator is a dianion of α-methylstyrene tetramer[21], so that the polystyrene has four α-methylstyrene units at the centre of the chain. These few α-methylstyrene units are not expected to affect the PS chain significantly as their structure is quite similar to that of PS. Moreover, they become increasingly unimportant as the molecular weight of the polymer increases.

1-Pentylpyrene was purchased from Molecular Probes Inc. and was used as the model compound. Beer's law was obeyed up to a concentration of 2.5×10^{-5} M in THF. The molar extinction coefficient of the model compound was found to be 4.40×10^{4} M^{-1} cm^{-1} in THF. It was found that after three precipitations in methanol the sample chromatograms showed no absorption peak for the free dye. The absorption and fluorescence spectra of the labelled sample and the model compound were identical. The absorption peaks are located at 313, 327 and 343 nm and the major fluorescence peaks are at 376, 396 and 416 nm. The excimer peak appears at about 480 nm.

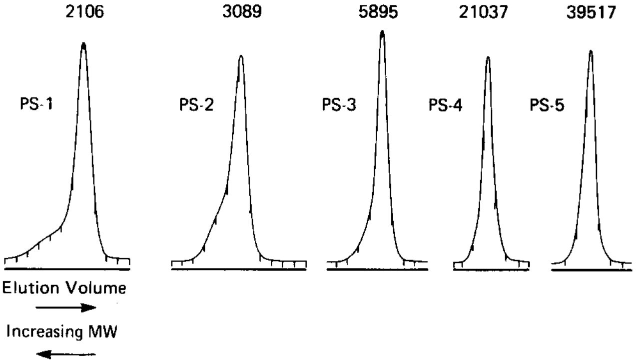


Figure 1 Gel permeation chromatograms of pyrene end-labelled polystyrene. The molecular weights at the peaks are also given

The complete characterization data of the five samples synthesized are given in *Table 1*. The g.p.c. chromatograms with the peak molecular weights are shown in *Figure 1*.

DISCUSSION

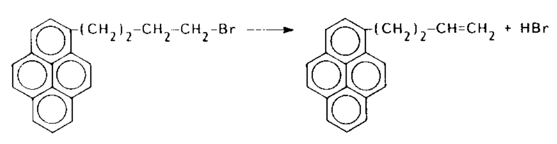
The end-labelling procedure

In *Table 1* the ratio of moles of BBPy added at the end of the polymerization reaction to the moles of carbanions are also given. Since the polymerization is done anionically, the molecular weight distribution is expected to be narrow. Flory[22] has shown that a Poisson distribution of molecular weight is expected for a termination-less polymerization reaction, and the polydispersity is inversely related to the degree of polymerization (DP):

$$\frac{\bar{M}_w}{\bar{M}_n}=1+\frac{1}{\mathrm{DP}} \tag{1}$$

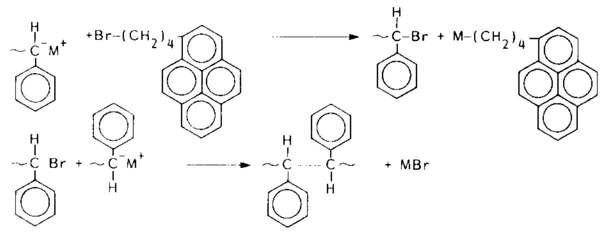
Our results in *Table 1* qualitatively agree with this prediction, although the actual molecular weight distribution is wider than the ideal value. This is not surprising since these reactions were done under purified argon and not with the much more laborious and difficult break-seal high vacuum technique[23]. Since the argon technique is more flexible and practical, it is encouraging to see that moderately high molecular weight samples (e.g. PS-4 and PS-5) with low polydispersity may be obtained.

Since BBPy is relatively unreactive, two side reactions were thought to be most likely to compete with the desirable nucleophilic substitution. The first is dehydrohalogenation of the bromoalkyl:



The HBr thus generated can terminate the carbanions prematurely, yielding only low molecular weight product.

The second possible side reaction is metal–halogen exchange:



This reaction can lead to coupling of the growing chain and, if present, will result in bimodal molecular weight distribution. The metal–halogen exchange has been shown to be important when lithium is the counter ion[24]. We specifically chose potassium as the counter ion to avoid this problem. The use of the polar solvent THF makes the carbanion more reactive since THF can solvate the anion, thus making the carbanion–potassium bond more ionic in nature. Therefore, nucleophilic substitution should be favoured. The relatively high labelling efficiencies and narrow molecular weight distributions of PS-4 and PS-5 demonstrate the success of the dye-labelling reaction. Since the absorption and fluorescence spectra for the labelled PS and the model compound are identical, no other side reactions seem to be present under our reaction conditions.

For the lower molecular weight samples (PS-1 and PS-2), the higher molecular weight shoulders are not likely to be caused by side reactions with the dye because in the PS-4 and PS-5 samples a much larger dye to carbanion ratio was used, yet the samples are quite monodisperse. It is possible that a small amount of O_2 may have leaked into the reactor during the dye-labelling reaction because a longer time was needed to complete the reaction in the case of PS-1 and PS-2 having low dye/carbanion ratios. It is well-known that O_2 can couple the living chains, giving higher molecular weight shoulders and broader molecular weight distributions[25]. The less than complete labelling efficiency is most likely caused by the trace amount of impurity in the THF solvent containing BBPy, since it was not treated with the initiator by the zero point technique as was done for the polymerization solvent. We believe that adding the BBPy in the powder form by using a vacuum tight powder addition funnel to react with the anionic chain ends may result in a higher labelling efficiency.

The glass transition of the labelled polystyrene

The availability of this series of pyrene end-labelled PS sample provides an excellent opportunity for examining two issues related to T_g. The first is the applicability of Couchman's theory of the glass transition of polymers to this type of end-labelled polymer, and the second is the influence of the bulky pyrene end groups on T_g values.

Couchman[26,27] recently developed a general thermodynamic theory for the molecular weight dependence of the T_g of polymers based on purely entropic considerations. He treated a polymer as a mixture of chain ends and the infinite molecular weight polymer. The general equation is

$$\ln T_g = \frac{(n-m)\Delta C_p^o \ln T_g^o + m\Delta C_p^m \ln T_g^m}{(n-m)\Delta C_p^o + m\Delta C_p^m} \qquad (2)$$

where ΔC_p is the heat capacity increment and the superscripts o and m denote the high molecular weight limit and the m-mer, respectively. If equation (2) is rearranged and the approximation $\ln(1+x) \approx x$ is used, then it can be shown that for $\Delta C_p^m/\Delta C_p^o = 1$, the well-known Fox–Flory equation[28,29] results:

$$T_g = T_g^o - (m/n)(T_g^o - T_g^m) \qquad (3)$$

Equation (2) has been found to fit the experimental data of a number of homopolymers very well[26,27]. However, since the theory treats the chain ends and the polymer as separate entities, it is of interest to determine whether equation (2) still holds for chain ends that are chemically different from the polymer constituent. The pyrene end-labelled PS provides such an opportunity.

Rudin and Burgin[30] compared the T_g values of anionic and thermally initiated PS and found no significant difference. Since the anionic PS has a butyl end group but the thermally initiated PS does not, they concluded that the end groups have little influence on the T_g of PS and that the free volume and main glass transition are not closely linked. However, the n-butyl end group is comparatively small and its effect on the T_g of PS may not be large enough to reveal a measurable difference. It is therefore of interest to examine this issue again using our pyrene end-labelled PS.

In *Table 1* the T_g values of the five samples are given. The T_g and $\bar{M}_n^{-1}$ of the samples are found to obey a linear relationship, as shown in *Figure 2*. The T_g of a series of standards ($\bar{M}_w/\bar{M}_n < 1.1$) purchased from Polymer Laboratories are measured with exactly the same instrument settings and procedure as for the labelled PS. These data are also shown in *Figure 2*, in which T_g results on PS from other workers[28,30,31] are included for comparison. We have plotted our data in the format of the Fox–Flory equation (equation (2)) to show the difference between the labelled and unlabelled PS. For our samples, the $\Delta C_p^m/\Delta C_p^o$ ratios are very close to 1 (we found ΔC_p^m of PS-1 was 0.400 of PS-1 was 0.400 and of PS-5 was 0.393 $J(g°C)^{-1}$) and for a relatively narrow range of molecular weight, equation (3) is a very good approximation of equation (2)[26,27]. Our data clearly show that equation (3) is obeyed within experimental error.

In *Figure 2* the T_g of the labelled PS is higher than the unlabelled PS standard. This difference widens as the molecular weight of the samples decreases. This is not due to the broader molecular weight distributions of our end-labelled samples because it has been shown for PS that a broader molecular weight distribution lowers the T_g[32]. The T_g values of the pyrene-labelled samples are consistently higher than the PS standards, approaching

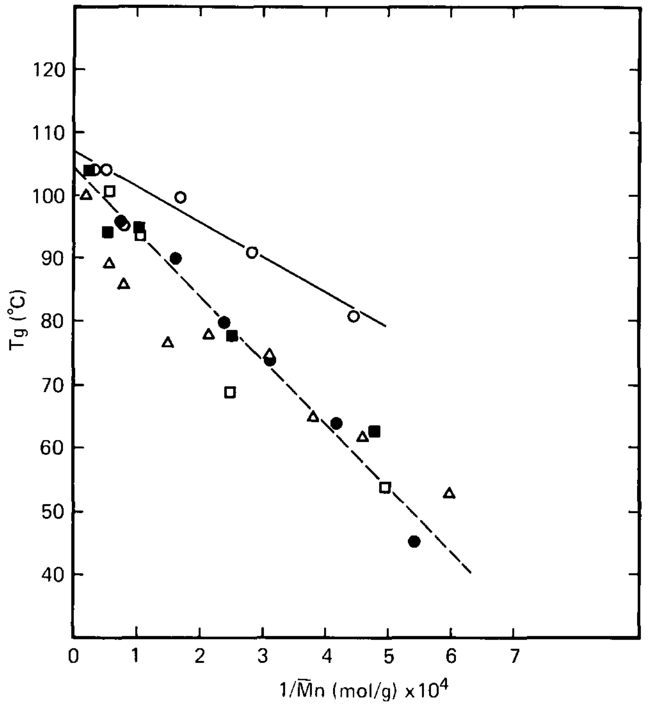


Figure 2 Glass transition temperature of labelled and unlabelled polystyrene. ○, Pyrene end-labelled PS; ●, PS standard; △, data of Fox and Flory[28]; ■, data of Rudin and Burgin[30] at 10°C min^{-1} heating rate; □, data of Blanchard *et al.*[31] at 10°C min^{-1} heating rate; ———, linear regression fit of the T_g data for the pyrene-labelled PS; – – –, linear regression fit of the T_g data for the unlabelled PS standard

values as much as 15–20°C higher for molecular weights lower than about 4000.

The influence of the four central α-methylstyrene units must be assessed for PS-1 and PS-2 because they assume higher proportions as the molecular weight of the total polymer decreases. The relationship between T_g and $\bar{M}_n^{-1}$ of poly(α-methylstyrene) (PMS) was found to be[33]:

$$T_g(\mathrm{K}) = 453 - 3.1 \times 10^5/\bar{M}_n \qquad (4)$$

From this equation, the T_g of PMS of molecular weight 3000 is 77°C, which is comparable to the PS standard of the same molecular weight (about 70°C, see *Figure 2*), but the T_g drops much more rapidly than PS as the molecular weight becomes lower. For molecular weight of 2000, T_g of PMS is only 25°C, while that of PS is about 60°C (see *Figure 2*). It is therefore not possible that the four α-methylstyrene units (FW = 473) could have pushed the T_g up for PS-1 and PS-2 by more than 15°C compared with the corresponding unlabelled PS.

We conclude that it is the bulky pyrene end groups that are the cause of these higher T_g values. In particular, it seems quite clear that the presence of the pyrene groups will lead to a drastic reduction in chain end mobility. As a result, the T_g would be expected to increase relative to small end groups. This is consistent with the generally accepted free volume theory of the glass transition in polymers[34]. It is important to note that the pyrene groups apparently did not become detached from the polymer chain as a result of high temperature because the sample was first heated up to 200°C, cooled down to room temperature and then the T_g was measured. The fact that the measured T_g was higher than the unlabelled PS shows that the end groups were intact. Otherwise, the T_g would be lower than the unlabelled PS as a result of a plasticization effect.

The T_d of our samples are listed also in *Table 1*. The T_d values are seen to be quite insensitive to molecular weight, in accordance with literature findings on unlabelled PS[35]. We have also measured the T_d of unlabelled PS under the same conditions and found that it is almost exactly the same as the labelled PS. Therefore, we conclude that the presence of the pyrene end groups has no effect on the thermal stability of PS.

CONCLUSION

The use of 1-bromobutylpyrene as a coupling agent at the end of anionic polymerization of PS results in pyrene end-labelled PS that has only non-polar linkages in the labelled chain. If the reaction conditions are suitably chosen, high labelling efficiency can be obtained. The T_g and molecular weight of these samples obeyed the Fox–Flory equation. These pyrene end-labelled PS have higher T_g than the unlabelled materials as a result of the decrease of chain end mobility caused by the bulky end groups. These samples are also shown to be very stable thermally.

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REFERENCES

1 Winnik, M. A. in 'Cyclic Polymers' (Ed. J. Semlyen) Elsevier, London, 1986, Ch. 9, 285
2 Lakowicz, J. R. 'Principles of Fluorescence Spectroscopy', Plenum Press, New York, 1983
3 Chen, R. F. and Edelhoch, H. 'Biochemical Fluorescence', Vols. I and II, Marcel Dekker, New York, 1975
4 Phillips, D. (Ed.) 'Polymer Photophysics', Chapman and Hall, 1985
5 Morawetz, H. *Science* 1979, **203**, 405
6 Guillet, J. E. 'Polymer Photophysics and Photochemistry', Cambridge University Press, New York, 1985
7 Haugland, R. R. 'Handbook of Fluorescent Probes and Research Chemicals', Product Catalog of Molecular Probes Inc.
8 Birks, J. B. 'Photophysics of Aromatic Molecules', Wiley–Interscience, New York, 1970
9 Semerak, S. N. and Frank, C. W. *Adv. Polym. Sci.* 1983, **54**, 31
10 Semerak, S. N. and Frank, C. W. *Macromolecules* 1981, **14**, 443
11 Gelles, R. and Frank, C. W. *Macromolecules* 1983, **16**, 1448
12 Fredrickson, G. H., Andersen, H. C. and Frank, C. W. *J. Chem. Phys.* 1983, **79** (7), 3572
13 Jeng, Y. H., Peterson, K. A., Zimmt, M., Fayer, M. D., Tang, W. T., Frank, C. W. and Hadziioannou, G. in preparation
14 Winnik, M. A., Redpath, A. E. C., Paton, K. and Danhelka, J. *Polymer* 1984, **25**, 91
15 Morrison, R. T. and Boyd, R. N. 'Organic Chemistry', 4th Edn., Allyn and Bacon Inc., 1983, Ch. 20
16 Hess, L. G. and Tilton, V. V. *Ind. Eng. Chem.* 1950, **42**, 1251
17 Tang, W. T. PhD Thesis, March 1987, Stanford University, California, 94305
18 Hadjichristidis, N. and Fetters, L. J. *Macromolecules* 1980, **13** (1), 191
19 Ushiki, H., Horie, K., Okamoto, A. and Mita, I. *Polym. J.* 1979, **11** (9), 691
20 Vogl, O. and Bryant, W. M. D. *J. Polym. Sci. A* 1964, **2**, 4633

21 Lee, C. L., Smid, J. and Szwarc, M. *J. Phys. Chem.* 1962, **66**, 904
22 Flory, P. J. *J. Am. Chem. Soc.* 1943, **65**, 372
23 Morton, M. and Fetters, L. J. *Rubber Chem. Technol.* 1975, **48**, 359
24 Szwarc, M. 'Carbanions, Living Polymers and Electron Transfer Processes', John Wiley and Sons Inc., New York, 1968
25 Mansson, P. *J. Polym. Sci.* 1980, **18**, 1945
26 Couchman, P. R. *J. Appl. Phys.* 1979, **50** (10), 6043
27 Couchman, P. R. *Polym. Eng. Sci.* 1981, **21** (7), 377
28 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
29 Fox, T. G. and Flory, P. J. *J. Polym. Sci.* 1954, **14**, 315
30 Rudin, A. and Burgin, D. *Polymer* 1975, **16**, 291
31 Blanchard, L., Hesse, J. and Malhotra, S. *Can. J. Chem.* 1974, **52**, 3170
32 Glandt, C. A., Toh, H. K. and Gillham, J. K. *J. Appl. Polym. Sci.* 1976, **20**, 1277
33 Malhotra, S. L., Minh, L. Y. and Blanchard, L. P. *J. Macromol. Sci. Chem.* 1978, **12** (1), 167
34 Hiemenz, P. C. 'Polymer Chemistry', Marcel Dekker, New York, 1984
35 Dickens, B. in 'Degradation and Stabilization of Polymers' (Ed. H. H. G. Jellinek) Elsevier, Amsterdam, 1983, Ch. 11