Reaction to effect the transformation of anionic polymerization into cationic polymerization: 3. Analysis of block copolymer formation by gel permeation chromatography

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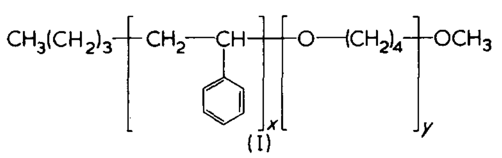
A study of the g.p.c. traces of AB poly(styrene-*b*-THF) materials prepared by anion-to-cation transformation reactions has established conditions under which very narrow molecular weight distributions may be obtained. Dispersities as low as 1.04 were consistently obtained using directly brominated polystyrenes as initiators, and there is evidence that this value is an upper limit controlled by machine broadening. Dispersities of about 1.15 were registered with block copolymers prepared from xylylene-bromide-terminated polystyrenes, but in neither system was there any evidence for a chain scission process to generate homo polyTHF.

INTRODUCTION

In parts 1 and 2[1,2], transformation reactions were reported for the preparation of AB poly(styrene-*b*-tetrahydrofuran) having the following structures:



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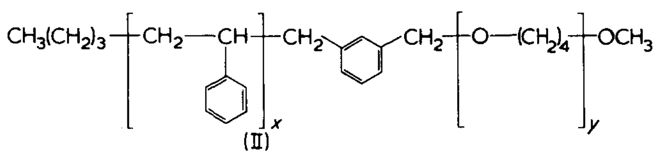

(II)

Briefly, polystyryl carbanions are reacted, either directly or via their Grignard compounds, with excess bromine[1], or with excess *m*-xylylene dibromide[2] to produce bromine-terminated polystyrenes. These may then be converted to polymeric carbenium ions by addition of a silver salt, such as the perchlorate or hexafluorophosphate and, when this is carried out in tetrahydrofuran (THF), polymerization ensues to create block copolymers of structures I or II. The end-groups of these block copolymers result from initiation with n-butyl lithium and termination with methanol.

Qualitative confirmation of block copolymer formation was provided by gel permeation chromatography (g.p.c.) with a chromatograph equipped with ultra-violet (u.v.) and refractometer (r.i.) detectors in series. Signals were recorded from both detectors at molecular weights higher than the initiating polystyrene. Since polyTHF is transparent to u.v. radiation at 254 nm, structures I and II were postulated for the high molecular weight product.

This paper reports on methods employed to characterize these block copolymers quantitatively, and thereby obtain a clearer insight into the efficiency of the transformation process. It will be shown that, under appropriate polymerization conditions, propagation by oxonium ions corresponds to a 'living' polymerization giving AB block copolymers with narrow distributions of molecular weight and composition.

EXPERIMENTAL

Block copolymers

The materials examined in this communication were prepared by the methods outlined in parts 1 and 2 of this series[1,2]. The samples are listed in *Table 1*.

Polymer standards

The polystyrene standards used to determine the g.p.c. molecular weight calibration curve were obtained from Waters Associates. A polystyrene standard with a molecular weight of 1800 was used to calibrate the responses of the u.v. and r.i. detectors.

The g.p.c. molecular weight calibration curve for polyTHF was established with samples kindly provided by Dr T. G. Croucher and Dr R. E. Wetton of Loughborough University

Table 1 AB poly(styrene-*b*-THF) copolymers and their conditions of preparation

Co-polymer	Struc-ture	Silver salt	Initiation T (°C)	Initiation Time	Propagation T (°C)	Propagation Time
IaClO_4	I	$AgClO_4$	−78	30 min	+15	6 days
IbPF_6	I	$AgPF_6$	−30	30 min	−10	1–4 h
IIaClO_4	II	$AgClO_4$	+20		+20	2 days
IIbClO_4	II	$AgClO_4$	+20		+20	16 h
IIcPF_6	II	$AgPF_6$	−10		−10	1–5 h

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Table 2 Average molecular weights of polyTHF standards[3]

$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	M_{peak} *	V_{peak}
6 790	8 660	1.28	7 670	26.80
10 120	12 110	1.20	11 070	25.75
16 960	19 180	1.13	18 040	24.35
32 620	37 980	1.16	35 200	22.55

* Molecular weight at the maximum peak height of the chromatogram

of Technology[3]. The polymerization of THF was initiated by triethyloxonium hexafluorophosphate using a procedure described elsewhere[4]. Propagation took place at −10°C in order to minimize transfer reactions, and the polymerization was terminated by adding acetic acid. Details of these narrow molecular weight distribution polyTHFs are given in *Table 2*. The low and high molecular weight standards were used to calibrate the response of the r.i. detector.

Gel permeation chromatography (g.p.c.)

Separations were performed at room temperature with THF as eluent using a Waters Associates model 301 gel permeation chromatograph with refractometer (thermostatted at 25°C) and ultra-violet (254 nm) detectors. The solvent (BDH) containing quinol stabilizer (0.1%) was dried and distilled before use. A series arrangement of four columns containing crosslinked polystyrene gel was used, consisting of two 10^3 Å and two 10^4 Å Styragels from Waters Associates. Elutions were conducted with a flow rate of 1 cm^3/min, and the retention volume (1 count = 5 cm^3) of the calibration standards was calculated from the initial point of injection to the appearance of the peak height maximum of the chromatogram. Polymer concentrations (w/v) were: polystyrene calibration $\leqslant$0.1%, polyTHF $\leqslant$0.3%, copolymers $\leqslant$0.3%, and all the polymer in the sample loop (2 cm^3) was injected.

Calibration of the detector responses was established with sensitivity settings of 8x and 32x for the r.i. and u.v. detectors respectively Experiments showed that doubling the proportionality constants (*Table 3*) was satisfactory with sensitivity settings for the r.i. and u.v. detectors of 4x and 16x. The chart speed was 12 cm/h. No corrections for chromatogram broadening were performed in calculations of number-average and weight-average molecular weights $\bar{M}_n$ and $\bar{M}_w$.

The g.p.c. was also used preparatively, and fractions from copolymer separations were collected from compositional analysis by proton magnetic resonance spectroscopy (^{1}H n.m.r.). Copolymer concentrations were in the range 1 to 2%.

Nuclear magnetic resonance spectroscopy

^{1}H n.m.r. spectra were recorded at 25°C on a Jeol PS-100 spectrometer at 100 MHz in the continuous wave mode. For the g.p.c.-separated samples, satisfactory spectra could be obtained in a single scan without the need for signal averaging. Typically, 25 ml of the eluent (5 counts) were evaporated on a vacuum line at room temperature to remove the THF solvent, and the residue was dissolved in dry carbon tetrachloride.

In addition to the expected peaks, the sample showed further absorptions which were identified as impurities formed by the aerial oxidation of the THF solvent. However, these peaks were in positions which did not interfere with the copolymer peaks. The compositions of the poly(styrene-*b*-THF) block copolymers were assessed by comparison of the areas of the styrene aromatic hydrogens and the $-OCH_2-$ hydrogens at 6.6 τ. Areas were measured using the instrument's electronic integrator, the average of six integrals being taken.

BLOCK COPOLYMER CHARACTERIZATION

Determinations of copolymer composition distribution by g.p.c. with dual u.v. and r.i. detectors have been reported by several workers[5–8]. Because of differences in nomenclature and methods in these publications, it is necessary to detail the procedures used in the present analysis for the following operations: determining the copolymer composition distribution, correcting the refractometer detector response to find the copolymer concentration, evaluating the g.p.c. molecular weight calibration curve for a block copolymer, and calculating average molecular weights and the polydispersities of the block copolymers.

Copolymer composition

The response $h_{uv}(V)$ of the u.v. detector as a function of retention volume V depends only on the weight w_s of styrene units in the copolymer, whilst the response $h_{ri}(V)$ of the r.i. detector depends on both w_s and the weight, w_T, of THF units in the copolymer. By starting with the relationships defined by Adams[6], an expression may be derived for the weight fraction, W_s, of styrene units in the copolymer. The detector responses are given by:

$$h_{uv}(V) = K_s w_s \qquad (1)$$

$$h_{ri}(V) = K_c(w_s + w_T) \qquad (2)$$

where K_s is a proportionality constant related to the u.v. extinction coefficient for styrene units in the copolymer, and K_c is a proportionality constant related to the specific refractive index increment of the AB block copolymer in the g.p.c. eluent. This increment is generally assumed to be related linearly to the values for the corresponding homopolymers[9], so that K_c is given by:

$$K_c = W_s K_A + (1 - W_s)K_B \qquad (3)$$

where K_A and K_B are the refractometer proportionality constants for polystyrene and polyTHF respectively. The weight fraction of styrene in the copolymer is:

$$W_s = \frac{w_s}{w_s + w_T} \qquad (4)$$

and substitution of equations (1) and (2) into equation (4), and elimination of K_c with equation (3), gives after rearrangement the following expression for W_s as a function of V:

Table 3 Proportionality constants for r.i. detector response (8X) and u.v. detector response (32X)

K_s	K_A	K_B
1.07	0.875	0.293

$$W_s(V) = \frac{K_B h_{uv}(V)/h_{ri}(V)}{K_s - (K_A - K_B)h_{uv}(V)/h_{ri}(V)} \tag{5}$$

Equation (5) is also derived from the relations given by Runyon *et al.*[5].

Copolymer concentration

If W_s varies as a function of V, it is clear from equations (2) and (3) that $h_{ri}(V)$ does not give directly the block copolymer concentration. An expression for $(w_s + w_T)$ is obtained by substituting equations (1) and (5) into equation (4). If the corrected refractometer response is represented by $h(V)$, which is directly proportional to $(w_s + w_T)$, then $h(V)$ is given by equation (6), in which the proportionality constant is omitted.

$$h(V) = (w_s + w_T) = \frac{h_{ri}(V)}{K_B} - \frac{h_{uv}(V)}{K_s K_B}(K_A - K_B) \tag{6}$$

Similar expressions derived by other authors differ from equation (6) only in that they give quantities which are proportional to $h(V)$. Runyon *et al.*[5] presented an equation for the total corrected response in terms of polystyrene, so that the right-hand side of equation (6) appeared multiplied by K_A. Grubisic-Gallot *et al.*[7] introduced the specific refractive index increment of the total block copolymer into their expression for the corrected refractometer response. Since we shall be interested in average molecular weights (see equation 10 and 11), and the average copolymer composition (see equation 15), rather than a pictorial view of the corrected refractometer chromatogram, the presence or absence of these constants will not affect the calculations. Relative values of $h(V)$ are sufficient, provided they are directly proportional to the block copolymer concentration as a function of V.

Copolymer calibration

Grubisic-Gallot, Rempp and Benoit[10] showed that a g.p.c. calibration plot of log $[\eta]M$ *versus* V was the same for homopolymers and copolymers, where $[\eta]$ is the intrinsic viscosity of the polymer in the g.p.c. eluent, and M is the molecular weight. At a given retention volume, it follows that:

$$\log [\eta]_c M_c = \log [\eta]_{PS} M_{PS} = \log [\eta]_{PT} M_{PT} \tag{7}$$

for a block copolymer (c), polystyrene (PS) and polyTHF (PT). With a viscometer detector on the g.p.c. instrument, the dependence of $[\eta]$ on V can be determined as polymer elutes from the chromatograph. Consequently, the $\log M_c$ *versus* V calibration curve can be calculated from the $\log M_{PS}$ *versus* V calibration curve determined experimentally with polystyrene standards. If no viscometer detector is available (as in the present case), then the $\log M_c$ *versus* V relationship has to be derived from the experimental M_{PS} and M_{PT} calibration curves.

Benoit and coworkers[11,12] have suggested that the molecular dimensions of block copolymers are not influenced by AB interactions. Consequently, the dimensions of an AB block copolymer in a theta solvent are linearly related to the dimensions of the homopolymers by the simple relation[7] where:

$$(\langle r^2\rangle_0/M)_c = W_s(\langle r^2\rangle_0/M)_{PS} + (1 - W_s)(\langle r^2\rangle_0/M)_{PT} \tag{8}$$

$\langle r^2\rangle_0$ is the unperturbed mean square end-to-end distance. G.p.c. separations are generally performed in good solvents, where polymers have similar polymer–solvent interactions and values for the chain expansion factor α. It follows that $\langle r^2\rangle_0$ is satisfactory as a universal calibration parameter for homopolymers in good solvents[13,14]. Donkai *et al.*[15] have confirmed experimentally the validity of $\langle r^2\rangle_0$ for the universal calibration of polystyrene ($M_{PS} \leqslant 51\,000$) and polyTHF ($M_{PT} < 20\,000$) in THF. At low molecular weights ($M < 20\,000$), the value of α is unity[14,16,17], and the two universal calibration parameters $[\eta]M$ and $\langle r^2\rangle_0$ are equivalent. The expression for $\log M_c$ at a given V is therefore:

$$\log M_c - \log M_{PS} = \log[(\langle r^2\rangle_0/M)_{PS}/(\langle r^2\rangle_0/M)_c] \tag{9}$$

Values for $(\langle r^2\rangle_0/M)_c$ are calculated at each value of V from equation (8), with the values of $W_s(V)$ determined from equation (5).

The present method gives parallel curves for M_{PS} and M_{PT} on a semi-logarithmic plot. The procedure proposed by Chang[18,19] also gives parallel curves and requires homopolymer calibrations and Mark–Houwink constants for the determination of M_c.

Average molecular weights

From the corrected refractometer response and the block copolymer calibration, number-average and weight-average molecular weights were calculated from equations (10) and (11).

$$\bar{M}_n = \frac{\Sigma h(V)}{\Sigma h(V)/M_c(V)} \tag{10}$$

$$\bar{M}_w = \frac{\Sigma h(V)M_c(V)}{\Sigma h(V)} \tag{11}$$

RESULTS AND DISCUSSION

Calibration of detector responses

The areas of the chromatograms of the homopolymer standards were determined as a function of the injected weight and are plotted in *Figures 1a* and *b*. The detector responses are linearly related to concentration giving the values of the proportionality constants listed in *Table 3.*

Some workers have observed that K_A is molecular weight dependent[20,21]. However, as all the copolymers in this study contained polystyrene with a molecular weight of 2000 and a narrow dispersity, this dependence need not be considered. In *Figure 1b* the data show no definite trend with molecular weight, and it was assumed that ethyl and acetate end-groups had no influence on the r.i. response of polyTHF in the molecular weight range of interest. The same assumption was therefore made for methoxy end-groups in the copolymers. As the g.p.c. concentration of the polyTHF standards was raised above 0.3%, both the retention volume and chromatogram broadening increased. Furthermore, the r.i. response for polyTHF was found to be related non-linearly to the injected weight of the polymer at high concentrations. Consequently, copolymer compositions were not determined from chromatograms obtained for the preparative separations.

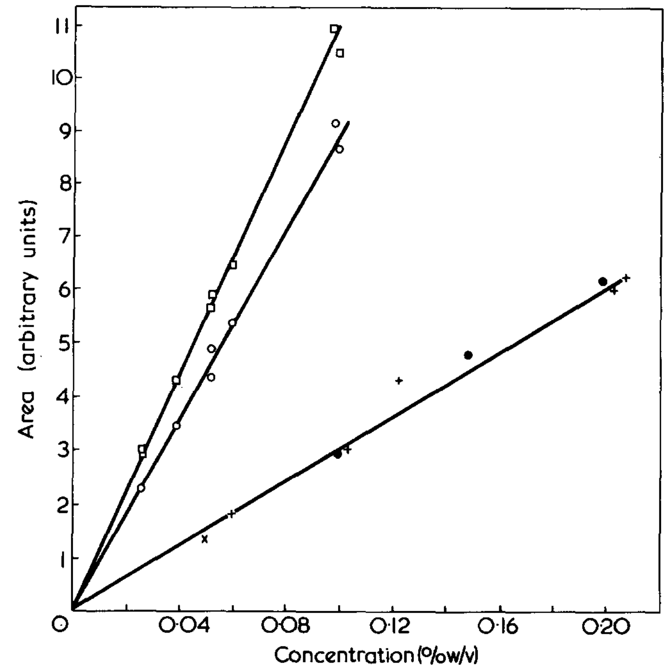


Figure 1 U.v. detector response (32X) (□); r.i. detector response (8X) (○) for polystyrene standards. R.i. detector response 8X for polyTHF standards: X, $\bar{M}_n$ = 6790; ●, $\bar{M}_n$ = 10 120; +, $\bar{M}_n$ = 32 620

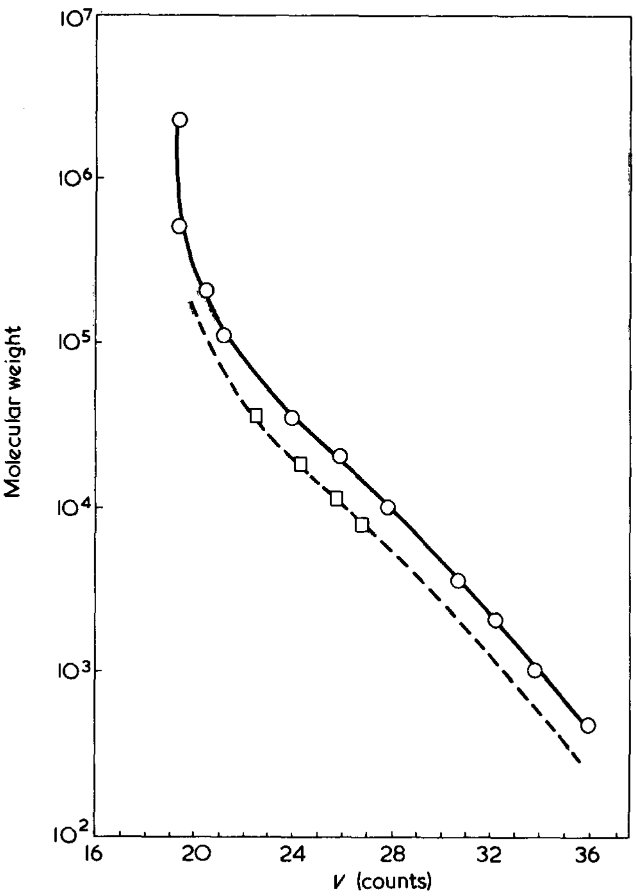


Figure 2 G.p.c. molecular weight calibration plot: ○, polystyrene standards; □, polyTHF standards; — — —, M_{PT} calibration from equation (12)

Molecular weight calibration

Experimental calibration curves for the polystyrene and polyTHF standards are shown in *Figure 2*. The results indicate that the assumption of parallel calibrations is satisfactory. The broken curve in the Figure was calculated with the following relation:

$$\log M_{PT} - \log M_{PS} = \log\left[(\langle r^2\rangle_0/M)_{PS}/(\langle r^2\rangle_0/M)_{PT}\right]$$

$$= \log\left[0.45/0.81\right] \qquad (12)$$

giving good agreement with the four polyTHF standards. Values of $\langle r^2\rangle_0/M$ were taken from Polymer Handbook[22], and were used in equation (8) in order to calculate the M_c calibration from equation (9).

Copolymer composition

If a copolymer possesses a narrow molecular weight distribution with little dependence of $W_s(V)$ on V, then the composition of the whole copolymer can be determined from the areas of the r.i. and u.v. chromatograms. G.p.c. traces are shown in *Figure 3* for copolymer IbPF$_6$/4. The two peaks at high V result from polystyrene of 2000 molecular weight (V_{peak} = 32.1 counts) which has not been transformed, and coupled polystyrene (V_{peak} = 30.2 counts) which was formed at the preparative stage. From the areas of the chromatograms at V_{peak} = 24.3 counts the copolymer composition can be determined with the data shown in *Figures 1a* and *b*, giving the value in *Table 4*. The same procedure was used to determine the compositions of the other IbPF$_6$ samples shown in this Table.

These samples were suitable for comparing g.p.c. and ^{1}H n.m.r. determinations of copolymer compositions. The ^{1}H n.m.r. values for fractions collected from preparative separations are given in *Table 4* where they are seen to be in good agreement with the g.p.c. results. The efficiency of the

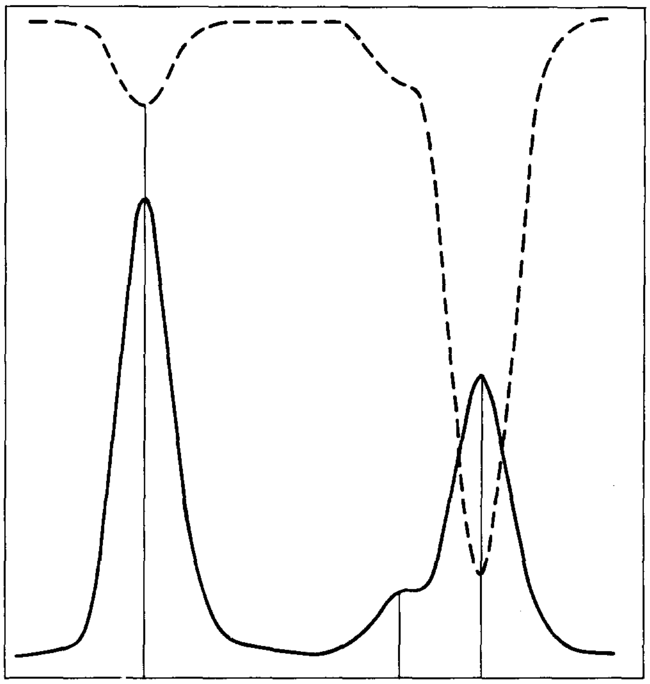


Figure 3 Chromatogram of product IbPF$_6$/4 containing copolymer (V_{peak} = 24.3 counts), coupled polystyrene (V_{peak} = 30.2 counts) and polystyrene, 2000 *MW* (V_{peak} = 32.1 counts). — — — —, U.v. 32X; ——— ; r.i. 4X

Table 4 Composition of $IbPF_6$ copolymers

			G.p.c. composition			
Copolymer[a]	V_{peak}	^1H n.m.r. composition	Chromatogram area[b]	$W_s(V)$ at V_{peak} [c]	$\bar{W}_s$ from equation (15)	$\bar{W}_s$ from equation (16)[d]
1	27.2	0.27	0.30	0.27	0.28	0.26
2	25.9	0.21	0.22	0.21	0.21	0.18
3	25.0	0.16	0.16	0.16	0.16	0.13
4	24.3	0.14	0.13	0.12	0.13	0.11

[a] Numbers refer to polymerization time (h) at −10°C; [b] assumes no dependence of *V* on composition; [c] from substitution of peak height maxima for the two detectors into equation (5); [d] assumes AB block copolymer

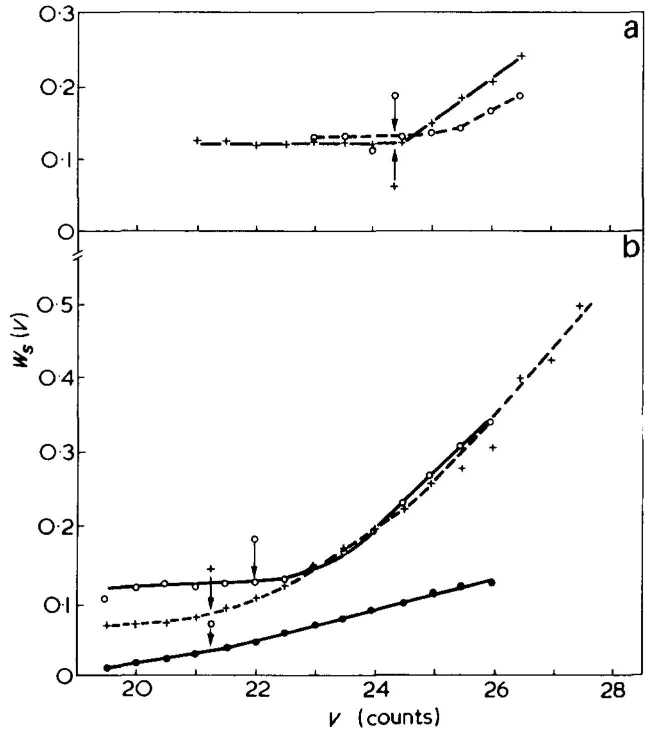


Figure 4 Dependence of copolymer composition on retention volume. (a) +, $IbPF_6/4$; ○, $IIcPF_6$. (b) ○, $IIbClO_4$; +, $IIaClO_4$; ●, $IaClO_4$. Arrows denote V_{peak}

separation was confirmed by reinjecting the fraction at low concentration into the chromatograph. Thus the composition for copolymer $IbPF_6/4$ from the chromatogram for the re-injected fraction was 0.12 using the area method as outlined in the previous paragraph. The somewhat higher value of sample $IbPF_6/1$ by the area method is probably caused by overlap of the tail of the copolymer chromatogram into the polystyrene peak at $V_{peak} = 30.2$ counts, whereas the n.m.r. sample is a fraction from the eluent collected between $V = 25$ counts and $V = 28$ counts. This overlap is not present in the other samples from this experiment, as exemplified by the chromatogram in *Figure 3*.

The assumption of a narrow composition distribution is checked by determining the dependence of $W_s(V)$ on V. Using the constants in *Table 3*, equations (5) and (6) simplify to:

$$W_s(V) = \frac{0.2925\, h_{uv}(V)/h_{ri}(V)}{1.07 - 0.5825\, h_{uv}(V)/h_{ri}(V)} \tag{13}$$

$$h(V) = 3.419\, h_{ri}(V) - 1.861\, h_{uv}(V) \tag{14}$$

Table 5 Average molecular weights of $IbPF_6$ copolymers

Co-polymer	Molecular weight at V_{peak} M_{PS}	M_c*	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	12 750	8045	7790	8120	1.04
2	20 000	12 200	11 300	11 900	1.05
3	26 000	15 600	15 060	15 600	1.04
4	32 000	18 800	18 000	18 750	1.04

* Calculated from equation (9), using $W_s(V)$ at V_{peak} (*Table 4*) in equation (8)

From the chromatograms in *Figure 3*, equation (13) gives the dependence of $W_s(V)$ on V for copolymer $IbPF_6/4$, as displayed in *Figure 4a*. For comparison, results for copolymer $IIcPF_6/5$ are also presented, and these will be discussed later.

Equation (13) may be used to calculate $W_s(V)$ at V_{peak} of the copolymer chromatogram. Values so obtained are given in *Table 4*, showing good agreement with ^1H n.m.r. values. The average composition $\bar{W}_s$ was calculated from the chromatogram using equation (15):

$$\bar{W}_s = \frac{\Sigma W_s(V) h(V)}{\Sigma h(V)} \tag{15}$$

Values for $h(V)$ were determined at intervals of $\Delta V = 0.5$ counts. Results for $\bar{W}_s$ given in *Table 4* show good agreement with the other determinations. Consequently, it can be concluded that the g.p.c. copolymer composition procedure is valid and that the $IbPF_6$ copolymers have narrow composition distributions.

Average molecular weights

From the dependence of $h(V)$ and $M_C(V)$ on V at intervals of $\Delta V = 0.5$ counts, values of $\bar{M}_n$ and $\bar{M}_w$ were calculated for the copolymers from equations (10) and (11). The results are given in *Tables 5* and *6*. The molecular weight distributions of these copolymers in the $IbPF_6$ series are nearly monodisperse. The value of $\bar{M}_w/\bar{M}_n$ for the initiating polystyrene with $M = 2000$ was 1.07 (determined by protonating a sample of the 'living' polystyryl anion and examining it by g.p.c.). Consequently these copolymers conform to a Poisson molecular weight distribution and confirm the kinetic analysis[1] in part 1 that propagation occurs without transfer or termination under these conditions.

It follows, therefore, that if the chromatograms at high molecular weight for the $IbPF_6$ copolymers correspond to

Table 6 Average molecular weights of IIcPF$_6$ copolymers

Copolymer	$W_s(V)$ at V_{peak}	^{1}H n.m.r. composition	Molecular weight at V_{peak}		$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
			M_{PS}	M_c*			
3	0.20	0.18	22 500	13 700	12 700	14 100	1.11
4	0.18	0.15	27 000	16 300	15 700	17 900	1.14
5	0.12	0.15	32 000	18 800	18 000	21 200	1.17

* Calculated from equation (9), using $W_s(V)$ at V_{peak} in equation (8)

pure AB block copolymers the copolymer composition may be calculated from equation (16):

$$\bar{W}_s = \frac{\bar{M}_n(\mathrm{PS})}{\bar{M}_n} \qquad (16)$$

where $\bar{M}_n(\mathrm{PS})$ is the number-average molecular weight (2000) of the polystyrene A block, and $\bar{M}_n$ is the value for the AB block copolymer (assumed to be the value in *Table 5*). Values of $\bar{W}_s$ from equation (16) are given in *Table 4*, showing reasonable agreement with other estimates of copolymer composition. Values obtained in this way may be expected to be lower than those determined by other procedures because of the assumptions involved in equations (8) and (9). The molecular weight calibration procedure is based on the absence of AB interactions between the two blocks, which has been suggested by Benoit and co-workers[11,12]. However, other observations[23,24] suggest that AB interactions are present, giving an expansion of the size of the AB block copolymer, so that the molecular dimensions predicted by equation (8) will be too low. Higher values of $(\langle r^2\rangle_0/M)_c$ will clearly lead to lower values of M_c in equation (9), thus lowering the copolymer $\bar{M}_n$ and raising the value of $\bar{W}_s$ in equation (16).

The IIcPF$_6$ series of copolymers were prepared under conditions similar to those of series IbPF$_6$ but, as the initiating polystyrene had been terminated with *m*-xylylene dibromide, they possess structure II. The results given in *Table 6* show that they have a significantly greater polydispersity than the IbPF$_6$ series. This broadening of the molecular weight distribution is accompanied by a broader copolymer composition distribution, as shown in *Figure 4a*.

It is significant that a plateau is obtained in the $W_s(V)$ *versus* V plot with this polymer also, and that the value of $W_s(V)$ in this range is very close to that obtained with IbPF$_6$. The existence of plateau in both these samples is very interesting as it implies that, within the accuracies of measurement, the materials are monodisperse over these ranges. The peak shapes obtained in the plateau regions must be principally determined by the intrinsic broadening of the g.p.c. instrument, so that the recorded dispersities are almost certainly significantly larger than the intrinsic dispersities of both materials.

Interestingly, in the IbPF$_6$ system the peak maximum falls at about the centre of the plateau range, whereas with IIcPF$_6$ the peak maximum occurs at its low molecular weight edge. Further, the increase in $W_s(V)$ after the plateau region is much more steep in the latter system than in the former. Both of these observations confirm that there is a larger lower molecular weight tail with material generated from xylylene-terminated product than with directly brominated polystyrene.

It was proposed[2] in part 2 that the xylylene-terminated polymers might, on initiation, undergo intramolecular hydride transfer and thus generate copolymer in which a proportion of the chains could be grafts. Because of their smaller radii of gyration, these graft copolymers would appear at higher V than their analogous block copolymers, and it would therefore be expected that the plateau would be observed to extend down to molecular weights lower than those observed with IIcPF$_6$. This has not occurred in the cases studied, and so the g.p.c. analysis cannot substantiate this proposal, unless the graft-initiation mechanism is coupled with a slower initial propagation step.

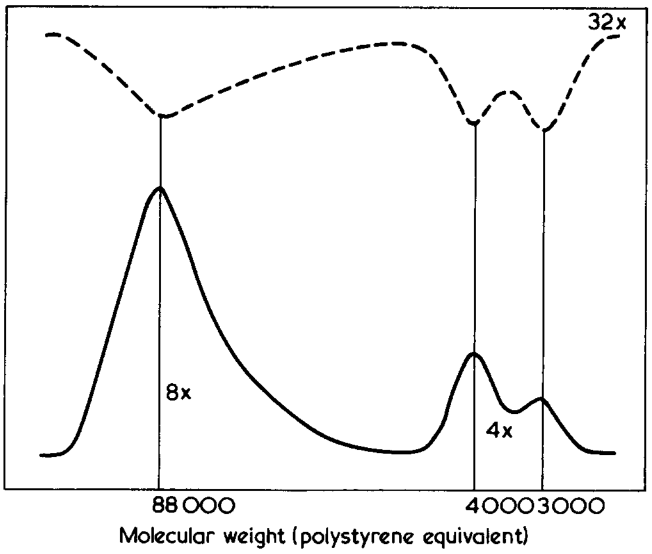
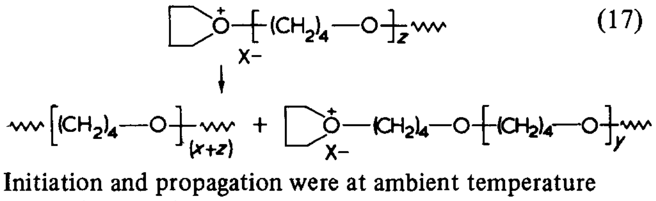


Figure 5 Chromatogram of product IIaClO$_4$ containing copolymer (V_{peak} = 21.6 counts), coupled polystyrene (V_{peak} = 30.2 counts), and polystyrene, 2000 *MW* (V_{peak} = 32.1 counts)

In some experiments carried out to study the nature and efficiency of the initiating process, the polymerization of THF was carried out under conditions in which it is known that molecular-weight broadening occurs, chiefly by chain scission reactions (equation 17):



Initiation and propagation were at ambient temperature using silver perchlorate as precipitant. It is of interest to examine the products of such experiments by g.p.c. to see the effect of the scission reaction on the traces obtained.

A typical trace (IIaClO$_4$) is shown in *Figure 5* where a

Table 7 Average molecular weights for copolymers formed by THF propagation at room temperature with perchlorate gegen ion

Copolymer	V_{peak}	$W_s(V)$ at V_{peak}	Molecular weight at V_{peak} M_{PS}	M_c*	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
$IaClO_4$	21.45	0.044	100 000	56 700	33 000	59 300	1.80
$IIaClO_4$	21.60	0.097	95 000	55 200	37 600	62 000	1.65
$IIbClO_4$	22.30	0.131	66 000	38 900	32 800	47 400	1.44

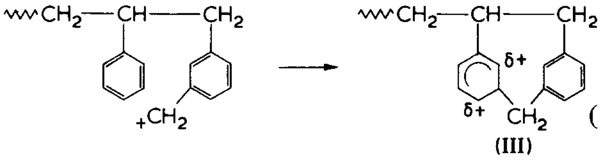
* Calculated from equation (9) using $W_s(V)$ at V_{peak} in equation (8)

much broader distribution is produced compared with that given in *Figure 3*. The high molecular weight component of such traces of the three perchlorate-initiated polymers listed in *Table 1* were analysed by the procedures for determining the copolymer composition and the molecular weight averages described previously. The results are listed in *Table 7*. It is evident that the polydispersities are much higher than those obtained under 'ideal' conditions, and that they increase with times of polymerization.

The dependences of $W_s(V)$ on V for these three polymers are plotted in *Figure 4b* where they may again be contrasted with those of the narrow dispersity materials. With the former polymers the plateau regions are seen to shrink as the polymerization times increase and the polymers approach the 'most probable' distribution. The value of $W_s(V)$ at high molecular weights also falls with time as the chain-scission mechanism generates homo polyTHF, being counterbalanced by a corresponding increase at lower molecular weights. Thus this chain-scrambling mechanism can be readily identified by g.p.c. techniques.

It is significant that the values of $W_s(V)$ recorded at a given retention time are appreciably higher with *m*-xylylene-bromide-terminated materials than with bromine-terminated polystyrene (*Figure 4b*). Calculations of $W_s(V)$ using the generalized form of equation (16) show close agreement with the latter polymer, but indicate that the values observed with the former materials are too high. This discrepancy results from an apparent increase in the u.v. absorbance of the block copolymer relative to that of the coupled polystyrene at 4000 molecular weight. Thus the increased absorption cannot be explained as due to more than one polystyryl chain being linked in some way into the block copolymer molecule, as this would not account for the observed diminution in the contribution of the 4000 molecular weight 'standard' to the total absorbance at 254 nm. Any explanation must therefore involve an increase in the average molar extinction coefficient of the polystyrene component. As this phenomenon only occurs with xylylene-bromide-terminated species (and with perchlorate as gegen ion), this moiety must be directly involved in the process causing this increased absorption.

A tentative suggestion is that the carbenium ion generated can attack the benzene ring of the adjacent styryl unit to yield species III in equation (18),



(18)

(III)

which is then still capable of additively polymerizing THF. The species resulting from this subsequent polymerization should exhibit considerably enhanced absorption at 254 nm, so that it need not be necessary to evoke this reaction as occurring with more than a fraction of the carbenium ions to account for the observed increase. Apart from showing by molecular models that the geometrical requirements for this intramolecular reaction can be easily met, no work has been carried out to test for its occurrence in these systems. It is also difficult to explain why it should occur when perchlorate rather than hexafluorophosphate is the gegen ion, unless it be that slower initiation with the former complex allows greater opportunity for the intra-molecular reaction to take place. Whatever the process involved, however, it does not significantly affect the efficiency of block copolymer formation.

CONCLUSIONS

The detailed examination of g.p.c. traces of AB poly(styrene-*b*-THF) materials prepared by anionic-to-cationic transformation reactions established the following points.

(1) Those polymers prepared at −10°C causing a PF_6^- gegen ion showed no evidence of chain scission to yield homo polyTHF, whereas those prepared at ambient temperature with a ClO_4^- gegen ion contained significant amounts of this material.

(2) Block copolymers prepared under 'living' conditions from directly brominated polystyrenes gave extremely narrow molecular weight distributions; the value of 1.04 obtained being determined by machine broadening.

(3) Block copolymers prepared under 'living' conditions from xylylene-bromide-terminated polystyrenes gave rather higher dispersity values (about 1.15); the principle cause for this was the presence of a low molecular weight tail.

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