Gradient High-Performance Liquid Chromatography of Statistical and Block Copolymers of Styrene and *t*-Butyl Methacrylate

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Synopsis

Copolymers of styrene (S) and *tert*-butyl methacrylate (TBMA) containing 24–92 mass % of the latter monomer were investigated using a silica column with isooctane/tetrahydrofuran (THF) gradients and on a phenyl bonded-phase column by methanol (MeOH)/THF gradients using UV detection. In both cases, retention decreased with increasing TBMA content of the sample. This is in contrast to the behavior of copolymers of S and methyl methacrylate (MMA) whose retention in gradient elution on silica columns increases with MMA content due to the polarity of this unit. The inversion of elution order is a result of the bulky TBMA residues shielding the polar groups of the ester units. For copolymers of varying composition, the gradation in retention on silica is quite sufficient for separating S/MMA but not for S/TBMA mixtures. The latter could be separated by composition on phenyl packings through MeOH/THF gradient elution. Block copolymers containing 80 or 92% TBMA could be baseline-separated. It was also possible to separate these samples from admixed PTBMA or PS homopolymers. Under the conditions used, the retention of a given block copolymer was somewhat higher than that of a statistical copolymer having the same composition. A block copolymer containing 80% TBMA was converted by transesterification into a S/MMA block copolymer. The elution of the latter fitted well in the sequence of S/MMA copolymers on silica column.

INTRODUCTION

High-performance liquid chromatography (HPLC) using elution gradients has proved suitable for the separation by composition of copolymers from styrene (S) and acrylonitrile,[1,2] S and methyl methacrylate (MMA),[3,4] S and methyl acrylate,[5] S and butadiene,[6] S and ethyl methacrylate (EMA),[7] and S and methoxyethyl methacrylate.[8] With UV detection, at least one kind of the constituting units must show absorption in the wavelength region where transparent solvents are available.

The variety of these applications indicates the versatility of the method. All the samples investigated so far were statistical copolymers. It is a challenging question as to whether or not gradient HPLC could also be applied to block copolymers. The present paper reports on the investigation of four block copolymers of S and *t*-butyl methacrylate (TBMA) samples by means of column gradient HPLC. In order to elucidate the effect of the block structure, we also investigated statistical copolymers from S and TBMA using the same equipment and solvents as with the block copolymers.

Balke and Patel[9] investigated statistical copolymers of S and *n*-butyl methacrylate with the aid of two size-exclusion chromatographic (SEC) systems which had been coupled according to the principle of cross fractionation. The term "orthogonal chromatography" was suggested by these investigators.[9] Balke[10] also reported on the separation of a copolymer containing 53.3% styrene units from both parent homopolymers.

Belenkij[11] investigated block copolymers of S and MMA by stepwise elution from a silica column through dichloromethane/methanol mixtures. Block copolymers of the same system have been studied by Inagaki et al.[12,13] who used development chromatography in a glass cylinder packed with silica gel. In the latter experiments, an isocratic mixture of 27.5% benzene in ethyl acetate was used for developing by absorbing the mobile phase into the dry column from the bottom. Thus, the procedure was similar to thin-layer chromatography, which also has been applied to block copolymers of the systems S/MMA,[14–16,19] S/butadiene,[17,19] S/ethylene oxide,[18,19] S/acrylonitrile,[19] S/γ-benzyl glutamate,[19] isoprene/α-methylstyrene,[19] MMA/butyl methacrylate,[19] and MMA/γ-benzyl glutamate.[19]

EXPERIMENTAL

Samples

Random copolymers from styrene and *t*-butyl methacrylate were obtained by radical copolymerization in bulk. In order to ensure homogeneity in composition, the degree of conversion was always limited to 16–26%. The procedure was performed according to an approved technique[20] but the crude polymerization products were precipitated from solutions in dichloromethane by pouring into an excess of methanol. The sample code and their characteristics are given in Table I. (Sample-composition data used in the text without additional remarks indicate mass % TBMA.)

AB-type block copolymers of S and TBMA were prepared by anionic polymerization at $-78°C$ in a break-seal apparatus.[21] Reagents were purified according to standard procedures.[21,22] Cumylpotassium was used as an initiator and potassium tetraphenyl borate was added as common-ion salt in order to suppress dissociation into free anions. First, styrene was added in bulk to the solution of initiator in THF. After full conversion, a small sample was withdrawn as a reference for the polystyrene (PS) block. Then TBMA was added in bulk, leading to an immediate decoloration. After conversion of the second monomer, methanol was added and the polymer was precipitated in water/methanol 1:1 and dried *in vacuo* at 50°C. The molecular weight distributions usually were narrow ($\overline{M}_w/\overline{M}_n \leq 1.2$). The composition measured by SEC (UV/RI ratio) agreed well with that calculated from monomer feed. However, due to partial chain termination at the addition of TBMA, some PS homopolymer was present in two of the block copolymers (ca. 15% in sample F and ca. 40% in sample E). Sample G contained ca. 40% of a TBMA–S–TBMA triblock copolymer of double molecular weight. This product was formed by a side reaction of cumylpotassium leading to bifunctional α-methylstyryl potassium.

TABLE I
Specification of the Copolymers from Styrene (S) and t-Butyl Methacrylate (TBMA) Used[a]

Sample code	A	B	C	D	E	F	G	H
Structure	Statistical copolymers				Block copolymers			
Composition: TBMA (mass %)	23.9	47.5	69.1	86.0	26	55	80	92
TBMA (mol %)	18.7	39.9	62.1	81.8	20.5	47	75	89
Molecular weight, $\bar{M}_w \times 10^{-3}$					300	240	92	112
Intrinsic viscosity (cm^3/g)	30	34	44	73				
Concomitant concentration in the respective sample (%, estimated)					PS	PS	ABA[b]	
					40	15	40	
$\bar{M}_w \times 10^{-3}$ of the concomitant					230	130	165	
Concentration of sample in mixture M-1 (mass %)	54.9	24.9	15.2	5.0				

[a] The S/MMA copolymers shown in Figure 11 contain the following percentage of methyl methacrylate (mass %): 11.4/23.8/37.0/49.5/64.0/76.2/88.5.
[b] Triblock copolymer, P(TBMA-b-S-b-TBMA).

An AB-block copolymer of S and MMA was prepared by hydrolysis of S–TBMA block copolymer G in THF containing 5% HCl (24 h reflux), followed by reesterification with diazomethane in THF. The polystyrene sample investigated ("PS 110 K") was an SEC calibration standard with narrow molecular-weight distribution and a weight-average of 110,000 (Pressure Chemical Corp.). "PS 2000" was an SEC standard purchased from Knauer (Bad Homburg, FRG) of nominal molecular weight 2,000,000.

Solvents. THF (BASF, Ludwigshafen, FRG) was distilled over potassium in a silver-coated column, which was 2-m long. The middle fraction was subsequently refluxed over potassium in a closed-circle apparatus from which it was taken immediately to the HPLC apparatus. The THF was continuously purged with helium. Sample solutions for direct injection into the HPLC apparatus were prepared using analytical-reagent grade THF, stabilized with 0.025% butylated hydroxy toluene (E. Merck, Darmstadt, FRG). Isooctane and methanol were HPLC grade (LiChrosolv), both purchased from Merck.

Size-Exclusion Chromatography (for Analytical Investigations). A Gynkotek HPLC pump M 600/200 (Gynkotek, München, FRG) was used with THF as an eluent at 1 mL/min flow rate; 0.1 mg of polymer was injected by means of a Knauer HPLC autosampler (injection volume: 0.1 mL). A Jasco Uvidec III variable wavelength detector at 260 nm (Japan Spectroscopic Co., Hachioji, Japan) and a Knauer differential refractometer 51.78 were used for monitoring the 260 and 230 nm UV signals and the refractive index (RI) signal, respectively. Two columns (1000 × 7.5 mm each) packed with PL-Gel 10 μm, 10^2 and 10^4 nm nominal pore size (Polymer Laboratories, U.K.) were employed. Calibration was performed by using PS standards (Pressure Chemical Corp.) and PTBMA homopolymers characterized by light scattering. The molecular weights of block copolymers were estimated as the weighed average of the values obtained from the PS and the PTBMA calibration curves. For the determination of block copolymer composition, the ratio of the RI and UV signals was compared to a calibration curve established by mixtures of homopolymers.

Gradient High-Performance Liquid Chromatography

HPLC Apparatus. A Liquid Chromatograph Model HP 1090 Series A (Hewlett Packard, Waldbronn, FRG) was used, equipped with a ternary DR 5 pump, an auto-injector with 250-μL syringe, diode-array detector, and data processing unit. A personal computer HP-85 was employed as a system controller.

HPLC Columns. Cartridge columns 60 × 4 mm (Knauer), packed with silica Nucleosil 50, 5-μm diameter particle size, pore size 5 nm ("silica column") or Nucleosil C_6H_5, 7 μm ("phenyl column").

HPLC Conditions. The samples were dissolved in THF (0.4 mg/mL). The eluent flow rate was 0.5 mL/min. The gradient dwell time was 2.3 min both for the silica column and the phenyl column. The column temperature was 50°C. The effective periods of the multilinear gradient programs used are listed in Table II. The subsequent return period included rinsing with THF at an increased flow rate (2 mL/min).

TABLE II
Effective Period of the Gradients Used[a]

No. 1	Time (min)	0	10	11	
	MeOH	100	0	0	
	THF	0	100	100	
No. 2	Time (min)	0	20	21	
	ISO	100	0	0	
	THF	0	100	100	
No. 3	Time (min)	0	19.6	21	
	ISO	98	0	0	
	THF	0	98	98	
	MeOH	2	2	2	
No. 4	Time (min)	0	12	14	
	MeOH	90	30	30	
	THF	10	70	70	
No. 5	Time (min)	0	12		
	MeOH	100	40		
	THF	0	60		
No. 6	Time (min)	0	1	11	13
	ISO	80	50	0	0
	THF	18	48	98	98
	MeOH	2	2	2	2
No. 7	Time (min)	0	12	13	
	ISO	80	20	0	
	THF	18	78	98	
	MeOH	2	2	2	

[a] MeOH = methanol, THF = tetrahydrofuran, ISO = isooctane (vol %). The transition from an eluent composition indicated to the next one is linear.

RESULTS

Statistical S / TBMA Copolymers

Figures 1(a, b) show the elution patterns of two statistical S/TBMA samples on the silica column. In terms of polarity, the gradient used (isooctane/THF) was a normal one which, together with the polar column, formed a proper normal-phase (NP) chromatographic system. The separation was much poorer than that of S/MMA copolymers under corresponding conditions,[4,24] and retention decreased with increasing content of the methacrylate ester in the copolymers, which also was in contrast with the behavior of S/MMA copolymers.

The small peaks in Figures 1 in the period between 3 and 6 min were caused by unknown impurities in the starting eluent which were collected on the column during the preinjection period and subsequently displaced by THF. The same phenomenon was observed in similar experiments with S/EMA copolymers, where it could be suppressed by using isooctane with 2% methanol as a starting eluent. Here, the disturbances could be eliminated in the same
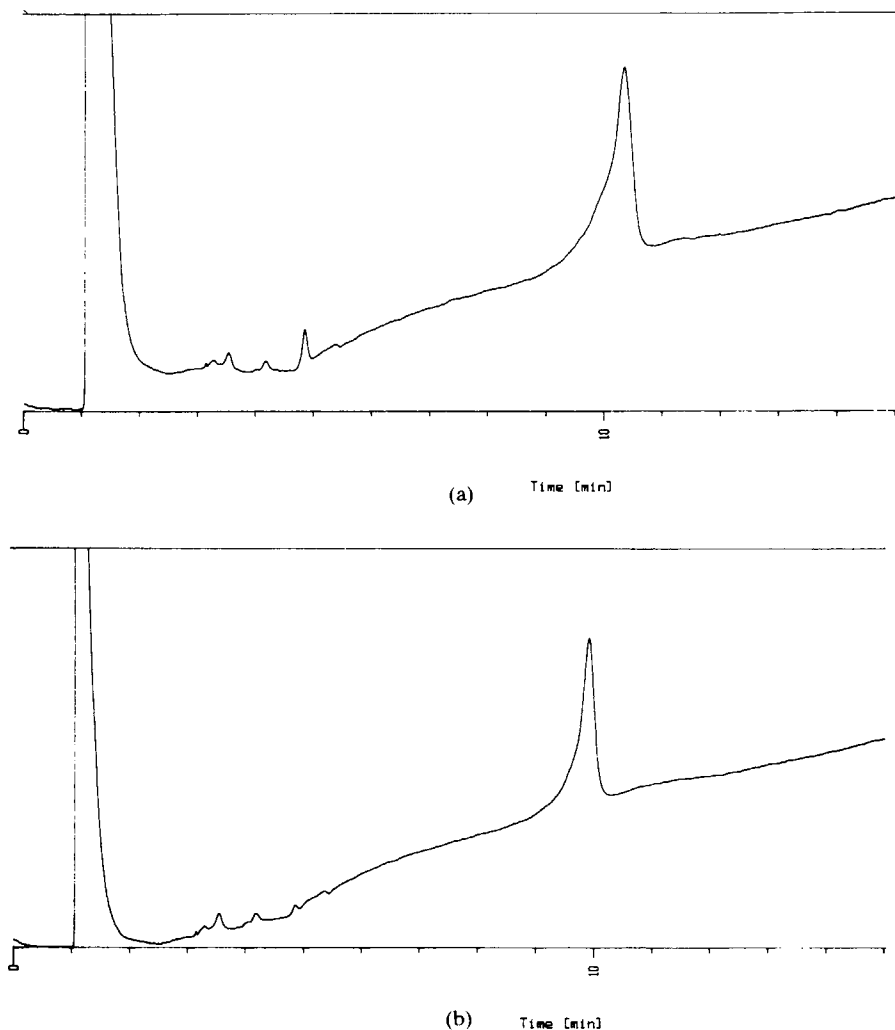
(a)   Time [min]

(b)   Time [min]

Fig. 1. Chromatograms of statistical copoly(styrene/t-butyl methacrylate) samples, silica column, $V_0 = 20\ \mu\mathrm{L}$, $m_0 = 8\ \mu\mathrm{g}$, gradient isooctane/THF (5%/min, no. 2), monitored at 259 nm wavelength, 25 mAU full scale: (1a) Specimen A (23.9% TBMA, $t_e = 10.37$ min); (1b) Specimen B (47.5% TBMA, $t_e = 9.93$ min).

way but unfortunately at the cost of the separating efficiency, which was small in any event.

The comparison of peak shapes in Figures 1 may cause suspicion concerning sample homogeneity. The peak in Figure 1(a) from the statistical copolymer A with 23.9% TBMA is broader than those obtained with the copolymers B or (not shown) C and D with a higher content in TBMA units. The copolymerization parameters for radical reactions at 60°C are $r_s = 0.56$ and $r_{\mathrm{TBMA}} = 0.60$. Thus, an azeotropic copolymer will contain 60.05% TBMA. Specimen A (23.9% TBMA) is rather far apart from this value and its peak seems to indicate some constituents with more TBMA (shorter retention) than the
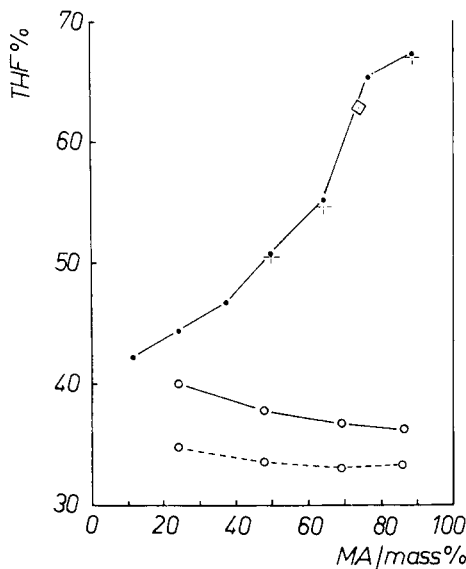
Fig. 2. Elution characteristics of statistical copolymers from styrene and t-butyl methacrylate (○) or methyl methacrylate (●, +) on silica column: (○——○) S/TBMA (samples A–D), gradient isooctane/THF (5%/min, no. 2); (○————○) S/TBMA (samples A–D), gradient iO + 2% MeOH/THF (5%/min, no. 3); (●———●) S/MMA, gradient iO + 2%MeOH/THF (5%/min, no. 7), data from Figure 11; (+) S/MMA, gradient iO + 2% MeOH/THF (5%/min, no. 6); (◇) S/MMA block copolymer from sample G by transesterification, gradient no. 7, data from Figure 11.

main portion of sample A. Before starting the investigation of this question, it was necessary to find conditions for better separation.

Figure 2 shows the elution characteristics of S/TBMA and S/MMA copolymers on the silica column. It is obvious that the chromatographic selectivity of the NP system is much better with S/MMA than with S/TBMA copolymers and that the addition of 2% methanol diminishes the small effect with the latter even more. Whereas S/MMA retention increases with MMA content, this is inverse for S/TBMA samples. Thus, the interaction between S/TBMA copolymers and the surface of the packing seems to be due predominantly to the phenyl groups of styrene.

Following this idea, we employed a phenyl bonded-phase column and used a THF gradient with 90% methanol in the starting eluent. In terms of polarity, this is a reversed-phase (RP) chromatographic system. Figure 3 shows the elution characteristic obtained, which indeed is steeper (and consequently more effective) than that of the NP system. The elution order is the same, i.e., increasing retention with increasing styrene content. Figure 4 shows the elution traces obtained after separate injections of samples A–D on the phenyl column. The differences in peak shape are still more obvious than in Figure 1.

In order to learn more about sample A, we performed HPLC investigation of SEC fractions from the mixture of this copolymer with small amounts of the B, C, and D added. The gradient chromatograms are shown in Figure 5. They support the assumption that sample A has a somewhat broader distribu-
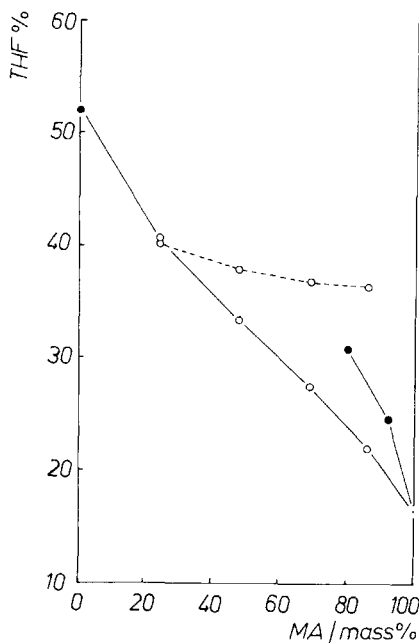
Fig. 3. Elution characteristics of copolymers from styrene and t-butyl methacrylate on phenyl column: (O———O) statistical S/TBMA copolymers A–D and TBMA homopolymer, gradient MeOH/THF (5%/min, no. 4), $V_0 = 40$ μL; (●———●) S/TBMA block copolymers G, H, and polystyrene PS 110K, gradient no. 4, $V_0 = 20$ μL; (O————O) statistical S/TBMA copolymers A–D on silica column (repeated from Fig. 2).

tion in composition than B, C, and D have. Especially the low-molecular SEC fractions contain species richer in TBMA than the bulk of sample A. These species certainly do not belong to the samples B–D whose molecular weight is higher and which are present in mixture M-1 only in small amounts (see Table I). The molecular-weight dependence of polymer retention in the RP system used may also have some influence. Information can in principle be derived from the peak shift seen in Figure 5.
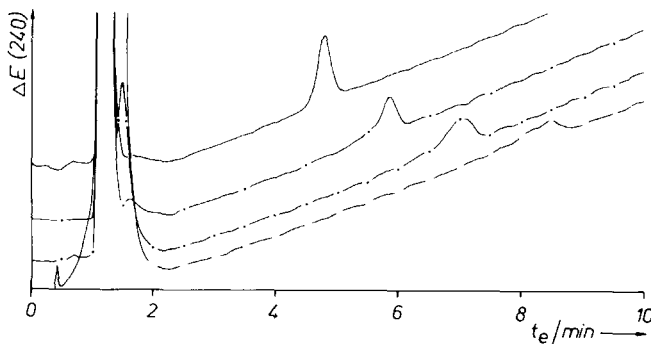

Fig. 4. Gradient elution of statistical S/TBMA samples D–A (from top to bottom) on phenyl column, $V_0 = 40$ μL, $m_0 = 16$ μg, gradient MeOH/THF (5%/min, no. 4), monitored at 240 nm wavelength, 50 mAU full scale.
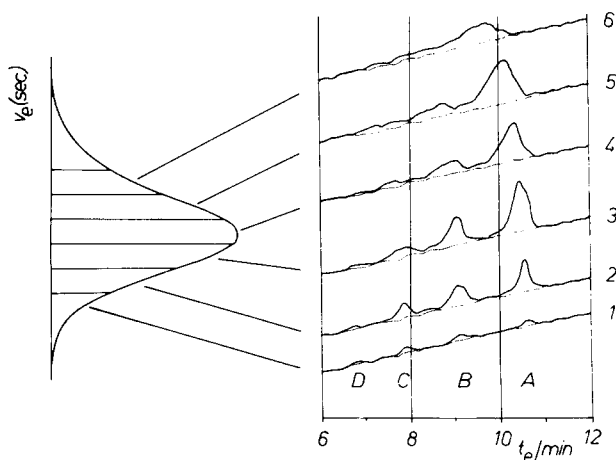
Fig. 5. Investigation of SEC fractions (obtained from 1.007 mg of mixture M-1 of four statistical S/TBMA samples) by gradient elution on phenyl column, gradient MeOH/THF (5%/min, no. 5), monitored at 259 nm wavelength. The injection volumes were 100 μL (fr. no. 1), 50 μL (fr. no. 2, 3, 5, 6), or 25 μL (fr. no. 4).

S / TBMA Block Copolymers

In analytical SEC, sample H produced a narrow peak without any significant difference between the UV and RI signal. The UV signal of sample E exhibited a shoulder at a slightly higher elution volume than the peak maximum had. The concomitant of sample F caused a small additional peak eluting at about 24.7 mL whereas the main portion of the sample was eluted at 23.3 mL. Sample G produced two distinct SEC peaks, i.e., a smaller one at about 24 mL (due to ABA triblock copolymer) and a larger one at 25.5 mL.

The traces obtained through gradient HPLC of the block copolymers on a phenyl column are shown in Figure 6. As with the statistical samples, reten-
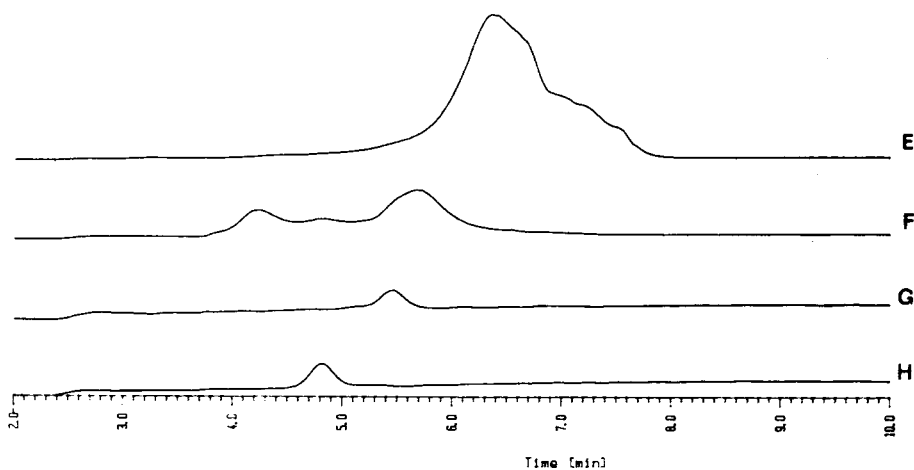

Fig. 6. Gradient elution of S/TBMA block copolymers E–H on phenyl column, $V_0 = 20$ μL, $m_0 = 8$ μg, gradient MeOH/THF (10%/min, no. 1), monitored at 259 nm wavelength, attenuation 500 (E), 250 (F), or 100 mAU full scale (G and H).

tion increased with styrene content. Since the chromatograms were monitored at 259 nm, the styrene units only contributed to the signal. This explains the differing area of the peaks which can be seen in Figure 6 in spite of the gradation in attenuation.

The broad band of sample F was unexpected. According to information derived from dual-detection SEC, this sample contains about 15% PS homopolymer. The latter would elute from the phenyl column used under the influence of gradient no. 1 at about 7.0–7.5 min. From the elution characteristics of samples G and H (see Fig. 3, filled circles) and the TBMA content of sample F, the composition of a methanol/THF eluent can be estimated at which sample F should be eluted. This composition corresponds to an elution range between 5.5 and 6.0 min where the greater part of the sample F really elutes (see Fig. 6).

In order to elucidate the reason of the unexpectedly broad band of sample F, we tried to extend the limits of detectability towards shorter wavelengths. In the region below 259 nm, e.g., at 230 nm, increasing THF concentration in the eluent causes baseline rise. This can be seen in Figure 7, where the chromatogram of sample F is plotted together with the recordings at 230 nm of the other block copolymers. Here, uniform attenuation could be applied. The presentation confirms the result shown in Figure 6.

As mentioned above, the combination of a phenyl column and a gradient formed by the addition of THF to methanol as a starting eluent determines an RP chromatographic system. In general, earlier elution in RP chromatography means higher polarity. However, in normal-phase (NP) chromatography, higher polarity would cause stronger retention, i.e., later elution. An NP system can result from the combination of a polar column, e.g., a silica column, with a gradient formed by the addition of THF to isooctane as a starting eluent. Figure 8 shows the elution patterns of the samples E–H in
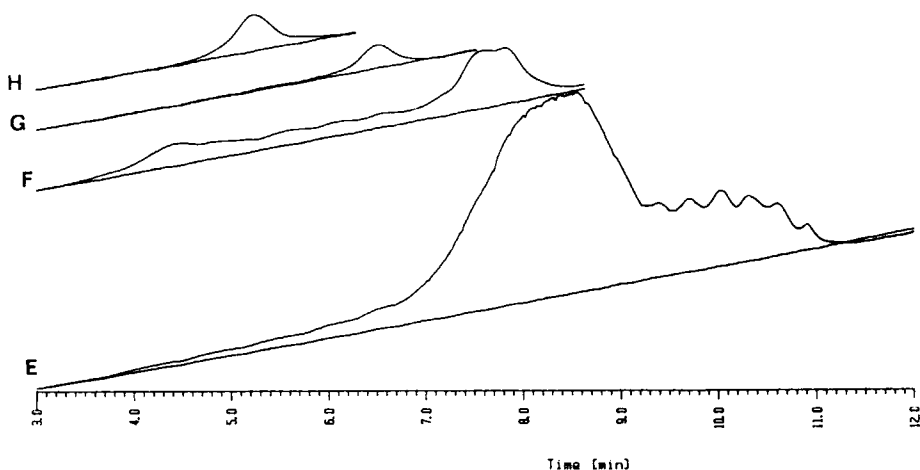

Fig. 7. Gradient elution of S/TBMA block copolymers E–H on phenyl column, $V_0 = 20 \mu L$, $m_0 = 8 \mu g$, gradient MeOH/THF (5%/min, no. 4), monitored at 230 nm wavelength, 160 mAU full scale. (The base line is the experimental one starting at the same zero level as the respective elution curve.)
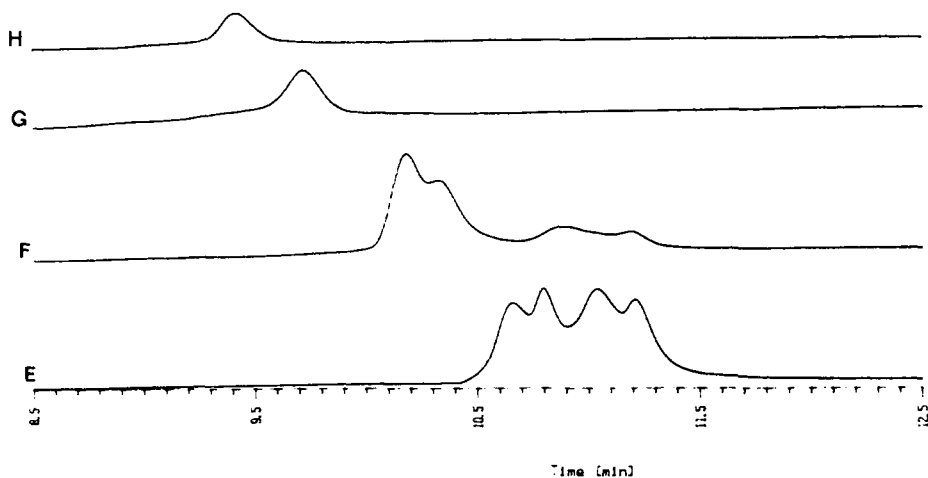
Fig. 8. Gradient elution of S/TBMA block copolymers E–H on silica column, $V_0 = 20 \, \mu l$, $m_0 = 8 \, \mu g$, gradient isooctane/THF (5%/min, no. 2), monitored at 259 nm wavelength, 100 mAU full scale.

this NP system. Retention slightly increases with styrene content. The main portion of sample F is eluted exactly at the expected position. The elution of the concomitant corresponds to that of PS.

In order to clarify whether the selectivity of the combination of a phenyl column with a gradient MeOH/THF would in principle suffice for separating S/TBMA block copolymers from admixed parent homopolymers, we investigated polystyrene (PS) together with either the block copolymer G or H. Both block copolymers show narrow bands in gradient HPLC, and their mixtures with polystyrene can be adjusted to give an average TBMA content corresponding to that of sample F. Figure 9 shows the elution of PS 110K at about
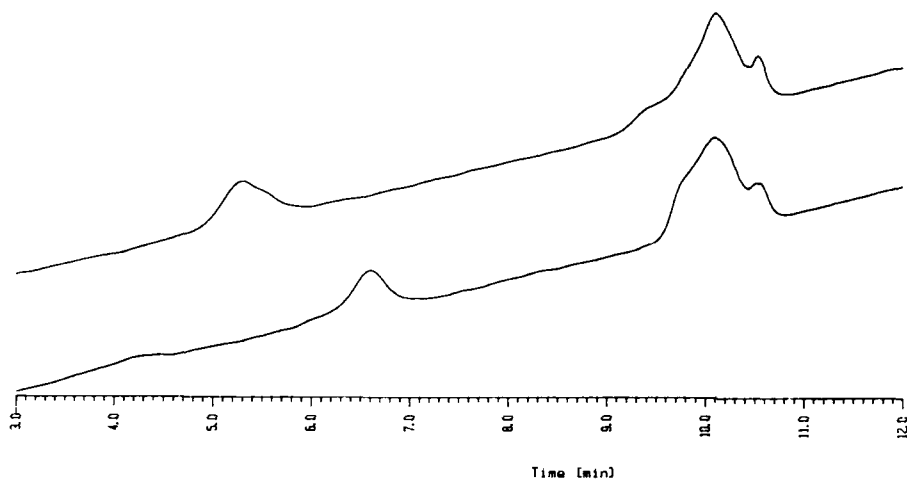

Fig. 9. Gradient HPLC on phenyl column of the mixture of PS with block copolymer H (upper curve) or G (lower curve), mixing ratio PS : (S/TBMA) = 1 : 5. $V_0 = 40 \, \mu L$, $m_0 = 16 \, \mu g$, gradient MeOH/THF (5%/min, no. 4), monitored at 230 nm wavelength, 125 mAU full scale.
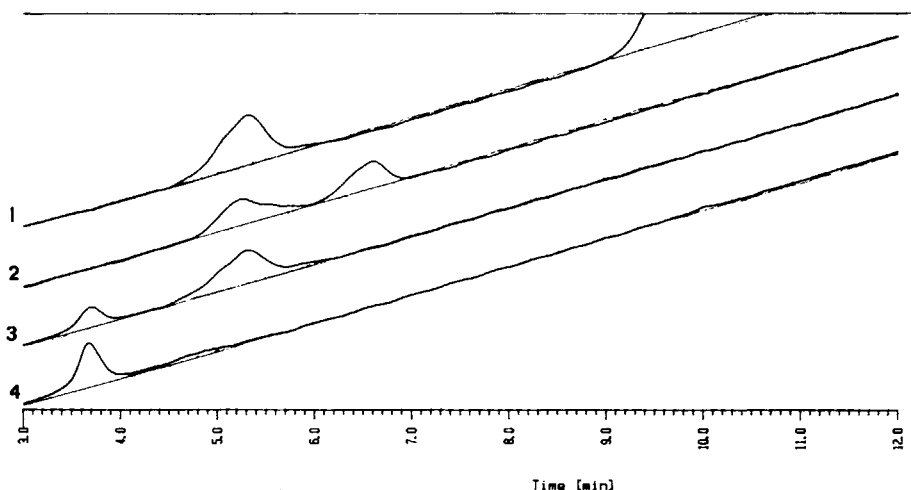
Fig. 10. Gradient HPLC of S/TBMA block copolymers on phenyl column: (1) block copoly-
mer H mixed with polystyrene (5:1); (2) block copolymers G and H (1:1); (3) block copolymer H
mixed with TBMA homopolymer (1:1); (4) poly(t-butyl methacrylate). $V_0 = 40 \mu L$, $m_0 = 16 \mu g$,
gradient MeOH/THF (5%/min, no. 4), monitored at 230 nm wavelength, 100 mAU full scale.

10 min and that of the block copolymers H and G at 5.2 or 6.5 min,
respectively. There is obviously no mutual disturbance on retention and
elution in these mixtures of block products and homopolystyrene.

One can object that this was an easy task since the gap in composition was
large. Therefore, we attempted also the separation of the samples G and H
from TBMA homopolymer. Figure 10 shows the result. The uppermost trace
once more shows the separation of the mixture of sample H (eluting between
4.8 and 5.6 min) and polystyrene (eluting from 9.2 min onwards). Chro-
matogram no. 2 in Figure 10 is from the mixture of the two block copolymers
G and H. Although the difference in composition is only 12%, both samples
were regularly eluted and baseline-separated. The third pattern was obtained
on injection of the mixture of sample H (92% TBMA) and TBMA homopoly-
mer. The lowermost trace is from this parent polymer without admixed
copolymer.

The crucial experiment was gradient elution of sample F together with
admixed PS. We used PS 2000 which is eluted distinctly later than the block
copolymer F. Increasing content of PS 2000 (20, 60, 100, 140% of amount of
sample F) in the mixture injected not only caused corresponding increase
of the PS peak but also two additional peaks between the traces of PS and of
block copolymer F. The area of these well-shaped peaks also increased in
proportion to the PS content of the mixture.[23]

Gradient HPLC of a S/MMA Block Copolymer

As a complement to the investigation of S/TBMA block copolymers, we
attempted to convert the TBMA blocks in MMA blocks by transesterification.
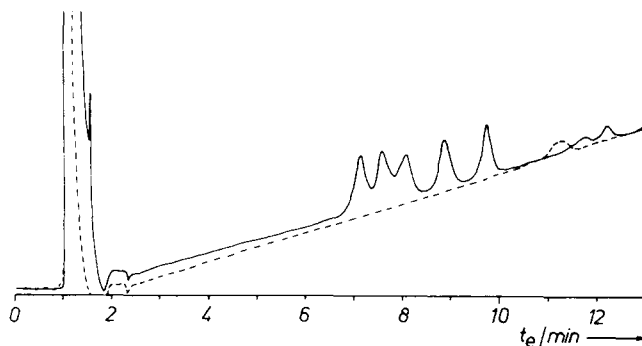These efforts were successful with specimen G which after transesterification

Fig. 11.   Gradient HPLC of S/MMA copolymers on silica column: (————) mixture of seven statistical copolymers; (— — —) block copolymer which was obtained by conversion of S/TBMA sample G into the corresponding methyl ester. $V_0 = 20 \mu L$, $m_0 = 8 \mu g$, gradient isooctate/THF (5%/min, no. 7), 259 nm wavelength, 30 mAU full scale.

contained 73.8 mass % MMA units. This sample was investigated under NP condition on the silica column. This procedure had been found suitable for S/MMA copolymers in previous investigations.[4, 24]

Figure 11 shows the chromatogram obtained from this sample (dashed curve) together with the corresponding one from a mixture of seven statistical S/MMA copolymers with compositions ranging from 11.4% MMA (eluting first) to 88.5%. (The position of these peaks was used in the calculation of the elution characteristic which has been shown in Fig. 2). The converted block copolymer was eluted in the position which corresponds to its content in MMA units. This can be seen from Figure 11 as well as from Figure 2.

CONCLUSIONS

In NP chromatography of S/MMA copolymers, retention increases with increasing content in methacrylate ester units in the samples. This and further features point to the fact that separation in this system is due to adsorption.[24] It is remarkable that the S/MMA block copolymer obtained by transesterification was eluted exactly in an eluent composition, which can be derived from the elution characteristics of statistical S/MMA copolymers (see Fig. 2). Thus, in this case the block structure seems to have only a minor influence on chromatographic retention.

The retention of S/TBMA copolymers decreases with increasing content in methacrylate in the sample. This indicates shielding of the polar ester group by the bulky t-butyl units. Separation by composition of these copolymers can be better achieved through the combination of phenyl interactions between solute and stationary phase with solvophobic interactions according to the principle of RP chromatography. Here, block copolymers have elution characteristics different from that of the statistical samples (see Fig. 3). This is an interesting effect, which possibly could facilitate separation by block length.

Finally it can be concluded that gradient HPLC has sufficient selectivity for application in the investigation of block copolymers. Thus, it can be a useful supplement to other methods as, e.g., SEC and NMR techniques.

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