

Separation of block copolymers from parent homopolymers by means of liquid chromatography at the critical adsorption point

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Summary

The characterization of a block copolymer consisting of blocks of tetrahydrofuran, THF, and methyl methacrylate, MMA, was attempted with the aid of liquid chromatography, LC, at the critical adsorption point, CAP. The conditions applying to the CAP at 30°C for the homopolymers are: PTHF: eluent composition: THF:acetonitrile = 50:50, w/w; column: Nucleosil C₁₈. PMMA: eluent composition: THF:n-hexane = 81.8:18.2, w/w; column: bare silica gel. The presence of homo PTHF and of homo PMMA in the crude block copolymer was evidenced. Moreover, chromatography at the CAP for PMMA showed that the block copolymer contains multiblock (triblock) fractions. The formation of triblock copolymer is expected when the polymerization of MMA is terminated (partially) by combination. In conclusion, LC at the CAP is a powerful tool to characterize block copolymers regarding the presence of homopolymer and multiblock (triblock) fractions.

Introduction

The synthesis of block copolymers, i.e. linear polymers consisting of blocks of chemically different repeating units, opens a way to adjust properties of polymeric materials. Multi-mode polymerization (1) is an elegant method to prepare block copolymers. In this case different kinds of propagating species are combined to form blocks of chemically differing repeating units. For example, block copolymers of methyl methacrylate (MMA) and tetrahydrofuran (THF), that are polymerizable by different propagation mechanisms, can be prepared by this method. The increasing utilization of block copolymers as materials with novel properties has provoked a need for analytical methods suitable for their proper characterization. The latter encompasses various aspects, such as the simultaneous existence of homopolymers and block copolymers in the product, the molar mass distribution of the block copolymer and the length distribution of the blocks. Frequently, the detection of homopolymer is quite important, because the homopolymer might affect significantly (sometimes in a devastating manner) the desired properties of the product and its removal might be necessary. Consequently, whenever block copolymers are synthesized it is important to know, whether and to which extent the products contain homopolymers.

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Size exclusion chromatography (SEC) is the most widely used liquid chromatographic method for molecular characterization of polymeric materials. However, the straightforward application of SEC to multi-component polymer systems is only possible if the hydrodynamic volume of the constituents differs so significantly that chromatographic resolution can be achieved by an appropriate column. For block copolymers an additional analysis method is required to distinguish between various blocks, because generally the SEC separates macromolecules according to their size and not to their composition. Here, the liquid chromatography at the critical adsorption point (LC CAP) (2, 3) appears to be a promising tool.

The present paper demonstrates how the LC CAP method can be applied to examine block copolymers consisting of methyl methacrylate and tetrahydrofuran blocks. Special emphasis was given to the detection of the parent homopolymers PMMA and PTHF in the polymeric product.

Principle of the LC CAP method

The LC CAP method is based on two separation mechanisms referring to size exclusion (entropic, size exclusion chromatography - SEC) and to adsorption (enthalpic, liquid adsorption chromatography - LAC). The critical adsorption point (CAP) for a certain polymer type corresponds to specific conditions (eluent composition, temperature, pressure, nature of the column packing material) at which the two mechanisms are mutually compensated. Consequently, separation according to molar mass differences does not take place at the CAP, where all macromolecules of a homopolymer sample irrespective of their molar mass are eluted from the column at the same elution volume. The latter is roughly equal to the total volume of liquid in the column. In the case of a sample consisting of two different homopolymers only one of them is eluted according to the size exclusion mechanism provided the conditions apply to the CAP of the other one. Therefore, the detection of homopolymer generated in parallel during the preparation of the block copolymer is feasible. Normally, the LC CAP method is applied twice for the determination of the molar mass distribution of each block in a diblock copolymer.

Experimental

Chromatography

All chromatographic separations were performed at 30°C with a liquid chromatography set-up comprising a model 510 pump (Waters, Milford, USA), a six-port three-way injection valve provided with a 20 µL loop (Knauer, Berlin, Germany), one or two columns, a model DDL-21 evaporative light scattering detector operated at 60°C (Cunow, Cergy Pointoise, France) and a column oven (Knauer, Berlin, Germany). The following columns were used: (a) a single analytical SEC column, 300x7.5 mm, packed with polystyrene-divinylbenzene (PS-DVB) gel, particle size 10 µm (Polymer Laboratories, Shropshire, UK), (b) a single column, 250x8 mm, packed with Biospher, bare silica gel, pore size 12 nm, particle size 10 µm (Labiog, Prague, Czech Republic), (c) a set of two columns, 250x4 mm, packed with Nucleosil C₁₈, silica gel bonded with C₁₈ groups, pore size: 30+100 nm, particle size: 5+7 µm, resp. (Knauer, Berlin, Germany). The detector signal was processed by means of a PC operated in conjunction with the baseline data acquisition system (Waters, Milford, USA). Polytetrahydrofuran standard samples of narrow molar mass distribution (Polymer Laboratories, Shropshire, UK) and

poly(methyl methacrylate) samples of relatively broad molar mass distribution (Röhm, Darmstadt, Germany) were used for the identification of the CAP.

Solvents

Tetrahydrofuran (THF) and its mixtures with either n-hexane or acetonitrile (ACN) were used as eluents. Mixed eluents were prepared on the weight basis of the components.

Synthesis of block copolymer

The block copolymer was prepared according to the following method (see Chart 1) (4): The living polymerization of THF was initiated by triethyloxonium ions at 25°C and the propagating chains were reacted with the N-oxide of 2-picoline resulting in PTHF terminated by 2-methyl pyridinium ions. The average molar mass of this *prepolymer*, $M_n = 7.8 \times 10^3 \text{ g mol}^{-1}$, was determined by SEC on the basis of the calibration with polytetrahydrofuran standards. Upon subjecting the prepolymer to UV irradiation in the presence of anthracene (photosensitizer) and MMA the polymerization of MMA was initiated. Noticeably, a block copolymer of the A-B type would be obtained by this method provided the termination of growing PMMA chains occurred exclusively by disproportionation. As inferred from the literature, this is, however, not the case. A relevant review on this aspect (5) reveals that the polymerization of MMA is terminated by both combination and disproportionation. However, there is considerable discrepancy in the precise values of the rate constant ratio k_{td}/k_{tc} . Most values are in the range 1 to 3 corresponding to a fraction of growing chains terminated by combination ranging from 50 to 25%. In our case termination by combination results in the formation of a block copolymer of the A-B-B-A type and the presence of such macromolecules in the polymeric product has to be considered.

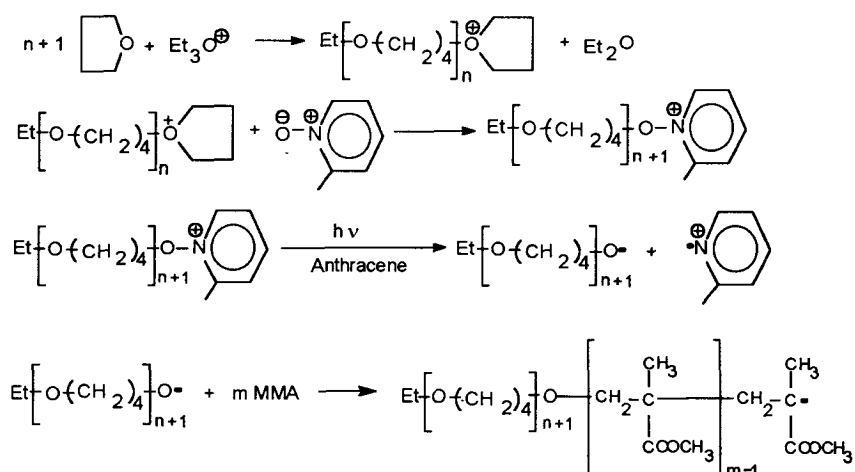


Chart 1. Synthesis of a copolymer consisting of polytetrahydrofuran and poly(methyl methacrylate) blocks

Results and discussion

Homopolymers

PTHF and PMMA are eluted in the SEC mode from chromatographic columns packed with PS-DVB gel, with silica gel bonded with C₁₈ groups or even with bare silica gel provided neat THF is used as the eluent. In all cases PMMA samples exhibit higher retention volumes than the PTHF samples of equal molar mass which is probably due to the smaller hydrodynamic volume of PMMA coils in THF solution. The weak adsorption of PMMA on silica gel increases this effect. In spite of this fact the separation of the components of about equal molar mass from PMMA/PTHF blends (1:1, w/w) was not achieved (using THF as eluent) when the SEC gel column was used and only an incomplete discrimination of the constituents was possible with the aid of the Biospher column.

Upon employing eluents consisting of two-components, THF/acetonitrile (ACN) in the case of PTHF and THF/n-hexane in the case of PMMA, the retention volume becomes larger with increasing content of ACN or n-hexane, respectively. At a certain eluent composition all polymer samples are eluted from the column at nearly the same retention volume regardless of the molar mass. The solvent composition applying to the CAP, also denoted as the "critical composition", is THF:ACN = 50:50, w/w, for PTHF (Nucleosil C₁₈) and THF:n-hexane = 81.8:18.2, w/w, for PMMA (bare silica gel). The CAP is very sensitive to slight changes in the eluent composition. If the eluent contains a small excess of the adsorption-promoting liquid, i.e. ACN or n-hexane, respectively, the elution occurs according to the liquid adsorption chromatographic (LAC) mode. Notably, PMMA is eluted in the SEC mode at the critical adsorption point for PTHF (Nucleosil C₁₈) and PTHF is eluted in the SEC mode at the critical adsorption point for PMMA (bare silica gel). This can be seen from Figs. 1 and 2 where calibration curves for PTHF and PMMA recorded at the CAP are presented.

Blends of homopolymers

In order to prove whether a separation of homopolymers is possible at the CAP 1:1 blends of PTHF and PMMA were analyzed. Typical results are also presented in Figs. 1 and 2. Fig.1 shows chromatograms of three PTHF/PMMA blends obtained with the Biospher column and THF/n-hexane eluent at the CAP for PMMA and Fig.2 shows chromatograms of two 1:1 PTHF/PMMA blends obtained with the Nucleosil C₁₈ column and THF/ACN eluent at the CAP for PTHF. It can be seen from Figs. 1 and 2 that under CAP conditions the homopolymers can be satisfactorily separated.

Block copolymers

(a) SEC

The SEC chromatogram of the crude block copolymer recorded with the Biospher column using THF as eluent consists of a large peak followed by a broad shoulder indicating a bimodal molar mass distribution (not shown). A small peak at high elution volume is ascribed to an impurity originating probably from the synthesis. The chromatogram recorded with the SEC gel column possesses Gaussian shape. Also here a small peak at high retention volume was noted (not shown).

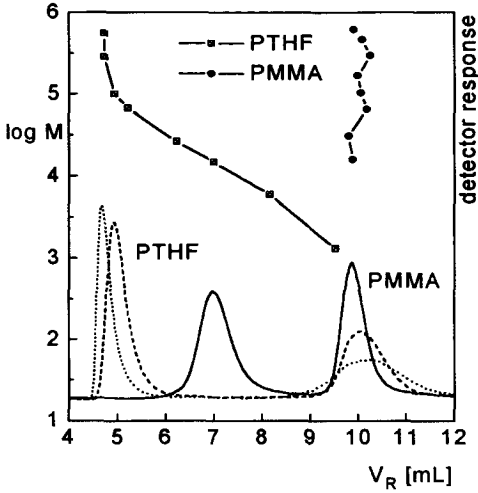


Fig.1 Calibration curves for PTHF and PMMA and chromatograms of PTHF/PMMA blends (1:1, w/w). Column: Biospher. Eluent: THF:n-hexane = 81.8:18.2, w/w.

—: PTHF 15000 g/mol + PMMA 16000 g/mol
 - - - : PTHF 99900 g/mol + PMMA 103000 g/mol
 : PTHF 283000 g/mol + PMMA 294000 g/mol

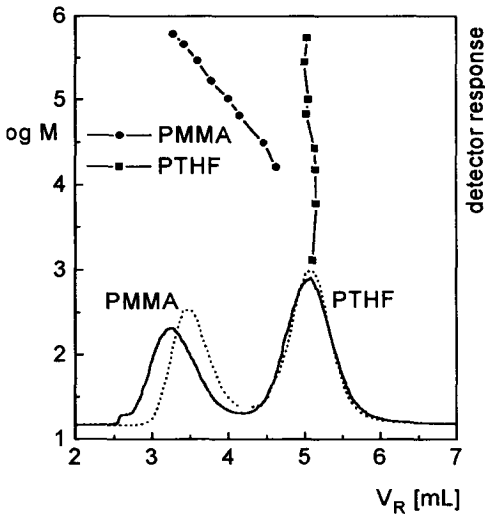


Fig.2 Calibration curves for PTHF and PMMA and chromatograms of PMMA/PTHF blends (1:1, w/w). Column: Nucleosil C_{18} . Eluent: THF:ACN = 50:50, w/w.

—: PMMA 613000 g/mol + PTHF 283000 g/mol
 : PMMA 294000 g/mol + PTHF 99900 g/mol

(b-1) LC at the CAP for PMMA

As can be seen from Fig.3 the chromatogram of the purified sample consists of a shoulder at $V_R \approx 4.8$ mL and peaks at $V_R \approx 5.0$ mL and $V_R \approx 5.9$ mL. Moreover, there is a very small peak at $V_R \approx 10$ mL which corresponds to homo PMMA. Obviously, the latter exists to an almost negligible amount in the product. The retention volume of the peak at $V_R \approx 5.9$ mL is equal to that of the peak of the PTHF prepolymer. Actually, at the CAP for PMMA, this polymer is chromatographically "invisible", i.e. both prepolymer and AB block copolymer are expected to be eluted simultaneously, in the present case at $V_R \approx 5.9$ mL. Since the (purified) block copolymer contains only a small portion of unreacted prepolymer (see Section b-2) the 5.9 mL peak is mainly due to AB block copolymer. Notably, no additional peaks were expected provided the product would consist exclusively of the diblock copolymer and the homopolymers. The existence of a shoulder and a peak at lower V_R , however, suggests that the product contains additional components and it appears plausible to attribute shoulder and peak at 4.8 and 5.0 mL, respectively, to multiblock copolymers. Although the assessment of the column resolution regarding such species is an objective of future research an assignment is attempted here: the 5.0 mL peak is attributed to triblock copolymer of type A-B-B-A, with A and B corresponding to THF and MMA moieties, respectively, and the 4.8 mL shoulder to multiblock copolymers of higher order.

(b-2) LC at the CAP for PTHF

Fig.4 shows that the chromatogram of the crude block copolymer is bimodal. Notably, the peak at the high retention volume is located at a position corresponding to that of the prepolymer (PTHF). Extraction of the crude polymer with ethanol resulted in a chromatogram (full line) possessing a weak shoulder at the PTHF position. This indicates that, although most of the prepolymer was removed, the purification was still incomplete. Fig. 4 also contains a chromatogram of a 1:1 blend of the purified block copolymer and the prepolymer. This chromatogram is bimodal, too, thus substantiating the interpretation of the chromatogram of the crude block copolymer.

Conclusion

The results obtained in this work demonstrate that liquid chromatography at the critical adsorption point can be employed to characterize block copolymers. Notably, the LC CAP method is quite appropriate to detect homopolymers in polymeric products obtained in the preparation of block copolymers. In the present study the presence of homo PTHF (actually prepolymer) and of homo PMMA in the polymeric product was evidenced. Moreover, it is noticeable that the LC CAP method provides a means to discriminate diblock and multiblock fractions in block copolymer samples prepared by free radical polymerization where termination by both combination and disproportionation is feasible.

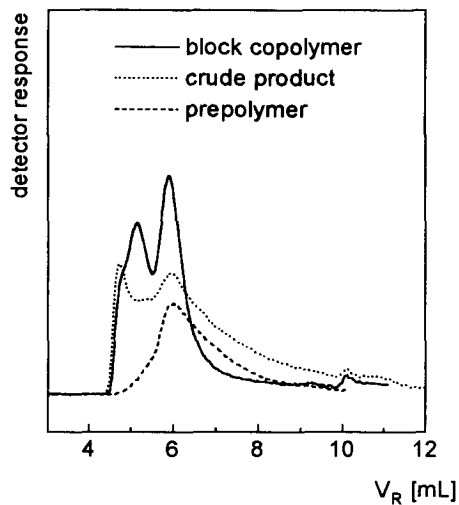


Fig.3. Chromatograms of block copolymer, crude product and prepolymer. Column: Biospher. Eluent: THF:n-hexane = 81.8:18.2, w/w.

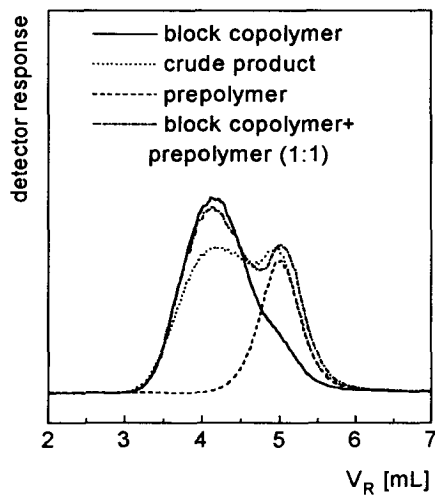


Fig.4 Chromatograms of block copolymer, crude product, prepolymer and 1:1 (w/w) blend of block copolymer and prepolymer. Column: Nucleosil C_{18} . Eluent: THF:ACN = 50:50, w/w.

Acknowledgement

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