

Fourier transform infra-red spectroscopic studies of gelation and crystallization of polystyrene/carbon disulfide solutions*

Xu-Ming Xie†, Akihiko Tanioka and Keizo Miyasaka

Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo Institute of Technology, Ookayama, Meguro-Ku, Tokyo 152, Japan

(Received 23 March 1992; revised 20 July 1992)

Dried gel and solution-cast films of atactic (at-) and isotactic (iso-)polystyrene/carbon disulfide (PS/CS₂) systems were investigated by Fourier transform infra-red spectroscopy (FTi.r.) and the relation between gelation and crystallization was studied. Iso-PS gel films dried at gelation temperature were less turbid than homogeneous solution-cast films made at room temperature. No difference was found in the i.r. spectrum of dried gel and solution-cast films of at-PS/CS₂. However, the i.r. spectrum of iso-PS dried gel film was different from that of solution-cast film. Comparison of these spectra indicated that spectral changes occurred at the bands near 1200, 560, 1085–1052 and 907–922 cm⁻¹. There were two bands at 909 and 922 cm⁻¹ for solution-cast films, while for dried gel films there was only one which shifted from 912 to 921 cm⁻¹ with increasing polymer concentration (10 to 40 g l⁻¹) of the original gel. I.r. spectra of dried gel films of low concentration gels were like those of solution and quenched iso-PS samples. The intensity of the crystalline band at 983 cm⁻¹ decreased with decreasing iso-PS gel concentration. This means that gel containing no crystals should be formed at very low polymer concentration; this is consistent with our previous conclusion that gelation of the PS/CS₂ system is independent of crystallization.

(Keywords: atactic; isotactic; polystyrene; carbon disulfide; gel; gelation; crystallization; FTi.r.; spectra)

INTRODUCTION

It has recently been shown^{1,2} that non-crystallizable atactic polystyrene (at-PS) can form thermoreversible gels from solutions of different solvents. This is evidence that some polymers form gels independently of crystallization; it was previously believed that only crystalline and stereoregular polymers form gels and that the gelation was induced by a particular mode of crystallization.

The relation between gelation and crystallization is very complex. Keller and co-workers^{3–6} studied the gelation of isotactic polystyrene (iso-PS)/decalin solutions, and found that a new crystal type formed in the gels with a different structure from the usual 3₁ helix. This suggests that junction points of the gel network are formed by the new crystal with a fringed micellar morphology. Atkins *et al.*⁷ and Painter *et al.*⁸ also carried out Fourier transform infra-red spectroscopy (FTi.r.) on iso-PS gels, and found that some new bands appear at 1061, 1069, 916 and 894 cm⁻¹. However, recent research^{9,10} on iso-PS/decalin gels has demonstrated some different results.

In our previous paper¹¹, it was found that iso-PS/carbon disulfide (CS₂) gels show two endothermal d.s.c. peaks while at-PS/CS₂ gels show one peak. The low-temperature peak was considered due to the melting of gel junction points and the high-temperature peak to the melting of crystals which were embedded in the gel

but did not work as the junction point. There was no significant difference between the gelation mechanisms of iso- and at-PS/CS₂ systems to suggest that gelation of iso-PS/CS₂ solutions occurred independently of crystallization. In this work, to elucidate the relation between gelation and crystallization of iso-PS/CS₂ solutions, dried gel films of at- and iso-PS were studied by FTi.r., and the spectra were compared with those of iso-PS/decalin gels.

EXPERIMENTAL

Materials and sample preparation

Commercially available at-PS (Wako Pure Chemical Industries, $M_w = 210\,000$, $M_w/M_n = 1.7$), at-PS (Nishio Kogyo, $M_w = 600\,000$, $M_w/M_n = 1.05$) and iso-PS (Polymer Laboratories, $M_w = 600\,000$, $M_w/M_n = 1.9$) were used as received. CS₂ of high purity grade was used after being dried over molecular sieves.

An at-PS/CS₂ solution sealed in a glass tube was kept at room temperature for 1 day. The solution was then poured into a shallow glass plate and quenched in a freezer at -25°C for 1 week to form gel film. The solvent was allowed to evaporate from the gel for 1 month, while the gel was kept at the gelation temperature. Finally the gel was dried further under vacuum of ~1.33 Pa at room temperature, until no solvent was detected by i.r. spectra.

Iso-PS dried gel films were prepared at -60°C in the same way as at-PS. However, since iso-PS was less soluble in CS₂ than at-PS, the sealed tubes were heated in boiled water to make solutions. It should be noted that the iso-PS/CS₂ homogeneous solution could be

* Presented in part at the 38th Meeting of the Society of Polymer Science, Japan, October 1989

† Present address: Department of Chemical Engineering, Tsinghua University, Beijing, P.R. China

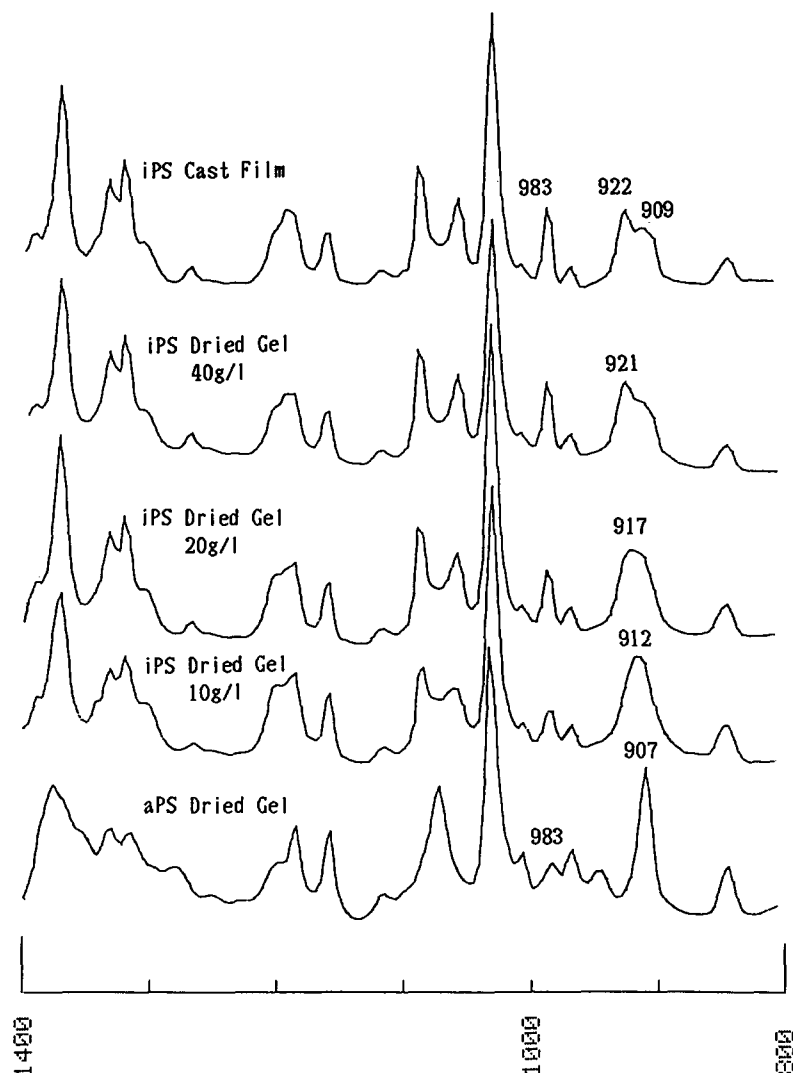


Figure 1 Comparison of the infra-red spectrum of at-PS dried gel, iso-PS gel dried from various polymer concentrations and solution-cast iso-PS film

obtained only at concentrations less than 40 g l⁻¹ in this case.

Iso-PS and at-PS cast films were prepared from the CS₂ solutions at room temperature, at which no gelation occurred at all.

FTi.r. measurement

I.r. spectra of samples were recorded on a Jasco model FT-IR3 spectrometer. Two hundred co-added interferograms at a resolution of 2 cm⁻¹ were used to obtain each spectrum. Composition absorption peaks were separated into each component peak with a Lorentzian shape, using the following equation:

$$D(\nu) = \sum_{i=1}^n \frac{a_i b_i^2}{b_i^2 + (\bar{\nu} - \nu_{oi})^2}$$

where $D(\nu)$ is absorbance at a frequency ν , b_i is band half width, a_i is peak height, $\bar{\nu}$ and ν_{oi} are wave number and band wave number, respectively.

RESULTS AND DISCUSSION

There was no detectable difference between FTi.r. spectra of at-PS dried gel and solution-cast films. FTi.r. spectra of iso-PS dried gels showed some changes with polymer concentration of the original gel, and were different from

the spectrum of the solution-cast film; this is illustrated in *Figure 1* for an at-PS dried gel, iso-PS gel films dried from various polymer concentrations and solution-cast iso-PS film. Some bands of interest are indicated, for example, the 907 cm⁻¹ band for at-PS dried gel. In the case of iso-PS dried gel films, this band tends to shift to the higher frequency side and increases in width with increasing polymer concentration of the original solution. In the case of iso-PS solution-cast film, it splits into two at 922 and 909 cm⁻¹, which have been assigned as the crystalline bands. It should be noted that the crystallinity of the dried gel films depends on the polymer concentration of solutions from which gels were formed. Crystallization takes place only during drying due to solvent evaporation at the gelation temperature. The spectra of iso-PS dried gel films of low polymer concentrations are very similar to those of the solutions and quenched iso-PS bulk reported by Kobayashi *et al.*¹². This means that crystallization occurs only with difficulty during drying of gel films with low polymer concentrations; this is partly related to the fact that the gelation of iso-PS/CS₂ is independent of crystallization, as already shown¹¹. The shifts of this band are shown in *Figure 2* as a function of polymer concentration in the wet gel state. The band at 912 cm⁻¹, for 10 g l⁻¹ dried iso-PS gel film, shifts close to 922 cm⁻¹ (assigned to out-of-plane C-H bending vibration related to crystalliza-

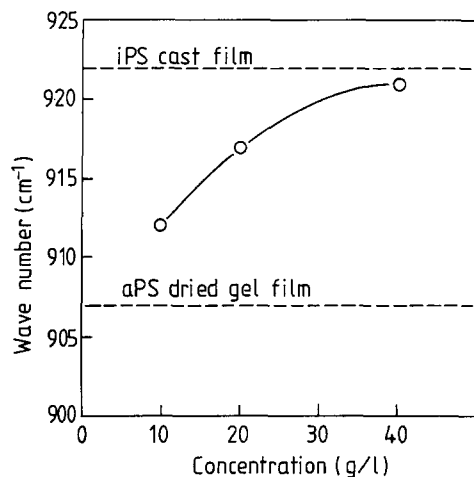


Figure 2 Plot of the shifts of the band at 912 cm^{-1} for dried 10 g l^{-1} iso-PS gel against the polymer concentration of the original solution

Table 1 Frequencies of observed bands of polystyrene between 1400 and 490 cm^{-1}

	at-PS dried gel	iso-PS dried gel (10 g l^{-1})	iso-PS dried gel (20 g l^{-1})	iso-PS dried gel (40 g l^{-1})	iso-PS cast film
1		1384	1384	1385	1386
2	1373				
3		1367	1366	1365	1365
4	1328	1327	1327	1327	1327
5	1313	1315	1315	1315	1315
6		1302	1302	1302	1302
7	1277				
8		1262	1262	1262	1262
9	1249	1251	1252	1252	1250
10	1225	1226	1227	1228	1227
11	1194	1195			
12				1186	1187
13	1182	1182	1182	1182	
14	1155	1155	1155	1155	1155
15	1112	1111	1112	1112	1112
16		1081	1082	1083	1083
17	1069				
18		1055	1054	1053	1053
19	1029	1026	1026	1026	1026
20	1004	1003	1003	1004	1004
21	980	982	983	983	983
22	965	965	965	965	965
23	943				
24	907	912	917	921	922
25					909
26					869
27	842	843	842	842	841
28					826
29		821			
30				818	
31					809
32	757	763	763	762	763
33	700	700	700	700	700
34					673
35	621	621	621	620	620
36		587	586	586	586
37	540	562	563	564	566
38		519	517	517	517
39			499	498	499

tion) with increasing polymer concentration of gels¹²⁻¹⁵. Figure 2 implies that gel containing no crystals is formed at very low polymer concentration, where the 912 cm^{-1} band of 10 g l^{-1} dried iso-PS gel film would shift close to the 907 cm^{-1} band of the atactic sample.

Painter *et al.*⁸ also found a new band at 916 cm^{-1} in

the spectrum of iso-PS/decalin gel. In this work, the bands at 912 , 917 and 921 cm^{-1} for iso-PS dried gel films should be assigned to the bands mixed with crystalline band 922 cm^{-1} and amorphous band 907 cm^{-1} .

The frequencies of the observed bands of PS between 1400 and 490 cm^{-1} are shown in Table 1.

It is well known that the band at 983 cm^{-1} is a crystalline band, and the intensity can be used as a measure of the crystallinity¹⁶. The intensity of the 983 cm^{-1} band for iso-PS dried gel films is plotted against the polymer concentration of the original gel in Figure 3. The crystallinity of iso-PS dried gel films decreases with decreasing polymer concentration in the wet gel state. This result also suggests that crystallinity becomes very low at a polymer concentration where gel containing no crystals should be formed. It is consistent with the result of Figure 2.

In the case of iso-PS/decalin gels, Atkins *et al.*⁷ and Painter *et al.*⁸ found that i.r. spectral changes are observed in bands near 1300 , 1200 and 1085 – 1050 cm^{-1} . In particular, the bands of gel appear at 1061 , 1069 , 916 and 894 cm^{-1} . These new bands were considered to relate to the new crystal which forms gel and is different from the usual 3_1 helix crystal. However, in the case of dried iso-PS/CS₂ gel films, the bands at 1182 and 1195 cm^{-1} of the dried gel of 10 g l^{-1} is similar to the bands at 1182 and 1194 cm^{-1} of at-PS samples. When the polymer concentration of the original gel increases, a band appears at 1187 cm^{-1} , between the 1182 and 1194 cm^{-1} bands which have been assigned to be associated with the intramolecular interaction in a helical chain having a three-fold screw axis¹⁷. The 1187 cm^{-1} band becomes stronger in the iso-PS solution-cast film, as shown in Figure 4. This indicates that the crystallization of the dried gel films occurs after gelation and depends only on the polymer concentration of the original gels, and hints that gelation is not always induced directly by crystallization.

No new band is found between 1085 and 1050 cm^{-1} in the spectra of iso-PS/CS₂ dried gel films, as illustrated in Figure 5. However, there is a doublet at 1081 and 1055 cm^{-1} in the dried 10 g l^{-1} gel, which appears as a singlet at 1069 cm^{-1} in the atactic sample and expands with increasing polymer concentration of the original gel. Finally, bands appear at 1083 and 1053 cm^{-1} in solution-cast films, as shown in Figure 5. The separation

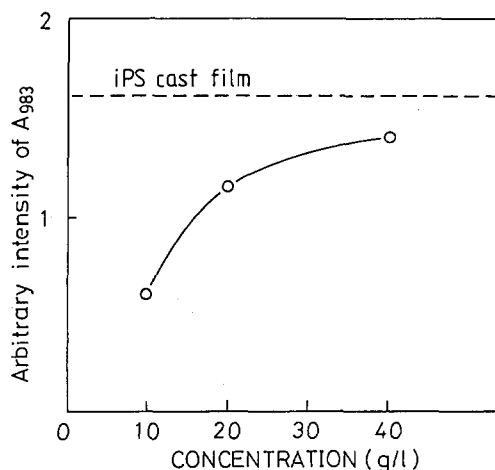


Figure 3 Plot of the intensity of 983 cm^{-1} band for iso-PS dried gel films against the polymer concentration of the original solution

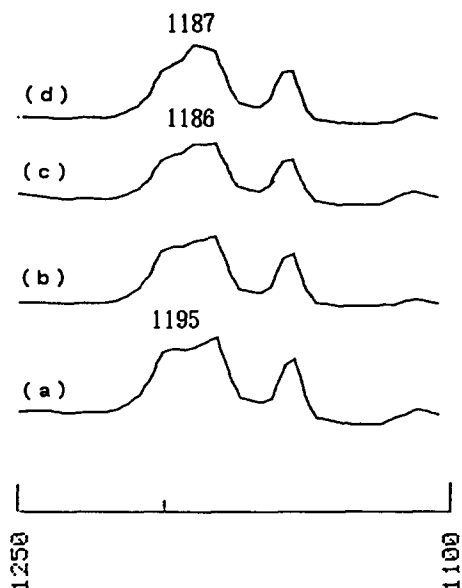


Figure 4 Infra-red spectrum (1250–1100 cm⁻¹) of iso-PS. (a) 10 g l⁻¹ dried gel film; (b) 20 g l⁻¹ dried gel film; (c) 40 g l⁻¹ dried gel film; (d) solution-cast film

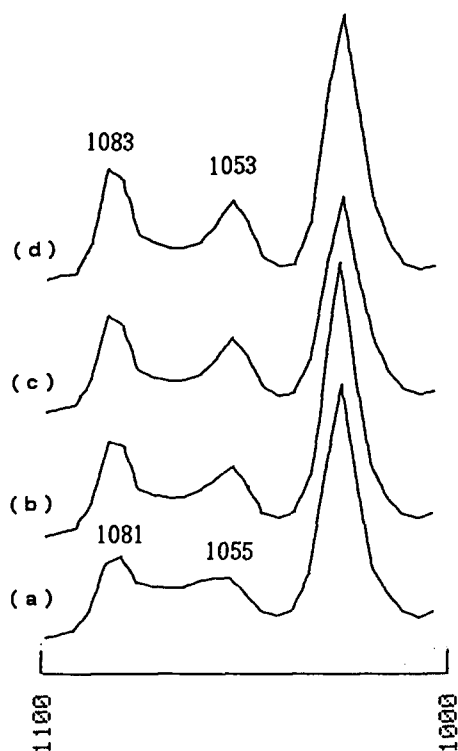


Figure 5 Infra-red spectrum (1100–1000 cm⁻¹) of iso-PS. (a) 10 g l⁻¹ dried gel film; (b) 20 g l⁻¹ dried gel film; (c) 40 g l⁻¹ dried gel film; (d) solution-cast film

of 1083 and 1053 cm⁻¹ bands was assigned to be associated with the difference in the sequence length of the conformation in the amorphous regions, which has a crystallization dependence¹⁸.

In order to investigate the conformational changes in at-PS and iso-PS gels, the 500–650 cm⁻¹ region, which is sensitive to conformation, was analysed. As shown in *Figure 6*, in this region, the spectrum of at-PS has three bands¹⁹ at 623, 556 and 540 cm⁻¹. The 540 cm⁻¹ band was assigned to relate to a sequence of four or more *trans*

carbon-carbon bonds, and the 556 cm⁻¹ band is due to the vibration of the benzene rings in the neighbourhood of *gauche* units. The 623 cm⁻¹ band is insensitive to conformation²⁰. The comparison of *trans* band (540 cm⁻¹) and *gauche* band (556 cm⁻¹) between the at-PS dried gel and solution-cast films is shown in *Table 2*. No detectable difference was found in the intensity of the *trans* conformation between the dried gel and solution-cast films.

The spectra of iso-PS dried gel and solution-cast film in the range 450–650 cm⁻¹ are shown in *Figure 7*. The 562 cm⁻¹ band of 10 g l⁻¹ dried gel shifts gradually towards the higher frequencies with increasing concentration of the original gel, and appears at 566 cm⁻¹ in the solution-cast film. According to Xu *et al.*²¹, the 562 cm⁻¹ band is related to the long helical *trans-gauche* conformational structure not yet involved in crystallites. When crystallization occurs, the band shifts to 566 cm⁻¹ to appear as a sharp absorption band. If this assignment is adopted in this case, the dried 10 g l⁻¹ gel films should contain almost no crystals, and the 563 and 564 cm⁻¹ bands for 20 g l⁻¹ and 40 g l⁻¹ dried gel films, respectively, may be assigned to a mixed band of 562 and 566 cm⁻¹, i.e. the 566 cm⁻¹ band is stronger with increasing crystallinity that is dependent only on polymer concentration. This result is also consistent with the conclusion that the gelation of the PS/CS₂ system is independent of crystallization. On the other hand, the 586 and 499 cm⁻¹ bands of solution-cast samples were assigned as crystalline (regularity) bands by Painter and Koenig¹⁸, whereas only one band appears at 587 cm⁻¹ in the spectrum of dried 10 g l⁻¹ gel.

SUMMARY

The spectral changes of dried iso-PS gel films are predominantly related to the crystallinity. The differences

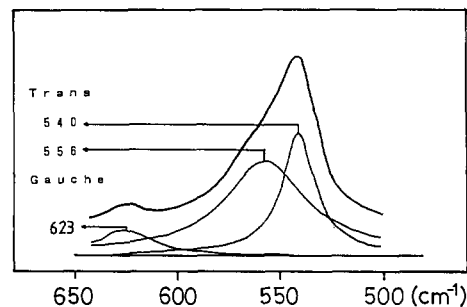


Figure 6 Curve analysis of the 500–650 cm⁻¹ range of the at-PS infra-red spectrum

Table 2 Comparison of *trans* band (540 cm⁻¹) and *gauche* band (556 cm⁻¹) for at-PS

	Percentage of peak height,	Percentage of peak area,
	$\frac{A_{540}}{A_{540} + A_{556}}$	$\frac{S_{540}}{S_{540} + S_{556}}$
Dried gel 1	57.80	33.90
2	58.32	33.46
3	57.50	33.80
Cast film 1	57.18	33.23
2	56.17	33.07
3	58.96	34.15

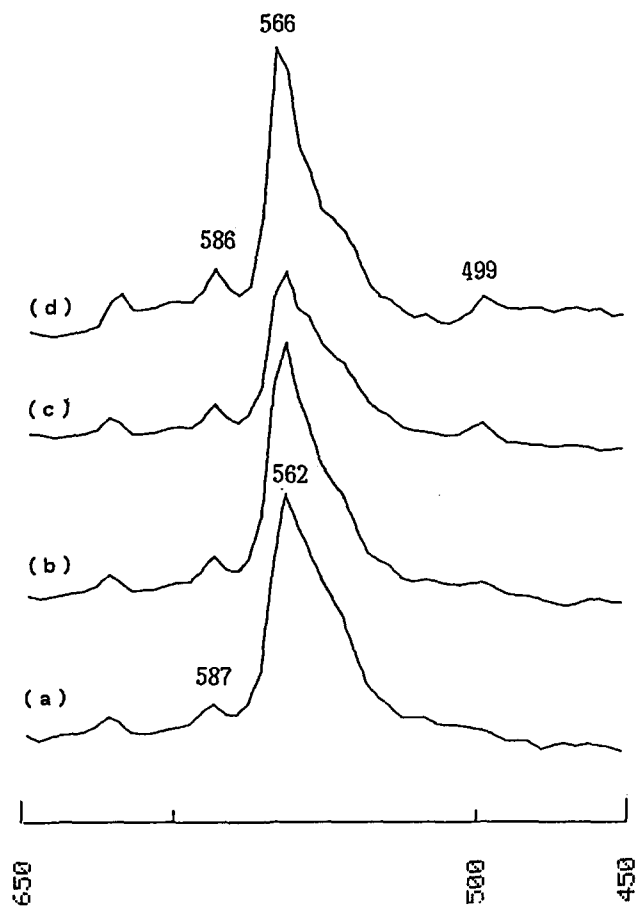


Figure 7 Infra-red spectrum (650–450 cm⁻¹) of iso-PS. (a) 10 g l⁻¹ dried gel film; (b) 20 g l⁻¹ dried gel film; (c) 40 g l⁻¹ dried gel film; (d) solution-cast film

in crystallinity of the dried gels are dependent only on the polymer concentration in the wet gel state, and the crystallization of the gels should take place only during drying, due to solvent evaporation at the gelation

temperature. Gel containing no crystal can be formed at low polymer concentration. This result is consistent with our previous conclusion that gelation of the PS/CS₂ system occurs independently of crystallization.

REFERENCES

- 1 Wellinghoff, S. T., Shaw, J. and Baer, E. *Macromolecules* 1979, **12**, 932
- 2 Tan, H., Hiltner, H., Moet, E. and Baer, E. *Macromolecules* 1983, **16**, 28
- 3 Girolamo, M., Keller, A., Miyasaka, K. and Overbergh, N. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 39
- 4 Atkins, E. D. T., Issac, D. H., Keller, A. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 211
- 5 Atkins, E. D. T., Issac, D. H. and Keller, A. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 71
- 6 Atkins, E. D. T., Keller, A., Shapiro, J. S. and Lemstra, P. J. *Polymer* 1981, **22**, 1161
- 7 Atkins, E. D. T., Hill, M. J., Jarvis, D. A., Keller, A., Sarhene, E. and Shapiro, J. S. *Colloid Polym. Sci.* 1984, **262**, 22
- 8 Painter, P. C., Kessler, R. E. and Snyder, R. W. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 723
- 9 Guenet, J. M. *Polym. Bull. (Berlin)* 1985, **14**, 105
- 10 Guenet, J. M. *Macromolecules* 1986, **19**, 1961
- 11 Xie, X.-M., Tanioka, A. and Miyasaka, K. *Polymer* 1991, **32**, 479
- 12 Kobayashi, M., Akita, K. and Tadokoro, H. *Makromol. Chem.* 1968, **118**, 324
- 13 Onishi, T. and Krimm, S. *J. Appl. Phys.* 1961, **32**, 2320
- 14 Tadokoro, H., Nishiyama, Y., Nozakura, S. and Murahashi, S. *Bull. Chem. Soc. Jpn* 1961, **34**, 381
- 15 Kobayashi, M. *Bull. Chem. Soc. Jpn* 1961, **34**, 560
- 16 Takeda, M., Iimura, K., Yamada, A. and Imamura, Y. *Bull. Chem. Soc. Jpn* 1960, **33**, 1219
- 17 Tadokoro, H., Nozakura, S., Kitazawa, T., Yasuhara, Y. and Murahashi, S. *Bull. Chem. Soc. Jpn* 1959, **32**, 313
- 18 Painter, P. C. and Koenig, J. L. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 1885
- 19 Theodorou, M., Jasse, B. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 445
- 20 Jasse, B., Lety, A. and Monnerie, L. *J. Mol. Struct.* 1973, **18**, 413
- 21 Xu, Z., Jasse, B. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 355