Studies on thermal degradation behaviour of anionically copolymerized styrene–divinylbenzene copolymers by high-resolution pyrolysis–gas chromatography

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Anionically and radically copolymerized styrene–divinylbenzene copolymers with comparable divinylbenzene contents have been synthesized and studied by high-resolution pyrolysis–gas chromatography. The considerable differences in thermal degradation behaviour observed between both copolymer systems were interpreted on the basis of differences in the expected network structures for the corresponding copolymer systems. In addition, thermogravimetric analysis was carried out to evaluate the thermal degradation behaviour of the copolymers.

(Keywords: high-resolution Py-g.c.; styrene–divinlybenzene copolymers; anionic copolymerization; radical copolymerization; thermal degradation behaviour)

INTRODUCTION

Previously, styrene–divinylbenzene (St–DVB) copolymers with various DVB contents, prepared by conventional radical copolymerization, were characterized using high-resolution pyrolysis–gas chromatography (Py-g.c.)[1]. In this work, the composition of the copolymers and St sequences between the network structures were estimated from the yields of the characteristic pyrolysates, such as toluene, St dimer and trimer and comparing them with those of monodisperse linear polystyrenes with known average molecular weights ($\bar{M}_n = 900–860\,000$). This estimation was made on the assumption that St sequences between the network structure behave similarly to those of linear polystyrene with corresponding average molecular weight during thermal degradation at relatively high temperatures. In general, the estimated St sequences between the crosslinking points decreased with an increase in the DVB content. The estimated values from St dimer and trimer were comparable with the reference values obtained from the measurement of glass transition temperature (T_g).

On the other hand, anionically prepared St–DVB copolymers with known St sequences have been extensively studied by Rietsch and co-workers[2–6]. In that work, various physicochemical measurements were made as for T_g, swelling ratio and stress-relaxation. Dependence of these properties on various parameters, such as average functionality of the crosslinking points, average molecular weight between the crosslinking points and the amount of free chains contained in the network structures, were interpreted on the basis of the related physicochemical theories. More recently, Errede *et al.*[7,8] correlated the ^{13}C n.m.r. linewidth of the associated signals with the crosslink density of anionically prepared St–DVB copolymers. Differences in the swelling behaviour between anionically and radically prepared gels were explained in terms of the distribution of the average molecular weight between the crosslinking points.

In the present work, St–DVB copolymers with known average molecular weight of St sequences between the crosslinking points were prepared by anionic copolymerization using pure *p*-DVB. Corresponding St–DVB copolymers prepared by suspension radical copolymerization were also used. Both copolymer systems were studied by high-resolution Py-g.c. with a fused silica capillary column. The thermal degradation behaviour of the anionically copolymerized gels was studied by comparing the yields of the common characteristic pyrolysates with those of the corresponding St homopolymers and the radically prepared copolymers. The considerable differences observed between both copolymer systems were interpreted on the basis of differences in the expected network structures for the corresponding copolymer systems. In addition, thermogravimetric analysis (t.g.a.) was carried out to study the thermal degradation behaviour of the copolymers.

EXPERIMENTAL

Conditions for Py-g.c.

A vertical microfurnace-type pyrolyser (Yanagimoto GP-1018) directly attached to a gas chromatograph (Yanagimoto G-3800) with a flame ionization detector (f.i.d.) was used. A high-resolution fused-silica capillary column (0.2 mm i.d. × 25 m length) coated with immobilized methylphenyl silicone (5 % phenyl) supplied

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Table 1 St–DVB copolymer samples utilized

Sample	Composition (wt%) St	Composition (wt%) p-DVB	Average molecular weight of St sequences[a]	p-DVB/living end ratio
Anionically copolymerized gels				
A-1	89.0	11.0	6.0×10^2	29
A-2	75.1	24.9	3.4×10^2	44
A-3	54.4	45.6	1.6×10^2	54
A-4	35.1	64.9	1.1×10^2	77
Radically copolymerized gels				
R-1	89.1	10.9	4.0	–
R-2	75.0	25.0	1.4	–
R-3	54.8	45.2	<1	–
R-4	37.7	62.3	<1	–

[a] Number-average degree of polymerization ($\overline{DP}_n$) by g.p.c. for anionically copolymerized gels and weight-average degree of polymerization ($\overline{DP}_w$) by Py-g.c. for radically copolymerized gels by the method in Ref. 1

from Hewlett-Packard was used in a temperature programming mode from 50 to 280°C at a rate of 4°C min^{-1}. The flow (30 ml min^{-1}) of the nitrogen carrier gas at the pyrolyser was reduced to 0.4 ml min^{-1} at the capillary column through a splitter. Samples of about 150 μg were pyrolysed at 600°C. Peak identification was usually carried out by a g.c.–m.s. system (Jeol JMS-DX300) attached to the pyrolyser.

Conditions for t.g.a.

T.g.a. measurements were made with a Rigaku-Denki thermobalance. About 8 mg of the sample weighed in a platinum dish was measured from room temperature to about 700°C at a rate of 10°C min^{-1} under nitrogen atmosphere.

Materials

Eight kinds of St–DVB copolymer samples utilised are listed in *Table 1*, which gives their compositions. samples A-1 to A-4 were synthesized by anionic copolymerization according to the method reported by Weiss *et al.*[9] using sodium naphthalene as an initiator. In this case, St homopolymers with living ends synthesized by homopolymerization of St were copolymerized with p-DVB to form network structures. Before adding p-DVB monomer, a portion of the polymerization mixture was sealed off to determine average molecular weight of the St homopolymers by gel permeation chromatography (g.p.c.). The St sequences between the crosslinking points for A-1 to A-4 are also the same as those of the corresponding St homopolymers. Molar feed ratios of p-DVB to one living end of the precursor are also given in *Table 1*. Samples R-1 to R-4 were synthesized so that they had comparable p-DVB contents to those of the anionically prepared gels by suspension radical copolymerization of St and p-DVB using benzoyl peroxide as an initiator. The weight-average degree of polymerization ($\overline{DP}_w$) of the St sequences between the network structures in the radically copolymerized gels estimated according to our previous work using St trimer[1] are listed in *Table 1*. Pure p-DVB monomer utilized was kindly supplied by Toyo-Soda Industry Inc.

RESULTS AND DISCUSSION

Typical high-resolution pyrograms of the anionically and radically copolymerized St–DVB copolymers are shown in *Figures 1* and *2*, respectively. The peak assignments on the pyrograms are basically consistent with those reported previously, except for some corrected assignments for DVB and ethylstyrene (ESt) isomers from m, p- and o- to m- and p-. Normalized peak intensities of the major pyrolysates on the pyrograms are listed in *Table 2*. Here, the normalization of peak intensity is carried out by dividing the peak intensity (count) by the sample amount (μg) utilized. As summarized in *Table 2*, the normalized intensities of the St monomer, dimer and trimer characteristic of St sequences decrease with the rise of DVB content in both copolymer systems, while those of p-DVB show the opposite tendency. The peak intensities for ethylbenzene, p-xylene, p-methylstyrene (p-MSt) and p-ESt, which are considered to be formed mostly from the p-DVB portion, also increase with the rise in p-DVB content. In addition, hybrid dimers and hybrid trimers between St and p-DVB are also observed on the pyrograms of both copolymer systems. As shown in *Table 2*, the intensities of these hybrid products from the radically prepared gels are always higher than those from the corresponding anionically prepared ones since the

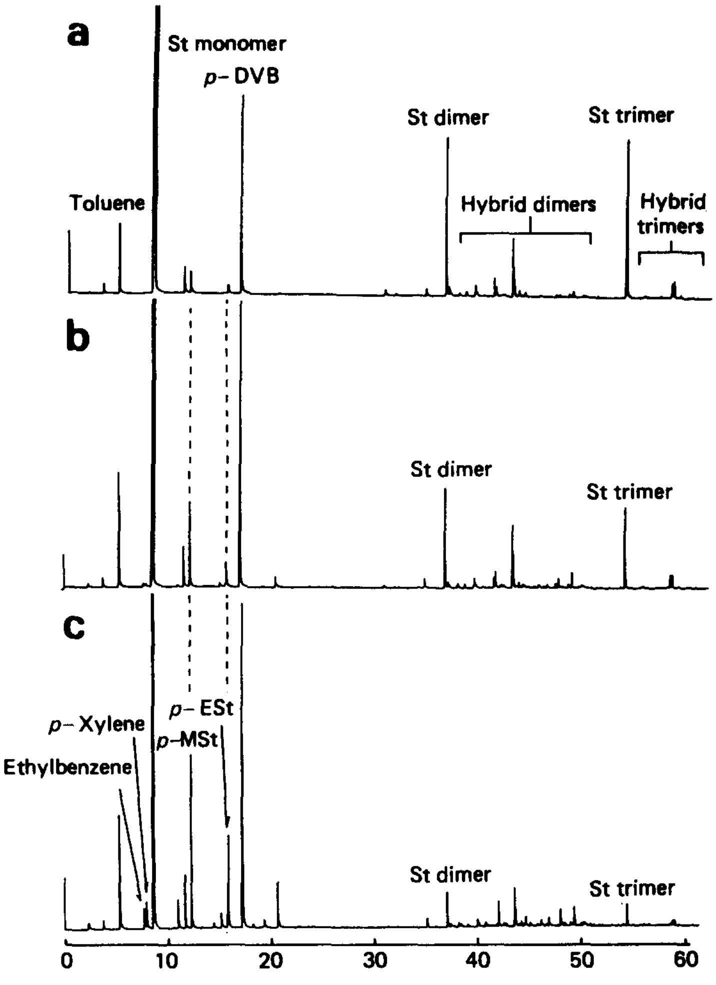

Figure 1 Typical high-resolution pyrograms of anionically copolymerized St–DVB copolymers (a) A-1: St = 89.0 wt%; (b) A-2: St = 75.1 wt%; (c) A-3: St = 54.4 wt%

junction numbers between St and *p*-DVB units for the former gels are much larger than those for the latter.

In order to develop a comparative discussion on the network structures, the yields of the pyrolysates characteristic of the St sequences, such as toluene, St monomer, dimer and trimer, defined as the peak intensity (count) normalized by the St amount (μg) contained in the samples utilized, are given in *Table 3* for the copolymers and the St homopolymers (A-1′ to A-4′) corresponding to anionic gels (A-1 to A-4). Similarly, *p*-DVB yields listed in *Table 3* are defined as the peak intensity normalized by the *p*-DVB amount (μg) contained in the sample utilized. The recovery data obtained by Py-g.c. and the observed residue in t.g.a. are also listed in *Table 3*. The recovery (%) is defined as the total peak intensity normalized by the sample amount (μg) when the value for poly(α-methylstyrene) is regarded as 100%. In general, the observed yields of St monomer, dimer and trimer, which are primarily formed through depolymerization and radical transfers in macroradicals with long St sequences, decrease with increasing *p*-DVB content since the average molecular weight of St sequences contained in the network structures decreases in both copolymer systems. On the other hand, the yields of toluene, which is formed mainly from the terminals of St sequences, show an opposite tendency. However, the yields of the characteristic pyrolysates for St homopolymers change only slightly with an increase in average molecular weight since even the lowest molecular weight St homopolymer utilized ($\overline{DP}_n = 1.1 \times 10^2$) are above the stabilization level ($\overline{DP}_n \approx 10^2$) at the pyrolysis temperature[10].

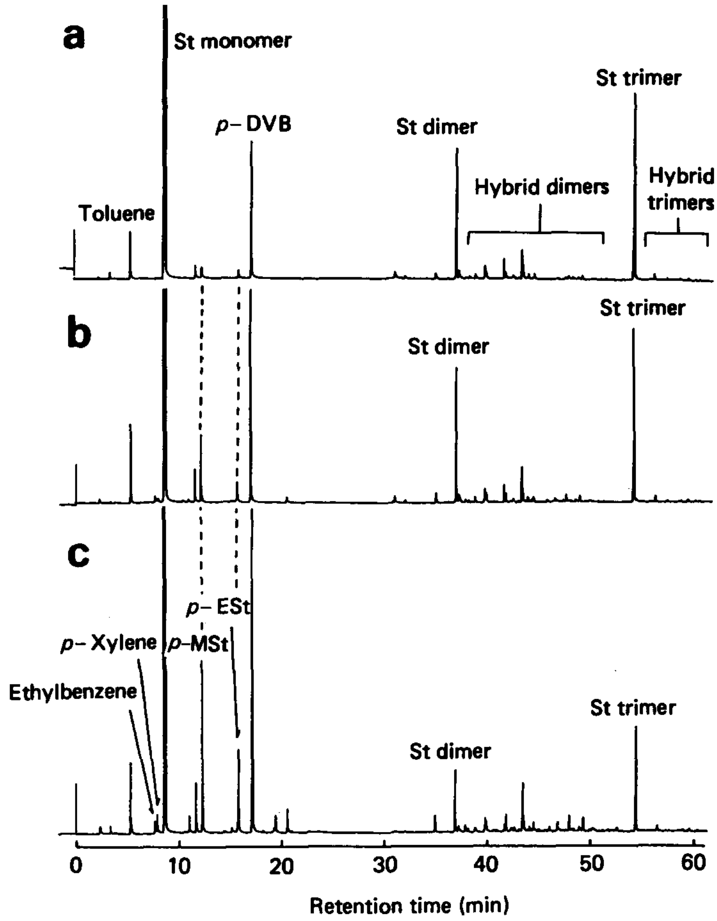

Figure 2 Typical high-resolution pyrograms of radically copolymerized St–DVB copolymers (a) R-1: St = 89.0 wt%; (b) R-2: St = 75 wt%; (c) R-3: St = 54.8 wt%

In comparing the two copolymer systems, the yields of St monomer, dimer and trimer for the anionic gels are always higher than those of the corresponding radically copolymerized gels and the yields of toluene show the opposite tendency. These phenomena are mostly attributed to differences in the average St sequences contained in the network structures. Here, it is interesting to note that the observed yields of the characteristic pyrolysates from the anionically copolymerized gels are significantly smaller than those of the corresponding St homopolymers, especially for the ones with larger *p*-DVB content, in spite of the fact that the St sequences contained in the corresponding samples are essentially the same. Moreover, although the ratios of the yield of St trimer to those of St dimer for radically copolymerized gels are in the range 0.43 to 0.80 and those for St homopolymers are in the range 0.65 to 0.76, the values for the anionically copolymerized gels, which range from 0.95 to 1.45, are much higher than those of the corresponding St homopolymers and radically copolymerized gels. These results suggest that the St sequences conained in the anionically copolymerized gels behave in a different manner from those of the radically copolymerized gels, for which the product ratios associated with St sequences are rather close to those for the St homopolymers.

The observed differences in thermal degradation

Table 2 Normalized peak intensity of the major pyrolysates on the pyrograms of St-DVB copolymers

		Normalized peak intensity (count μg^{-1})										
Sample	DVB (wt%)	Toluene	St monomer	St dimer	St trimer	*p*-MSt	*p*-ESt	*p*-DVB	Hybrid dimers	Hybrid trimers	Other	Total[a]
Radically copolymerized gels												
R-1	10.9	153	3550	226	138	37	11	245	174	51	325	4900
R-2	25.0	127	2960	121	79	91	36	487	232	45	373	4550
R-3	45.2	114	1960	48	18	187	96	716	226	13	527	3900
R-4	62.3	80	488	4	3	326	210	802	242	–	712	2870
Anionically copolymerized gels												
A-1	11.0	71	3880	211	201	41	13	213	132	–	379	5130
A-2	24.9	59	3310	180	186	76	33	317	180	–	320	4660
A-3	45.6	71	2160	76	92	167	79	537	213	–	466	3860
A-4	64.9	56	939	17	24	299	168	669	224	–	715	3110

[a] Total peak intensity normalized by the sample amount

Table 3 Yields of characteristic pyrolysates for St–DVB copolymers and St homopolymers

Sample	DVB (wt%)	Yield (count μg^{-1}) Y_{tol}	$Y_{monomer}$	Y_{dimer}	Y_{trimer}	$Y_{p\text{-DVB}}$	Recovery on pyrogram (%)	Residue on t.g.a. (wt%)
Radically copolymerized gels								
R-1	10.9	172	3980	254	155	2250	86.9	0.8
R-2	25.0	169	3950	162	106	1950	80.0	3.6
R-3	45.2	208	3570	87	34	1580	69.3	8.1
R-4	62.3	211	1300	10	8	1290	50.9	17.7
Anionically copolymerized gels								
A-1	11.0	80	4350	237	226	1940	91.0	0.5
A-2	24.9	78	4410	239	248	1280	82.7	2.4
A-3	45.6	130	3980	140	170	1180	68.5	7.7
A-4	64.9	160	2680	47	68	1030	55.2	12.5
St homopolymers[a]								
A-1′	–	62	4300	377	286	–	96.1	–
A-2′	–	63	4080	375	268	–	91.8	–
A-3′	–	73	4180	379	259	–	95.1	–
A-4′	–	101	4120	375	243	–	95.9	–

[a] St homopolymers A-1′ to A-4′ correspond to anionically copolymerized gels A-1 to A-4, respectively

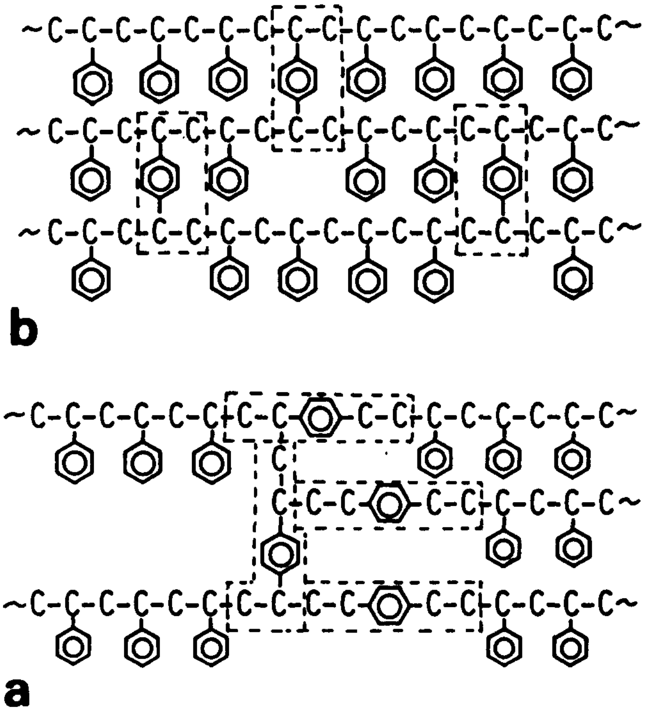

Figure 3 Expected network structures for (a) anionically copolymerized and (b) radically copolymerized St–DVB copolymers

behaviour could be attributed to structural differences in the expected networks as shown in *Figure 3*. In the network structures of the radically copolymerized gels, *p*-DVB units are distributed in an isolated way among St sequences. The favoured thermal cleavages at the tertiary C–C bond near the *p*-DVB crosslinking points mostly yield macroradicals with the corresponding St sequences in the network structures. On the other hand, the *p*-DVB portions in the anionically prepared gels exist as branched clusters in which the number of branching is closely related to the functionality. Further, there are no tertiary C–C bonds at the junctions of *p*-DVB units and St sequences which are preferentially cleaved to yield macroradicals with the corresponding St sequences.

Figure 4 shows the relationship between *p*-DVB content of both copolymers and the normalized peak intensities of the products characteristic of the *p*-DVB moiety in the gels such as *p*-DVB, *p*-MSt and *p*-ESt. Although almost linear relationships are observed for the sum of the normalized intensities (*p*-DVB + *p*-ESt + *p*-MSt), apparently nonlinear curves are observed for the *p*-DVB intensities. These phenomena suggest that the *p*-DVB monomer recoveries generally decrease with a rise in the density of crosslinking while the total recoveries of the products characteristic of the *p*-DVB moiety are almost constant. On the other hand, *p*-DVB yields for radically copolymerized gels are always greater than

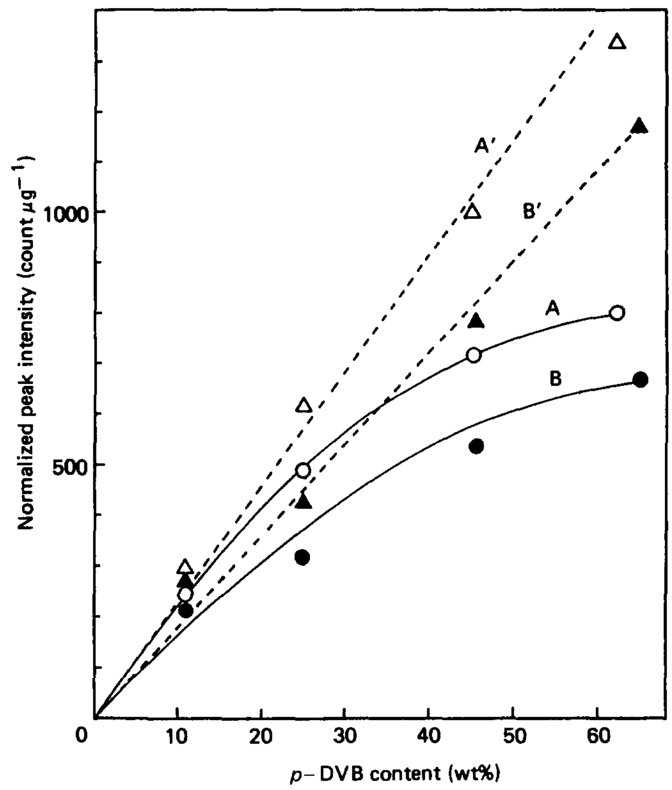

Figure 4 Relationships between *p*-DVB content and the normalized peak intensities of the pyrolysates characteristic of the *p*-DVB moiety in the anionically and radically copolymerized St–DVB copolymers: A, *p*-DVB (radical gel); B, *p*-DVB (anionic gel); A′, *p*-DVB + *p*-ESt + *p*-MSt (radical gel); B′, *p*-DVB + *p*-ESt + *p*-MSt (anionic gel)

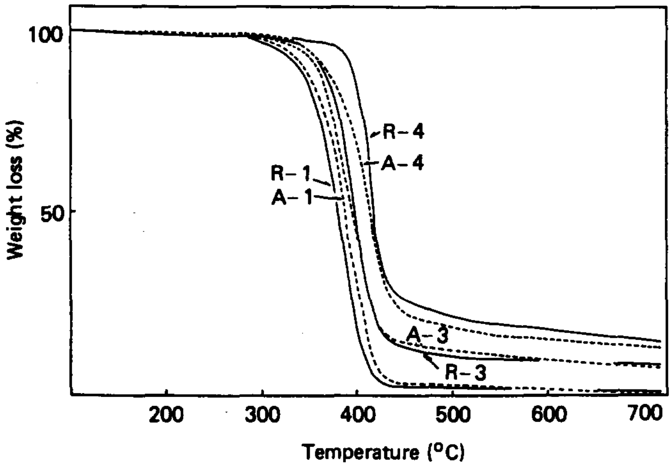

Figure 5 T.g.a. weight loss curves of anionically and radically copolymerized St–DVB copolymers

those for the corresponding anionically copolymerized gels. This result indicates that the monomer recoveries from the isolated DVB sequences in the radically prepared gels are always higher than those from the clustered ones in the anionic gels. This phenomenon could be explained by the neighbour effect of monomer units in copolymer chains where the monomer yield during pyrolysis is affected by the neighbouring monomer units along the polymer chain, depending on the difference in the ease of depolymerization for both monomer units[11].

The thermal stabilities of the two copolymer systems were also examined from t.g.a. data. Typical t.g.a. weight loss curves of the anionically copolymerized gels and the corresponding radically copolymerized ones are shown in *Figure 5*. The fact that the weight loss curves generally shift to the higher temperature with increasing *p*-DVB content suggests that the overall thermal stability of the copolymers increases together with the *p*-DVB content. Although the amount of residue as shown in *Table 3* also increases with the rise of the *p*-DVB content, there are no significant differences between the weight loss curves of the anionically and corresponding radically copolymerized gels for the samples with lower *p*-DVB contents. However, the initial weight loss for the radically copolymerized sample R-4 occurs at a considerably higher temperature than that of the corresponding anionically copolymerized sample A-4. From this result, it is apparent that the overall thermal stability of the radically copolymerized gels with the higher *p*-DVB content is higher than that for the corresponding anionically copolymerized ones since the randomly distributed network structures in the radically copolymerized gels contribute to the higher thermal stability than the locally distributed ones.

Another important factor which may contribute to the thermal degradation behaviour of the anionically prepared gels is the functionality of the crosslinking points, which could be altered by changing the molar feed ratio of *p*-DVB to the living ends of St homopolymers. This is confirmed by the fact that a sample corresponding to sample A-3 with an extremely low *p*-DVB/living end ratio gave significantly larger yields of the pyrolysates characteristic of both St sequences and the *p*-DVB moiety. The influence of functionality of the anionically copolymerized gels on thermal degradation behaviour may also be an interesting subject to study systematically using high-resolution Py-g.c.

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REFERENCES

1 Nakagawa, H. and Tsuge, S. *Macromolecules* 1985, **18**, 2068
2 Rietsch, F., Daveloose, D. and Froelich, D. *Polymer* 1976, **17**, 859
3 Rietsch, F., Brault, A. and Froelich, D. *Polymer* 1978, **19**, 1043
4 Brault, A., Rietsch, F. and Froelich, D. *Polymer* 1978, **19**, 1047
5 Rietsch, F. *Macromolecules* 1978, **11**, 477
6 Rietsch, F. and Froelich, D. *Eur. Polym. J.* 1979, **15**, 361
7 Errede, L. A., Newmark, R. A. and Hill, J. R. *Macromolecules* 1986, **19**, 651
8 Errede, L. A. *Macromolecules* 1986, **19**, 654
9 Weiss, P., Hild, G., Herz, J. and Rempp, P. *D. Makromol. Chem.* 1970, **135**, 249
10 Tsuge, S., Okumoto, T. and Takeuchi, T. *J. Chromatogr. Sci.* 1969, **7**, 250
11 Tsuge, S., Kobayashi, T., Nagaya, T. and Takeuchi, T. *J. Anal. Appl. Pyrol.* 1979, **1**, 133