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Separation of copolymers according to composition with special emphasis on the effect of block structure

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ABSTRACT

Block copolymers are a separate but important branch of copolymers. Like all copolymers, they are made of two (or more) different monomers, usually in a sequential manner. The characterization of block copolymers requires, among other things, the measurement of the precursor and other by-products. Gradient high-performance liquid chromatography, which has been used for the separation of statistical copolymers according to composition, can, under suitable conditions, also separate block copolymers with different molecular structures. This method has proved to be efficient even in cases where size-exclusion chromatography has failed. Block copolymers have longer retention times than statistical copolymers of the same composition. This is a result of the cooperative effect of adjacent repeat units.

INTRODUCTION

The objective of this paper is to review block copolymer synthesis and characterization methods, with an emphasis on the detection of homopolymer by-products.

BLOCK COPOLYMERS AND STATISTICAL COPOLYMERS

Copolymers are produced from at least two kinds of monomers. In the straightforward copolymerization of a binary mixture, the monomer reactivity ratios

$$r_A = k_{AA}/k_{AB} \quad (1)$$

$$r_B = k_{BB}/k_{BA} \quad (2)$$

govern the addition of either monomer A or B to the terminal A or B unit of a growing macromolecule.

Statistical copolymers usually consist of rather short sequences and can be described by the average sequence lengths

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$$L_A = 1 + r_A G \tag{3}$$

$$L_B = 1 + r_B/G \tag{4}$$

where $G = [A]/[B]$ is the molar ratio in the monomeric mixture.

Apart from systems with very high r values, or bipolymers with an extreme content of one of the monomers, the average sequence lengths of statistical copolymers are small in comparison with the degree of polymerization P. The lower limit is represented by alternating copolymers with $L_A = L_B = 1$, which are produced if $r_A = r_B = 0$ and $0 < G \ll \infty$.

A block copolymer is a copolymer in which the sequence lengths are of the same order of magnitude as P, *e.g.*, $L_A = L_B = P/2$ for a diblock copolymer with an equal molar content of the A and B units.

SYNTHESIS OF BLOCK COPOLYMERS

Block copolymers are produced in special reactions, usually in a sequential manner. In a sequential preparation, the A block of all the macromolecules is formed first, with the subsequent addition of the B block. Sequential copolymerization can be achieved by living polymerization of monomer A and (after the complete consumption of monomer A) continuation of the polymerization by the addition of monomer B. Diblock copolymers can be obtained by a termination reaction after the consumption of monomer B, whereas coupling reactions of the living A–B diblock copolymers can be used for the synthesis of A–B–A triblock copolymers.

A living polymerization reaction may be anionic or cationic in nature. Of these reactions, group transfer polymerization (GTP) [1–4] was found to be capable of producing polyacrylates or polymethacrylates with a narrow molecular weight distribution. As is common in proper living polymerizations, the molecular weight of the polymers (number average, M_n) obtained by GTP is controlled by the molar ratio of the monomer to the initiator. GTP was shown to yield binary block copolymers when two different kinds of monomer were fed successively [4,5].

If the addition of the second monomer causes deactivation of some of the precursor chains by side-reactions, the resulting block copolymer will be contaminated by a corresponding portion of precursor homopolymer. Coupling occurring as a side-reaction in the termination step of diblock copolymer synthesis also causes contamination of the desired product.

Block copolymers can also be obtained by free radical polymerization using, *e.g.*, multifunctional initiators. Using a polyester peroxide with five or six peroxide bridges within its backbone, commercial block copolymers were produced by polymerizing methyl methacrylate (MMA) at 65°C and, subsequently, styrene (S) at 75°C. The rather broad distribution in products of this kind, which is to be expected from the statistical processes of peroxide cleavage and chain termination, has been studied experimentally [6]. Block copolymers of vinyl acetate and styrene were also prepared by the stepwise decomposition of polymeric peroxides. The separation of three samples by gradient high-performance liquid chromatography (HPLC) and size-exclusion chromatography (SEC) revealed a broad distribution in chemical composition [7]. The molecular weight of fractions increased with vinyl acetate content.

The synthesis of block copolymers through free radical polymerization is also feasible by subjecting an initial homopolymer (poly-A) to mechanical stress in the presence of monomer B. Mechanical forces created by, *e.g.*, ball milling, mastication, or freezing and thawing of aqueous solutions may break the polymer chains. The segments are polymeric free radicals. The ends where the break occurred can, under favourable conditions and in the absence of radical-capturing agents, add units of monomer B by free radical polymerization, thus forming di- or triblock copolymers, AB or ABA, respectively.

Block copolymers can be obtained by transformation of a suitable end-group of a precursor polymer into a group capable of initiating another polymerization of a different monomer (with the incorporation of the precursor chain) or by the coupling of different kinds of prepolymers through mutually reactive end groups.

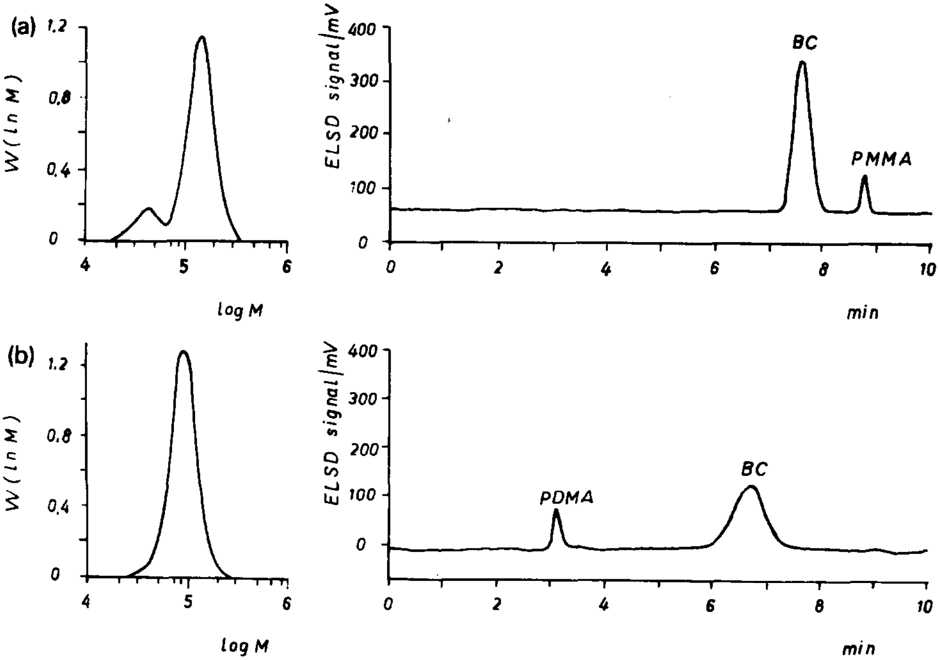

Fig. 1. (a) Block copolymer 9-16 (methyl methacrylate–decyl methacrylate, 36 mol% MMA, M_n = 155 500) containing 13.5% (w/w) PMMA precursor (M_n = 31 000). Left panel: molecular weight distribution (MDW) by SEC on a bank of two PS gel columns (TSK GMH6, 600 × 7.5 mm each, Toyo Soda, Tokyo Japan) with THF eluent, flow-rate 1 ml/min, injection volume 0.3 ml of a 1 g/l sample solution in THF, PMMA calibration. Right panel: gradient HPLC on a cyanide (CN) bonded phase column (60 × 4 mm, packed with Nucleosil 5 CN, $d_0 \leqslant 5$ nm, $d_p = 5$ μm) at 40°C and 1 ml/min flow-rate; injection volume 5 μl of a 5 g/l solution in THF. Gradient: iso-octane–THF (1% constant for 1 min, followed by 1–81% within 8 min). Detection by evaporative light scattering detector (ELSD). Molecular weight of the whole sample (block copolymer + PMMA contaminant), 101 000. Experimental results from ref. 25. (b) Block copolymer 9-13 (decyl methacrylate–methyl methacrylate, 27.5 mol% MMA, M_n = 89 600) containing 10.6% (w/w) PDMA precursor (M_n = 76 700). Left panel: MWD by SEC, conditions as in (a). Right panel: gradient HPLC; for conditions see (a). Molecular weight of the whole sample (block copolymer + DMMA contaminant), 88 000. Experimental results from ref. 25. BC = Block copolymer.

DETECTION OF BY-PRODUCTS

The sequential synthesis of block copolymers allows the measurement of (1) the precursor molecular weight, *i.e.*, $M_{n,A}$ and $M_{w,A}$ (weight average) and (2) the molecular weight of the final product, *i.e.*, M_n and M_w. The ratio $M_{n,A}/M_n$ should equal the weight fraction of monomer A in the copolymer and also the weight fraction of monomer A in the monomeric feed. Deviations indicate side-reactions.

As a result of the limited accuracy of molecular weight measurements, agreement between experimental and calculated molecular weights cannot sufficiently prove the absence of side-reactions. The latter can be detected this way only if they occur to a relatively high degree.

A similarly pessimistic view holds for any other method which measures average values. Thus, separation techniques are required which are capable of discriminating between the actual block copolymer and possible by-products. Unfortunately, the familiar methods of fractionation by precipitation or dissolution are often not efficient enough for these difficult separations [8–11]. Density-gradient ultracentrifugation has been used for the estimation of homopolymer impurities in block copolymers [12,13].

SEC has often been used for revealing the presence of by-products [14–24]. Of course, a prerequisite is a sufficient difference in molecular weight between the unreacted precursor and the block copolymer. The left panel of Fig. 1 shows the results obtained by Müller *et al.* [25] which demonstrates success (Fig. 1a) or failure (Fig. 1b) of SEC investigations on different block copolymers of the monomer systems decyl methacrylate (DMA) and methyl methacrylate (MMA). The upper chromatogram (left panel of Fig. 1a) shows a small peak due to the polyMMA (PMMA) content of the sample, the block copolymer portion of which was eluted in a large peak. In this instance, SEC was successful. The lower chromatogram (left panel of Fig. 1b) shows only an unimodal SEC peak for a sample which consists of a block copolymer and a polyDMA (PDMA) homopolymer. In this instance, SEC failed to separate the two components.

CHROMATOGRAPHIC SEPARATION ACCORDING TO COMPOSITION

Methods for separation by chemical composition rather than by molecular weight should be better suited for the evaluation of by-products. Inagaki and coworkers used thin-layer chromatography (TLC) for the characterization of S–MMA [26–29] or S–butadiene (Bd) block copolymers [30]. Belenkii and Gankina [31] also performed TLC of S–MMA block polymers [31]. A paper by Gankina *et al.* [32] presents TLC analyses of poly(S–*b*–MMA), poly(S–*b*–Bd), poly(S–*b*–ethylene oxide), poly(S–*b*–acrylonitrile), poly(BG–*b*–S–*b*–BG), poly(MMA–*b*–BG) as well as poly(I–*b*–MS–*b*–I) and mentions poly(MMA–*b*–BMA), where *b* = block, BG = γ-benzyl glutamate, I = isoprene, MS = α-methylstyrene, and BMA = butyl methacrylate.

Gradient HPLC is well suited for separating statistical copolymers by composition [33–36] (for survey, see refs. 37,38,59). Gradient HPLC was also applied to block and statistical copolymers of styrene and *tert.*-butyl methacrylate (TBMA) [39].

Copolymers of S and MMA [34,40,41] or ethyl methacrylate [42] can be separated according to composition on polar columns, *e.g.*, packed with silica [34,40], cross-linked poly(acrylonitrile) [41] or a nitrile bonded phase [42], through gradients increasing with eluent polarity, *e.g.*, iso-octane–tetrahydrofuran (THF). These chromatographic systems yielded retention times increasing with methacrylate content, *i.e.*, these separations of synthetic copolymers followed the principles of normal-phase separations. Attempts to separate the statistical copolymer S–TBMA in this manner have so far failed. Samples with a TBMA content between 24 and 86% (w/w) were, on a silica column, eluted in iso-octane–THF mixtures whose composition varied by less than 5% [39].

What was remarkable in this work was the fact that retention slightly decreased with increasing methacrylate ester unit content, the opposite of the behaviour of the corresponding copolymers with methyl or ethyl methacrylate units. This surprising effect indicated that *tert.*-butyl alcohol groups diminished the adsorption of –COO groups on silica to such an extent that the remaining interactions between the solute and stationary phase were due to the styrene units of the copolymer. Thus injections were repeated on a phenyl bonded phase column with a gradient methanol–THF, *i.e.*, employing a reversed-phase chromatographic system. This yielded a pronounced increase in retention with rising styrene content and a substantial gain in selectivity [39]. The combination of methanol–THF gradients with a C_{18} bonded phase column was also effective in separating S–TBMS copolymers.

GRADIENT HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY FOR THE MOLECULAR SEPARATION OF BLOCK COPOLYMERS

The failure of familiar fractionation techniques [8–11] is due to the tendency of block copolymers to form micelles by association of the less solvated blocks when the solvent strength decreases. Hence, it is interesting to see if gradient HPLC is capable of separating block copolymers on a molecular level. The possibility of forming aggregates must not be ignored because, to obtain the correct retention, the solvent strength of the eluent may be low in gradient HPLC.

Of the S–TBMA block copolymers investigated, two samples [with 26 or 55% (w/w) TBMA containing 40 or 15% polystyrene precursor, respectively] eluted from the phenyl column in broad bands, whereas block copolymers containing 80 or 92% TBMA formed well shaped peaks. Mixtures of these samples with either polyS (PS) or polyTBMA (PTBMA) homopolymers yielded patterns which showed the admixture baseline separated from the block copolymer, the peak of which remained almost unchanged. The mixture of both copolymers also yielded two separate peaks without mutual interference. These results indicate a molecular separation [39].

Separation on a molecular level was found also by Augenstein and Müller [43] in the investigation of poly(DMA-*b*-MMA) samples on a cyanide bonded/phase column through gradients iso-octane–THF. Mixtures of two or three block copolymers yielded tracings which were simply the superimposition of individual chromatograms.

A quantitative determination was also carried out [43] by measured additions of PDMA homopolymer to a DMA–MMA block copolymer and integration of the PDMA signal. The block copolymer was obtained with a PDMA precursor and a monomer feed of 75:25 mol% DMA–MMA. The results from the measured addition of PDMA adhered to a linear calibration which was established by injections of

PDMA alone in the range 4–10 μg, thus indicating the separation of the PDMA homopolymer from the block copolymer. Subtracting the known addition of homopolymer from the amount calculated from the peak area, the content of PDMA precursor in the block copolymer was also determined with excellent reproducibility. The PDMA precursor was 10.6 ± 0.1% (w/w) (mean value of duplicate injections at five different levels of PDMA addition). The result, which was confirmed by repetition on a silica column, enabled the block yield to be calculated with similar precision.

The procedure marks a real advance in the characterization of block copolymers. The importance of this should be appreciated, because the block copolymer was that mentioned earlier, which showed an apparently monotonous SEC peak due to a precursor molecular weight amounting to 85.6% of the final molecular weight (89 000).

In contrast to these favourable results, a warning must be given against the association phenomena which may occur under other chromatographic conditions. Augenstein and Müller [43] observed the puzzling elution behaviour of DMA–MMA block copolymers under reversed-phase conditions with gradients of methanol–THF. This observation matches observation with a certain S–TBMA block copolymer on the addition of a PS homopolymer [44] where the PS molecular weight affected the type of associations formed.

PROLONGED RETENTION OF BLOCK COPOLYMERS

Under equivalent chromatographic conditions, block copolymers were retained longer than statistical copolymers of the same composition. This was found with S–TBMA samples [39] (Fig. 2a). A similar result can be deduced from the observations in a paper dealing with the separation by composition of S–Bd copolymers [45]. This was recently confirmed on the basis of a thorough investigation of DMA–MMA copolymers [25,43] (Fig. 2b) in which the excess retention of block copolymers was larger than with S–TBMA copolymers. This is due to the large difference in adsorption between MMA and DMA units in contrast to a more moderate difference between TBMA and S units.

The effect of block length on retention can be understood on the basis of a model [37] which takes into account the fact that polymers consist of repeat units which, on adsorption, form a "trains". For the adsorption of n repeat units with retention factor k'_u for each unit, the retention factor of the whole train becomes:

$$k'_{\text{total}} = (k'_u + 1)^n - 1 \qquad (5)$$

With homopolymers, n is large, which has a significant effect on k'_{total}. Even k'_u values which only slightly exceed zero give rise to high k'_{total} data.

The diffent kinds of repeat units in copolymers will under given chromatographic conditions, be adsorbed differently. The consequences of this are diffent k'_u values for unlike constituting units. As, by eqn. 5, extremely small k'_u values suffice for k'_{total} data of the usual order ($2 \leqslant k'_{\text{total}} \leqslant 10$), the retention of copolymers will mainly be caused by the adsorption of only one kind of constituting unit. These units interact with a stationary phase under conditions where, for the chromatographically weaker units, k'_u is virtually zero.

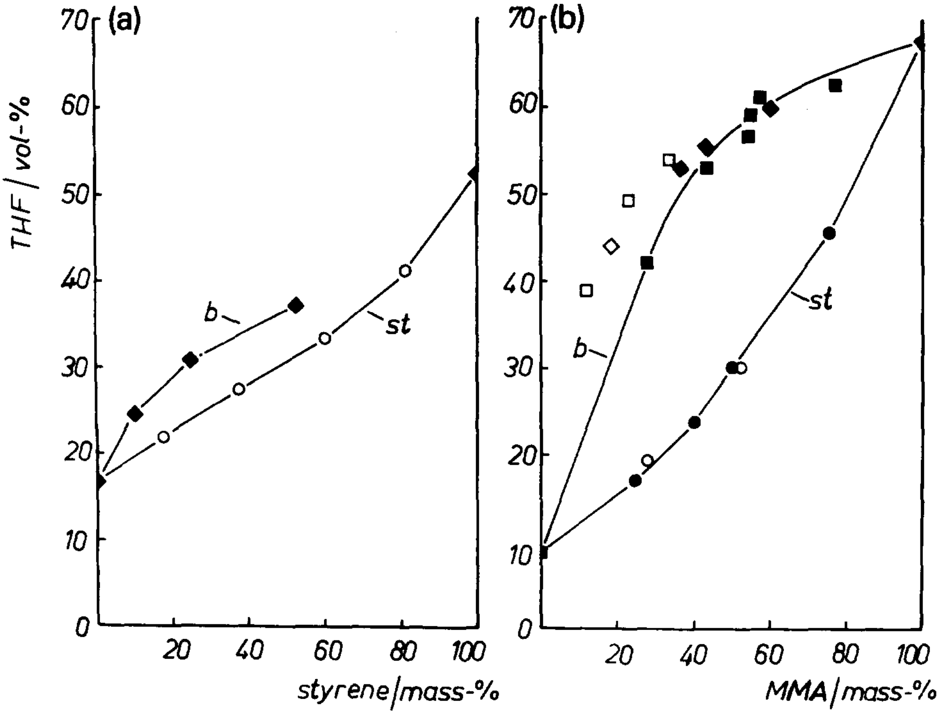

Fig. 2. (a) Elution characteristics of copolymers from styrene and *tert.*-butyl methacrylate of either statistical (○) or block architecture (◆). Phenyl bonded phase column (60 × 4 mm, $d_0 \leqslant 5$ nm. $d_p = 7$ μm) at 50°C and 0.5 ml/min flow-rate; injection volume 40 μl (statistical) or 20 μl (block copolymers) of 0.4 g/l solutions in THF. Gradient, methanol–THF (10–70% within 12 min), UV signal at 254 nm. Data from ref. 39 (b) Elution characteristics of copolymers from methyl methacrylate and decyl methacrylate of either statistical (circles) or block architecture (squares). (●) Statistical copolymers from group transfer polymerization; (○) same, from free radical polymerization; (■) block copolymers from group transfer polymerization, precursor PDMA; (◆) same, precursor PMMA; (□) and (◇) same, but molecular weight ⩾ 160 000. CN bonded phase column (60 × 4 mm, packed with Nucleosil 5 CN, $d_0 \leqslant 5$ nm, $d_p = 5$ μm) at 40°C and 1 ml/min flow-rate; injection volume 5 μl of a 5 g/l 1 min, followed by 1–81% within 8 min). Detection by evaporative light scattering detector. Data from ref. 43.

As a result of the small values of average sequence length in statistical copolymers the latter can, towards a stationary phase, expose only rather short trains of chromatographically active units, whereas block copolymers expose much longer trains. The larger number of consecutive repeat units in the latter give rise to a higher exponent *n*, which accounts for the stronger retention observed with block copolymers.

EFFECT OF MOLECULAR WEIGHT

The chromatographic behaviour of copolymers is determined by chemical composition and molecular weight. The latter effect can be described by:

$$\varphi_{NS} = A - B\,M^{-0.5} \tag{6}$$

where φ_{NS} is the volume fraction of the non-solvent (or weak eluent) at peak elution and A and B are constants. Originally stated for the effect of molecular weight on polymer solubility [46]. eqn. 6 was also found to be fulfilled by chromatographic results with excellent correlation, even under conditions where solubility is possibly not the predominant mechanism of retention [47–49]. Usually, the molecular weight effect on retention is small in comparison with the influence of copolymer composition. The parameter B is especially small when adsorption prevails and increases when solubility contributes substantially to retention. (For a discrimination between adsorption and solubility effects in polymer HPLC see, *e.g.*, ref. 50).

From eqn. 5 it was deduced that, under the given chromatographic conditions, the retention increases with the length of an adsorbed train. With block copolymers, the block length of chromatographically active units increases with the overall content in these units and the molecular weight of the polymer. Doubling of either of these values would double the number of the anchoring groups. This reasoning indicates that a molecular effect will be more pronounced in block copolymers than in statistical copolymers.

This has been reported by Augenstein and Müller [43], who measured a rather large value of $B = 40$ (see eqn. 6) for the MMA blocks in poly(DMA-*b*-MMA). They found that DMA–MMA block copolymers eluted earlier than PMMA homopolymers with a length similar to that of the MMA block in the copolymers. This indicates a "dragging" effect of the non-adsorbed DMA block on the adsorbed MMA block and demonstrates that, in contrast to low-molecular-weight adsorption, the interaction of polymer solutes with the mobile phase must not be ignored. Increasing the length of a dragging tail should increase its loosening effect. This expectation is in line with the slightly earlier elution of block copolymers of $M_n \approx 200\,000$, in comparison with other copolymers with the same PMMA block lengths but $M_n \approx 160\,000$. This exception aside, the common plot of eluent composition *versus* MMA block length for multifarious DMA–MMA block copolymers resembles a prediction of the critical elution theory [51–54].

ELUTION OF POLYMERS UNDER CRITICAL CONDITIONS

The critical elution conditions of polymers refer to a narrow intermediate state in the transition from SEC retention to retention due to adsorption. Here, at given eluent strength and temperature, the elution is independent of polymer molecular weight. This was first measured by Tennikov *et al.* [55] with PS standards on silica columns and confirmed by numerous other workers. For a survey, see ref. 56.

Among the features of critical elution is the important fact that oligomers can be separated exclusively by functionality when the elution conditions meet the critical conditions for the polymer chain [57]. Under these circumstances, the polymer portions of the molecules become "invisible". Theory predicts [54] that with block copolymers either of the constituting blocks may also become "invisible" under its critical conditions, which would allow the exclusive separation according to the length of the other blocks.

Critical conditions can be established on stationary phases, the pore size of which would also allow the SEC separation of the polymer under investigation. The results with poly(DMA-*b*-MMA) samples which showed retention (almost) exclusively due to the MMA blocks were obtained on small-pore packings (pore diameter $d_0 \approx 5$ nm). Thus, although similar in appearance, the observed effect is certainly not caused by critical elution of DMA blocks.

TLC experiments with poly(S–*b*–MMA) samples, where either the PS or the PMMA block is "invisible", have been performed by Gankina [58]. Under the critical conditions for the styrene block, the retention of the block copolymers increased with MMA block length due to the adsorption of the latter. Under critical conditions for the MMA block, the retention decreased with increasing size of the S block due to an SEC mechanism.

CONCLUSIONS

The paper has shown that reliable characterization of the by-products in block copolymers require separation methods. Gradient HPLC was found to be more efficient for this purpose than SEC or fractionations based on solubility differences.

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