BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 22, pp. 4309-4313, 1995

0032-3861/95/$10.00+0.00

Bulk copolyesterification of azelaic acid, *o*-phthalic anhydride and trimethylolpropane. Statistical distributions of acid branches on triol units studied by ^{13}C n.m.r.

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(Received 14 July 1994; revised 14 November 1994)

The mechanisms of tri-dimensional polyesterifications in bulk at 180°C of ternary mixtures of *o*-phthalic anhydride (P) + azelaic acid (Z) + trimethylolpropane (T), as well as the distributions of acid branches on the potential crosslinking T units, have been studied by liquid ^{13}C n.m.r. before (sol) and after (gel) gelation. The critical time for gelation is found to decrease when Z increases, and in all cases the actual critical conversions are larger than those calculated by the classical statistical Flory–Stockmayer relation. Transesterification reactions actually occur during polyesterification. Before as well as after gelation, the distributions of P and Z in diesters and triesters of T follow two slightly different Bernouillian statistics because of the better reactivity of Z than P.

(Keywords: bulk copolyesterification; transesterification; Bernouillian statistics)

INTRODUCTION

Although some known papers have dealt with the identification and quantitative determination by ^{13}C n.m.r. of copolyesters synthesized with trimethylol propane (triol)[1] or pentaerythritol (tetraol)[2,3], these only concern very low molecular weight and soluble polycondensates. For insoluble crosslinked high molecular weight polycondensates, ^{13}C n.m.r. examination of swollen gels only refers to the identification of the nature of the polyol and aromatic acid and some modifiers present in air-dried alkyd paint binders[4]. Most of the published works in the field of insoluble crosslinked polyurethanes or polyesters deal with physical mechanical properties. There are no known quantitative ^{13}C n.m.r. studies relating to gelled polyesters.

In our preceding paper[5], the mechanism of the tri-dimensional copolyesterificaton in bulk and at high temperature of trimethylolpropane† (T) by azelaic acid† (Z) and *o*-phthalic anhydride (P), which gives insoluble reticulated gels, was studied by ^{13}C liquid n.m.r. In-depth quantitative ^{13}C n.m.r. examinations of the homogeneous swollen copolyester gels have shown that: (i) Z is more reactive than P; (ii) the two acid functions of Z and P as well as the three alcohol functions of T do not have the same reactivity because of the steric hindrance created by the first esterification reaction(s); and (iii) in all cases, the actual critical conversions are larger than those calculated from classical statistical Flory–Stockmayer theory[6].

Concerning particularly the reticulated and insoluble copolyester obtained from the 0.5P + 0.5Z + 0.8T mixture (where quantities of reagents are expressed in mol), it has been shown that the distributions of P and Z on the mono-, di- and triesters of the potential crosslinking T units follow Bernouillian statistics. For P-rich mixtures, well before gelation, Z is found to almost reach its esterification limit. In contrast, esterification of the less active P continues until the gel point. In other words, the Z/P ratio slowly decreases in the copolyesters and this gives rise to the probability of a drift of the distributions of Z and P on T from Bernouillian statistics.

The present work concerns the in-depth ^{13}C n.m.r. study of the distributions of P and Z in the copolyesters

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† Systematic names: azelaic acid = nonanedioic acid, trimethylolpropane = 2,2-bis(hydroxymethyl) butane-1-ol

obtained from different pP + zZ + 0.8T mixtures – with COOH/OH = 0.8 – before and after the gel points.

EXPERIMENTAL

Reagents, polyesterification apparatus and procedures, ^{13}C n.m.r. spectroscopy

All these have been described in detail in ref. 5.

Reagent mixtures and polyesterification

Three mixtures have been studied: 0.75 P + 0.25 Z + 0.8 T, 0.5 P + 0.5 Z + 0.8 T and 0.25 P + 0.75 Z + 0.8 T, with COOH/OH ratio = r = 0.83. All the polycondensations were performed in bulk at 180°C. Conversions and distributions of Z and P have been determined by quantitative ^{13}C n.m.r. spectroscopy on liquid or/and swollen gels in deuterated dimethylsulfoxide (DMSO-d_6) and tetrachloroethane ($CDCl_2$–$CDCl_2$) as specified in ref. 5. For overlapped ^{13}C resonances, quantitative determinations were achieved by simulations using the Bruker LINESIM program.

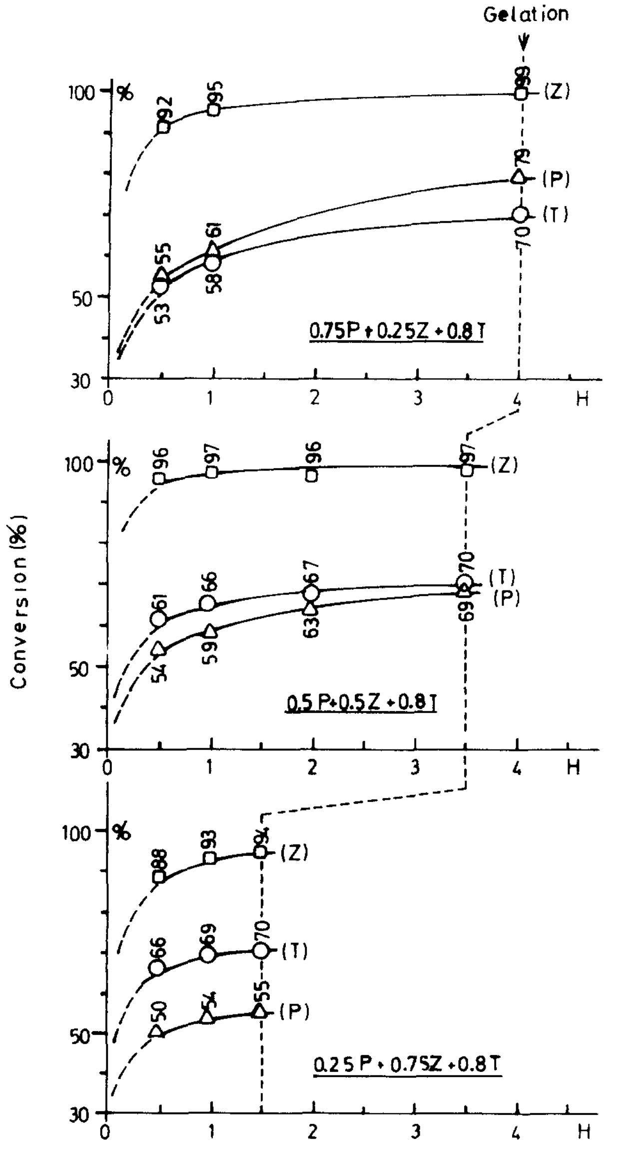

Figure 1 Polyesterifications in bulk at 180°C of o-phthalic anhydride (pP) + azelaic acid (zZ) + trimethylol propane (0.8 T) with $p + z = 1$ and COOH/OH = 0.83. Conversions of hydroxyls (○),and acid groups of P (△) and Z (□) *versus* reaction times (in h). Vertical figures are conversions (%)

RESULTS AND DISCUSSION

It was shown in our preceding study[5] that, in the bulk copolyesterification of o-phthalic anhydride (pP) + azelaic acid (zZ) + trimethylolpropane (tT) systems with $p + z = 1$ (in mol fractions), reticulation is mainly due to Z. That is, owing to its long chain of nine carbon atoms, Z is more able than P to crosslink copolyester chains. With P only, no reticulation has been observed.

Conversion at gel point

In bulk and at 180°C, with r = COOH/OH = 0.83, the critical time (t_c) for reaching the gel point decreases from 4 to 1.5 h when the z/p mole ratio increases from 1/3 to 3 (*Figure 1*). It is of interest that the observed overall critical conversion of acid groups ($C_c(\mathrm{COOH})_{\mathrm{obs}}$) amounts to 0.83–0.84 (equation (1)) and that of hydroxyls ($C_c(\mathrm{OH})_{\mathrm{obs}} = C_c(\mathrm{T})_{\mathrm{obs}}$) is 0.70 when the calculated critical conversion $C_c(\mathrm{COOH})_{\mathrm{calc}}$ or C_c(COOH) (FS), owing to the classical statistical Flory–Stockmayer (FS) relation, (equation (2)) equals only 0.77 (*Table 1*).

$$C_c(\mathrm{COOH})_{\mathrm{obs}} = p \times C_c(\mathrm{P}) + z \times C_c(\mathrm{Z}) \qquad (1)$$

where C_c(P) and C_c(Z) are the critical conversions of acid functions of P and Z, respectively (*Figure 1*), and

$$\begin{aligned} C_c(\mathrm{COOH})_{\mathrm{calc}} &= C_c(\mathrm{COOH})\ (\mathrm{FS}) \\ &= \{r[1 + \rho\,(f_{\mathrm{T}} - 2)]\}^{\,1/2} \\ &= (2r)^{-1/2} \\ &= 0.77 \end{aligned} \qquad (2)$$

with f_{T} (the functionality of T) = 3 and $\rho = 1$, because no other polyol is present.

The values of $C_c(\mathrm{OH})_{\mathrm{obs}}$ determined by ^{13}C n.m.r. may be checked using equation (3):

$$C_c(\mathrm{OH})_{\mathrm{obs}} = C_c(\mathrm{COOH})_{\mathrm{obs}}/r \qquad (3)$$

with $r = 0.833$.

As was found previously, all the observed critical

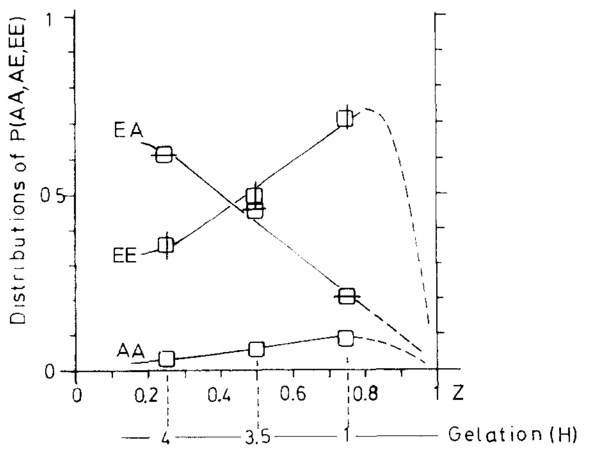

Figure 2 Distributions of free (□), mono-(□) and diesterified (□) o-phthalic anhydride (P) *versus* azelaic acid (Z) mole fraction

Table 1 Copolyesterifications in bulk at 180°C of *o*-phthalic anhydride (P) + azelaic acid (Z) + trimethylolpropane (T) with r = COOH/OH = 0.83 and different proportions of P and Z. Critical times (t_c), critical conversions (C_c) and distributions of free (aaa), mono- (aae), di- (aee) and triesters (eee) of T in gelled copolyesters

	p, z			
	0.75, 0.25	0.5, 0.5	0.25, 0.75	0, 1 (ref. 5)
Critical time, t_c (h)	4	3.5	1.5	1.6
Critical conversions:				
Acid $C_c(P)_{obs}$	0.79	0.69	0.55	–
Acid $C_c(Z)_{obs}$	0.99	0.97	0.94	0.82
Acid $C_c(P+Z)_{obs}{}^a$	0.84	0.83	0.84	0.82
Alcohol $C_c(T)_{obs}$	0.70	0.70	0.70	0.70
Alcohol $C_c(COOH)_{calc}{}^b$	0.77	0.77	0.77	0.77
Alcohol $C_c(OH)_{calc}{}^c$	0.64	0.64	0.64	0.64
Distributions:				
T (aaa)	0.03	0.03	0.04	0.04
T (aae)	0.19	0.19	0.16	0.18
T (aee)	0.45	0.46	0.44	0.44
T (eee)	0.33	0.34	0.35	0.35

[a] From equation (1)
[b] From equation (2)
[c] From equation (3)

conversions in this study are larger than those calculated:

$$\Delta C_c(COOH) = C_c(COOH)_{obs} - C_c(COOH)_{calc}$$
$$= 0.06\text{–}0.07$$
$$\Delta C_c(OH) = C_c(OH)_{obs} - C_c(OH)_{calc} = 0.06$$

Distributions of different copolyester species at gel point

Irrespective of the relative concentrations of P and Z at the gel point, the distributions of free T (aaa = 0.03–0.04; a = alcohol), mono- (aae = 0.16–0.18; e = ester), di- (aee = 0.44–0.46) and triesters of T (eee = 0.33–0.35) are remarkably constant within experimental error. Gelation always occurs when 1/3 of the potential crosslinking T units are triesterified (*Table 1*) as was observed previously[5].

For $z/p \leq 1$, far before the gel point, after 1 h of reaction the conversion of the more reactive Z's acid groups has almost reached its limit while that of the less reactive P's acid groups continues to increase (*Figure 1*, top and middle) until complete reticulation. Then copolyesterification reactions drastically slow down. The proportion of diesterified-P (EE; E = ester) *versus* Z increases almost linearly, while that of monoesterified-P (AE; A = acid) symmetrically decreases (*Figure 2*). The maximum of EE should lie around $z = 0.8$. It is worthy to note that, simultaneously, the proportion of trapped free anhydride P (AA) also increases. It is plausible to assume that, for Z-rich mixtures, free P is more easily trapped because of the fast gelation.

Distributions of the four T-triesters and transesterification

For simplicity, the four triesters are represented by PPP, PPZ$^+$ (PPZ + PZP + ZPP, owing to the order of esterification of T by P and/or Z), PPZ$^+$ (PZZ + ZPZ + ZZP) and ZZZ. The quantitative determinations of these four triesters were achieved by simulations of the envelope of the T-quaternary carbon resonances at 40.5–41.5 ppm (ref. 5). The variations of these four triesters *versus* reaction times for the three

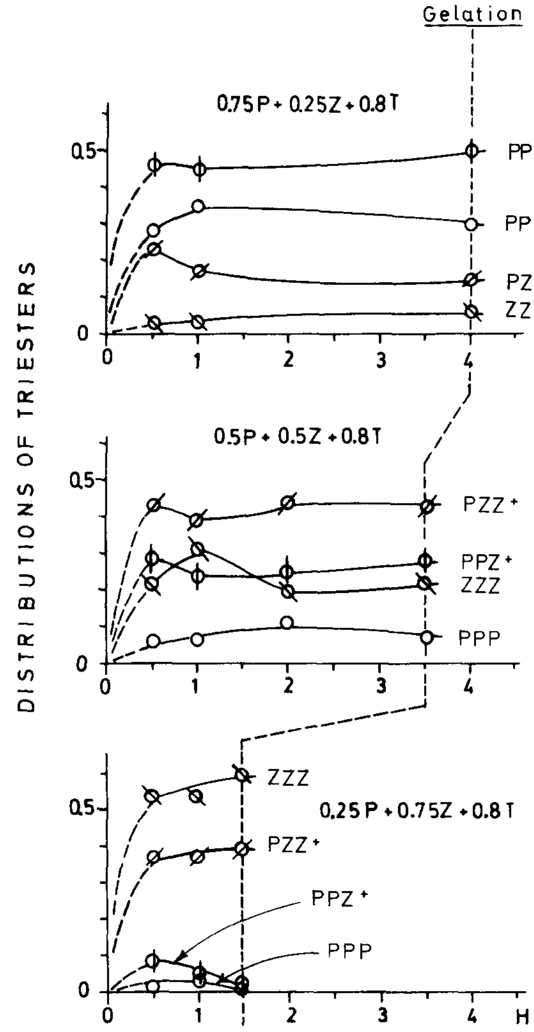

Figure 3 Distributions of the four triesters of trimethylolpropane *versus* reaction times: top, 0.75P + 0.25Z + 0.8T; middle, 0.5P + 0.5Z + 0.8T; bottom 0.25P + 0.75Z + 0.8T. ○, PPP; ⦶, PPZ$^+$; ⌀PZZ$^+$; ⦻ ZZZ

Table 2 Copolyesterifications in bulk at 180°C of *o*-phthalic anhydride (P) + azelaic acid (Z) + trimethylolpropane (T) with $r = COOH/OH = 0.83$. Probabilities of presence of P ($p(P)$) and Z ($p(Z)$) on T ($p(P) + p(Z) = 1$) at different reaction times

	Reaction time (h)					
	0.5	1	1.5	2	3.5	4
0.75 P + 0.25 Z						
p(P)	0.64	0.66				0.71^{a}
p(Z)	0.36	0.34				0.29^{a}
0.5 P + 0.5 Z						
p(P)	0.36	0.38		0.40	0.42^{a}	–
p(Z)	0.64	0.62		0.6	0.58^{a}	–
0.25 P + 0.75 Z						
p(P)	0.16	0.16	0.17^{a}			–
p(Z)	0.84	0.84	0.83^{a}	–		–

^{a} Swollen gel

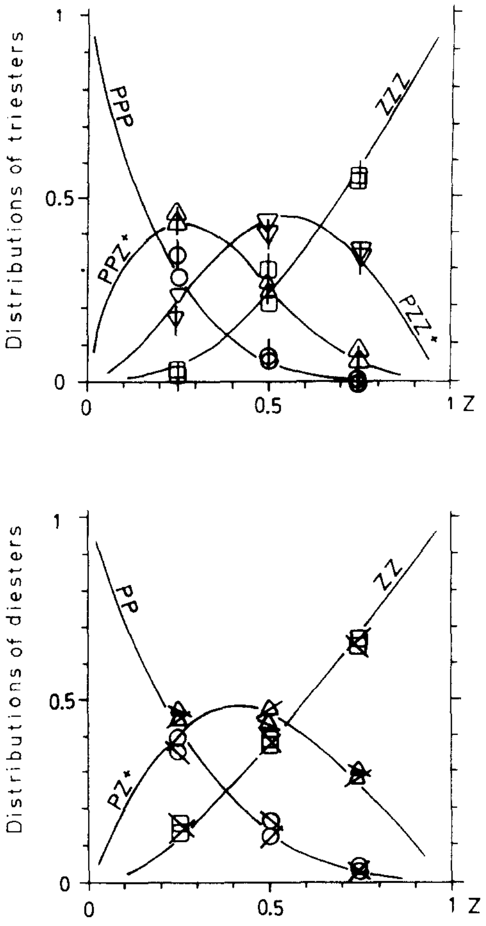

Figure 4 Distributions of diesters and triesters in soluble copolyesters ($pP + zZ + 0.8T$) obtained before gelation *versus* Z mole fraction, with $p + z = 1$ and COOH/OH = 0.83. Solid curves: calculated Bernouillian probabilities of presence. Bottom,diesters: PP (⊘ = 0.5 h; ⌀ = 1 h), PZ^{+} (△ = 0.5 h; △ = 1 h), ZZ (◫ = 0.5 h; ◫ = 1 h). Top, triesters: PPP (○ = 0.5 h; ⦶ = 1 h), PPZ^{+} (△ = 0.5 h; △ = 1 h), PPZ^{+} (▽ = 0.5 h; ▽ = 1 h), ZZZ (□ = 0.5 h; ◫ = 1 ⊇

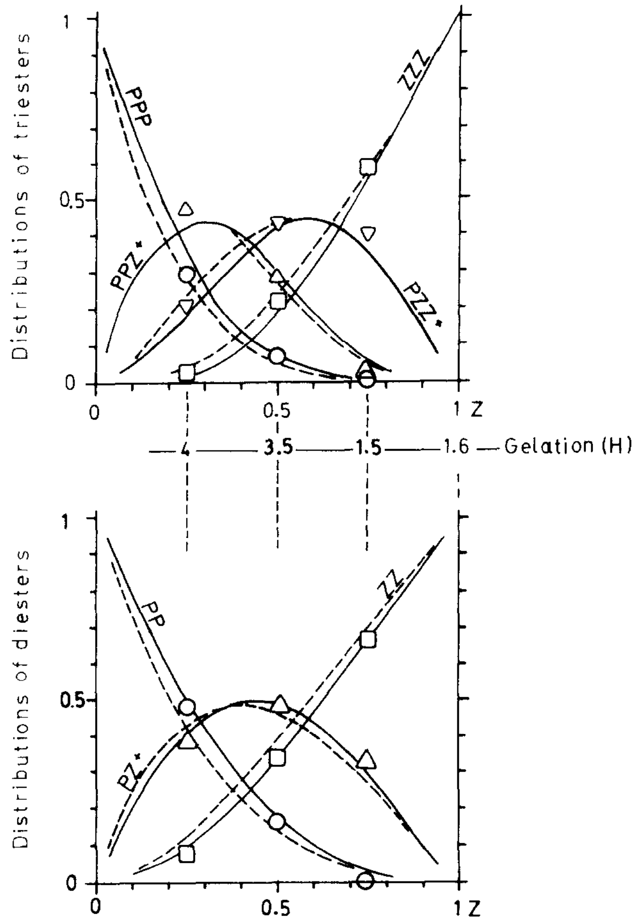

Figure 5 Distributions of diesters and triesters in copolyester swollen gels ($pP + zZ + 0.8T$) obtained after gel point *versus* Z mole fraction, with $p + z = 1$ and COOH/OH = 0.8. Solid curves: calculated probabilities of presence for swollen gels. Dotted curves: calculated probabilities of presence for soluble copolyesters (identical to the solid curves of *Figure 4*). Bottom, diesters: PP (○), PZ^{+} (△), ZZ (□). Top, triesters: PPP (○), PPZ^{+} (△), PPZ^{+} (▽), ZZZ (□)

copolyesterifications are illustrated in *Figure 3*. Shifts of the triester distributions – the natures and trends of which depend on z/p – are observed during the reactions. For $z/p \leq 1$, the drastic decreases of PZZ^{+} ($z/p = 1/3$; *Figure 3*, top) and ZZZ ($z/p = 1$; *Figure 3*, middle) for the benefit of PPZ^{+} and PPZ^{+} + PZZ^{+}, respectively, should simultaneously be due to the slow and continuous esterification of T by P and transesterification. Transesterification is even more clearly seen with $z/p = 3$ (*Figure 3*, bottom): PPZ^{+} and PPP are almost absent at the gel point.

Statistical distributions of azelaic and phthalic branches on di- and triesters of T

The probabilities of the presence of P (p(P)) and Z (p(Z)) on T, calculated[5] from their respective conversions (*Figure 1*) at different reaction times, are reported in *Table 2*. Examination of *Figure 1* and *Table 2* shows that, if for the Z-rich mixture ($z/p = 3$; *Figure 1*, bottom) p(P) and p(Z) remain the same before (sol) and after (gel) the gel point with the P-rich mixture ($z/p = 1/3$; *Figure 1*, top), in contrast, one has:

$$p(\mathrm{P})_{\mathrm{gel}} = 0.71 > p(\mathrm{P})_{\mathrm{sol}} = 0.65$$

because P continues to react while Z has almost reached its limit. So a question arises concerning a possible difference in the statistics of distributions of *o*-phthalic and azelaic branches in the sol and gel states of the copolyesters obtained from the same P-rich mixture.

Assuming that the relative reactivities of P and Z remain the same for di- and triesterification, irrespective of the order of esterification by P or Z (Bernouillian statistics)[5], one gets two sets of theoretical probabilities of presence of (i) the three diesters (p(PP), $p(PZ^+) = p(\mathrm{PZ} + \mathrm{ZP})$, p(ZZ)) and (ii) the four triesters (p(PPP), $p(\mathrm{PPZ}^+)$, $p(\mathrm{PZZ}^+)$, p(ZZZ)), calculated from the p(P) and p(Z) values of *Table 2*. These calculated $p(\ldots)$ give the solid curves of *Figure 4* (sol) and *Figure 5* (gel). The asymmetrical feature of these curves with regard to the vertical $\mathrm{Z} = 0.5$ is due to the better reactivity of Z.

Before gelation, the experimental distributions of the three diesters (*Figure 4*, bottom) as well as those of the four triesters (*Figure 4*, top) determined by ^{13}C n.m.r. fit quite well the corresponding calculated solid curves within experimental error. These experimental distributions are actually Bernouillian irrespective of the z/p ratios.

Concerning the copolyester gels, Bernouillian distributions have been found for the $0.5\mathrm{P} + 0.5\mathrm{Z} + 0.8\mathrm{T}$ reticulated copolyester[1]. Here, the experimental distributions of the two other gels ($z/p = 1/3$ and 3) also fit quite well the second Bernouillian statistical curves (*Figure 5*, solid curves), calculated by using the p(P) and p(Z) values of swollen gels in *Table 1*, slightly different from those of the sols (*Figure 5*, dotted curves).

REFERENCES

1 Hvilsted, S. *Makromol. Chem. Macromol. Symp.* 1991, **52**, 199
2 Newmark, R. A. and Palazzoto, J. *Appl. Spectroscopy* 1990, **44**, 804
3 Newmark, R. A., Runge, M. L. and Chermack, J. A. *J. Polym. Sci. Polym. Chem. Edn* 1981, **19**, 1329
4 Marshall, G. L. and Lander, J. A. *Eur. Polym. J.* 1985, **11**, 959
5 Petiaud, R., Waton, H., Coyard, H. and Pham, Q. T. *Polymer*, 1992, **33**, 5056
6 Odian, G. 'Principles of Polymerisation', 2nd Edn, Wiley, New York, 1981, p. 116