Macromolecules **2000,** *33,* 3687−3693

Characterization of Block Copolymers by Liquid Adsorption Chromatography at Critical Conditions. 1. Diblock Copolymers

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Received November 10, 1999; Revised Manuscript Received February 29, 2000

ABSTRACT: Liquid adsorption chromatography at critical conditions (LACCC) in normal and in reversed-phase modes provides independent information on the molar mass distributions of both blocks of poly(methyl methacrylate)-*block*-poly(*tert*-butyl methacrylate), even if no information about the precursor is available. In addition, the amount of unreacted precursor can be determined, even if its molar mass is comparable to that of the total block copolymer. The reversal of elution order by changing of stationary and mobile phases makes it possible to independently characterize each block in the SEC mode of the LACCC system. Thus, complete structural information is obtained even without using two-dimensional chromatographic techniques.

Introduction

Block copolymers represent a versatile class of functional materials for a multitude of applications because they combine the properties of incompatible but well-known monomers. Among other properties, the ability of these polymers to modify interfacial properties and to enhance the compatibility of polymer blends make this polymer type attractive for applications. New synthetic strategies in the field of living polymerization make an increased number of block copolymers available.[1]

Block copolymerization by sequential monomer addition has to be controlled effectively, e.g., by determination of precursor content. Beside the characterization of molar mass distribution this includes the characterization of chemical heterogeneity. As an example, remaining precursor affects the phase properties and application possibilities of the finished polymer. Thus, the complete characterization of block copolymers, i.e., the measurement of molar mass distribution in combination with the chemical distribution of the components of the desired architecture (diblock, triblock, multiblock), is necessary for optimization of synthesis methods.

Classical methods for determination of molar mass distribution the characterization in the last years were dominated by Size exclusion chromatography (SEC).[2] Selective detection in SEC has been used for the determination of chemical heterogeneity.[3,4] This method is limited by the determination of the calibration function for block copolymers. A linear interpolation of the calibration functions for the corresponding homopolymers which is often used has no theoretical background. The hydrodynamic volume of a block copolymer is not necessarily a linear function of the copolymer composition. Moreover, homo- and block copolymers of the same hydrodynamic volume cannot be distinguished by SEC.

The separation of chemically heterogeneous polymers based on solubility is very time-consuming and needs information about solvent/nonsolvent properties as a function of molar mass.[5] Liquid adsorption chromatography (LAC) in the gradient mode is a further established method, which separates statistic and block copolymers with respect to their molar mass and chemical composition.[6] Gradient elution of copolymers which separates the homopolymers according to the polarity can be complicated by precipitation/dissolution as elemental processes.[7]

Liquid chromatography at critical conditions of adsorption (LACCC) is a recent and most powerful method for the characterization of block copolymers according to the chemical heterogeneity. The method was established by Belinki et al.[8] and Entelis et al.[9] The theory and experimental details for determination of critical conditions have been described by Pasch.[10] Separation of polymers at critical conditions of adsorption allows for the elution of homopolymers independent of their molar mass on porous separation phases using mixed mobile phases. Under these conditions, homopolymers can be separated according to the number and nature of functional groups, e.g., end groups (functionality type distribution).

By changing the thermodynamic quality of the mobile phase, the temperature, and the adsorption properties of a porous stationary phase, the elution mode of the separation can be varied from SEC to LAC. The critical conditions are between those of SEC and LAC, and they are typical for a polymer with a given repeat unit in a chromatographic system.

Theory

The separation coefficient, K_D, of a porous column is related to the change in free energy ΔG according to the distribution of the solvated molecule between the mobile and the stationary phase

$$K_D = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{\Delta H}{RT}\right)\exp\left(\frac{\Delta S}{R}\right)$$

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10.1021/ma991903j CCC: $19.00

where K_D is the distribution coefficient, i.e., the ratio of concentration of polymer molecules between stationary and mobile phases, ΔH is the adsorption enthalpy of the macromolecule, and ΔS is its entropy. The separation coefficient K_D is related to the retention factor, k, and the volume of mobile (V_m) and stationary phase (V_s) by

$$K_D = kV_m/V_s$$

with $k = (V_e - V_m)/V_m$, where V_e is the elution volume and V_m is the dead volume, i.e., the retention volume of an unretarded component.

In general, ΔG of a homopolymer molecule is influenced by the contribution A of the polymer chain and the contribution B for heterogeneities (functional groups or a second block)

$$\Delta G_{AB} = \sum n_A \Delta G_A + n_B \Delta G_B$$

where n_A is the number of repeat units and n_B is the number of heterogeneities (e.g., end groups or repeat units of a block B).

Two thermodynamically different processes create the separation process. In ideal size exclusion, the separation of macromolecules is caused by change of entropy inside the pore, i.e., by change the conformation without interaction with the surface of the pores. Large molecules elute earlier because they do not fit into all pores. In contrast, in ideal adsorption chromatography, the repeat units can interact with the surface, resulting in an enthalpy change. Adsorption of long molecules is stronger that that of short ones, so they will elute later. Depending on the column material, the thermodynamic quality of the solvent mixture, and temperature, one of the two processes will be dominating. At a certain solvent/nonsolvent composition at a given temperature, critical conditions are reached where the enthalpic and entropic contributions compensate each other and all molecules with the same chemical composition (repeat units, end groups) will elute at the same elution volume. Experimentally, the critical solvent composition will be determined with polymers of the same type and different molar masses.

In SEC mode, K_D varies in the range between 0 and 1 and in the adsorption mode between 1 and ∞. At critical conditions for a given polymer, K_D depends on the type of interaction and the number of groups in the macromolecule which are different from the repeat units. Cyclic homopolymers will be separated exactly at $K_D = 1$. The repeat unit does not contribute to the change of free energy. The molecule is chromatographically "invisible".[9]

For AB diblock copolymers at critical conditions for block A retention is determined only by the length of block B. Each monomer unit of the second block B of the copolymer can be regarded as a chemical heterogeneity. Depending on the relative polarity of A and B units elution will occur either in SEC mode or in adsorption mode. The second "noncritically" eluting block determines the chromatographic elution mode. Block B will elute in SEC mode, if $K_{D,B} < K_{D,A}$. In contrast, for $K_{D,B} > K_{D,A}$, block B elutes in adsorption mode. Thus, two theoretical cases exist for the optimal elution conditions for the "noncritically" eluted block or homopolymer. In the SEC elution mode of block B in LACCC, the relation of K_D should be analogous to SEC. In a first approximation this is a semilogarithmic relation between molar mass and elution volume, log = $A - BV_e$, where A and B are positive constants. Under adsorption conditions, the elution volume increases with the degree of polymerization (Figure 1).

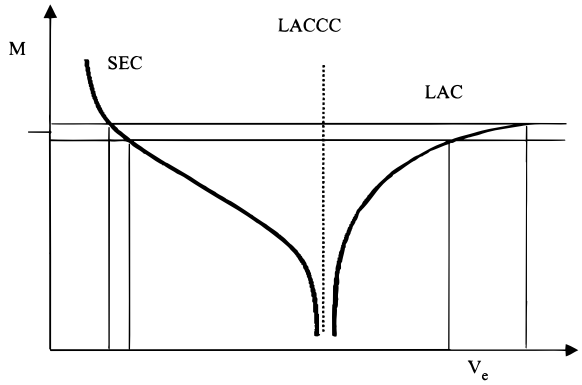

Figure 1. Dependence of elution volume on molar mass for the three modes of chromatography.

Experimental Section

Synthesis of Block Copolymers. Poly(methyl methacrylate)-*block*-poly(*tert*-butyl methacrylate), PMMA-*b*-PtBMA, was synthesized by living anionic polymerization using a novel initiator system reported recently.[11,12] Ethyl α-lithioisobutyrate was used as an initiator in the presence of a 2:1 complex of $AlEt_3$ and NBu_4Br in toluene at −20 °C. In one set of experiments, MMA was polymerized first, a sample was taken as precursor, and then *tert*-butyl methacrylate was introduced for the second block. To obtain different block lengths for the second block, samples were taken at different conversions. In a second experiment, the order of monomers was reversed. The initiator used leads to an end group which is very similar in structure to the repeat units, PMMA and PtBMA standards were obtained in a similar way.

Chromatography at Critical Conditions of Adsorption The measurements were conducted on a Hewlett-Packard (HP1090) HPLC system using a diode array UV detector and an Evaporative light scattering detector (SEDEX 45, ERC). The flow rate was 0.5 mL/min; 25 μL of about 2 wt % polymer solutions were injected.

(a) Reversed Phase System: Two Nucleosil RP18 columns (250 × 4 mm i.d.) were used: 1 × 300 Å pore size, 5 μm average particle size, and 1 × 1000 Å pore size, 7 μm average particle size. The eluent was a mixture of tetrahydrofuran and acetonitrile. The critical solvent compositions contain 49.5 wt % THF for PtBMA and 8.5 wt % THF for PMMA. Premixing of the mobile phase by weight is necessary for a constant and exact composition.

(b) Normal Phase System: Two Nucleosil Silicagel columns of 5 μm average particle size were used, 100 Å pore size (150 × 4 mm i.d.) and 300 Å pore size (250 × 4 mm i.d.). The eluent was a mixture of tetrahydrofuran and *n*-hexane. The critical solvent compositions are 43:57 wt % for PtBMA and 82:18 wt % for PMMA.

Size Exclusion Chromatography:. The SEC experiments were performed on a Hewlett-Packard (HP1050) HPLC modular system, including a Mistral column oven (SunChrom). For detection the Evaporative light scattering detector (SEDEX 45, ERC) and additionally a variable wavelength UV detector (230 nm) were used. The flow rate was 2.0 mL/min. Two linear SDV-gel columns (PSS Mainz), 5 μm average particle size (300 × 8 mm i.d.) as well as a guard column (50 × 8 mm i.d.) and tetrahydrofuran as mobile phase were used. A 100 μL aliquot of a 1 wt % polymer solution was injected. Calibration was performed using PMMA and PtBMA standards, respectively. The mean values of molecular weight are measured by ELSD.

Two-Dimensional Chromatography The crossover of LACCC fractions in SEC mode was performed by two combined electrical Rheodyne six-port switching valves. The measure-

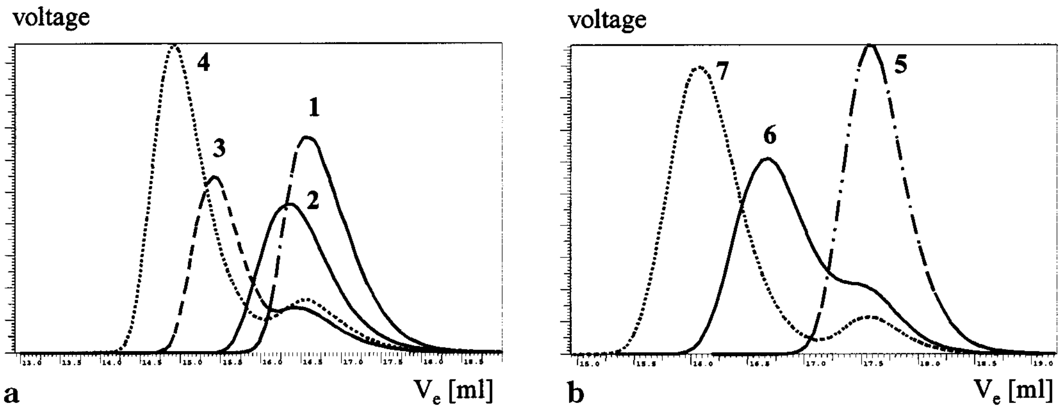

Figure 2. (a) SEC chromatograms of PtBMA-*b*-PMMA **2**, **3**, and **4** with different PMMA block lengths and of PtBMA precursor **1** (M_n = 73 000 g/mol). (b) SEC chromatograms of PMMA-*b*-PtBMA **6** and **7** with different PtBMA block lengths and of PMMA precursor **5** (M_n = 31 000 g/mol).

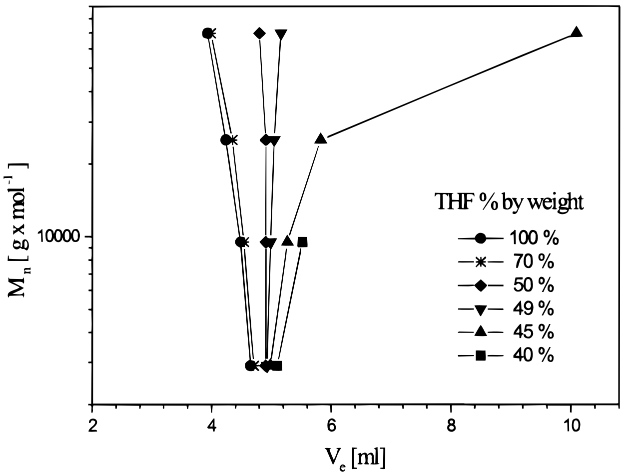

Figure 3. Elution volume of PtBMA as a function of molar mass at different mobile phase compositions.

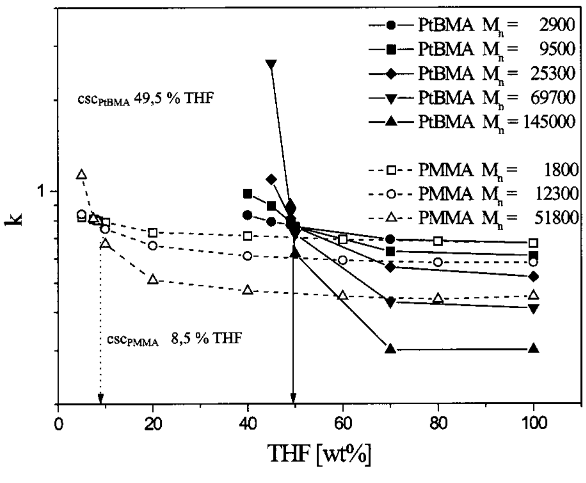

Figure 4. Determination of the critical solvent compositions for PtBMA and PMMA in mixtures of tetrahydrofuran/acetonitrile (RP system).

ments were evaluated by using the PSS WinGPC and PSS 2D software.

Results and Discussion

Two sets of PMMA-*b*-PtBMA block copolymers were synthesized. In the first one tBMA was used as the first monomer (PMMA block lengths were varied) and in the second set MMA (PtBMA block lengths varied) was used; see Tables 1 and 2.

SEC Experiments. For first information on molar mass distribution, a SEC analysis of all products was performed. The chromatograms are shown in Figure 2. As can be seen from SEC alone, samples **3**, **4**, **6**, and **7** are bimodal. The elution volume of the second peak is the same as that of the precursors **1** and **5**. Thus, SEC can give information on the molar mass distribution of the precursors in **3**, **4**, **6**, and **7**. However, it is not possible to get information about the precursor content in sample **2**. Furthermore, SEC offers no possibility to accurately determine the content of PMMA and PtBMA, respectively, in the block copolymer.

The M_n of the block copolymer can be estimated by using a PMMA/PtBMA calibration curve weighted by composition. For an estimation of M_n of the second block that of the precursor peak can be subtracted. This procedure has many deficiencies: (i) the precursor must be seen as a separate peak (which is not the case in sample **2**), (ii) the eluogram of the precursor must be available which is not the case for unknown samples), and (iii) the linear interpolation of the homopolymer calibration curves has no theoretical background. The hydrodynamic volume of a block copolymer is not necessarily a linear function of the comonomer composition.

LACCC Experiments: Reversed phase. Next, the critical solvent compositions (csc) of PtBMA and PMMA homopolymers were determined using RP columns. In Figure 3 the molar mass of PtBMA is represented as a function of elution volume for different solvent/nonsolvent compositions. The csc's for PMMA and PtBMA were determined by plotting the retention factor, *k*, vs solvent/nonsolvent composition. From the PMMA data points in Figure 4 it is obvious, that elutes in SEC mode at the csc of PtBMA. In contrast, PtBMA cannot be determined at critical conditions of PMMA in adsorption mode because of too strong adsorption leading to high retention values.

The comparison of LACCC chromatograms of PtBMA (Figure 5) and PMMA homopolymers at critical conditions of PtBMA (Figure 6) shows that PtBMAs elute at the same retention time of 9.95 min independent of their molar mass, but the retention time of PMMA depends on molar mass in the range from 6.6 to 9.4 min. From the chromatograms of PMMA standards, a calibration curve can be established (Figure 7). With the help of this calibration curve the block length of the PMMA block in PtBMA-*b*-PMMA can be determined. First, the

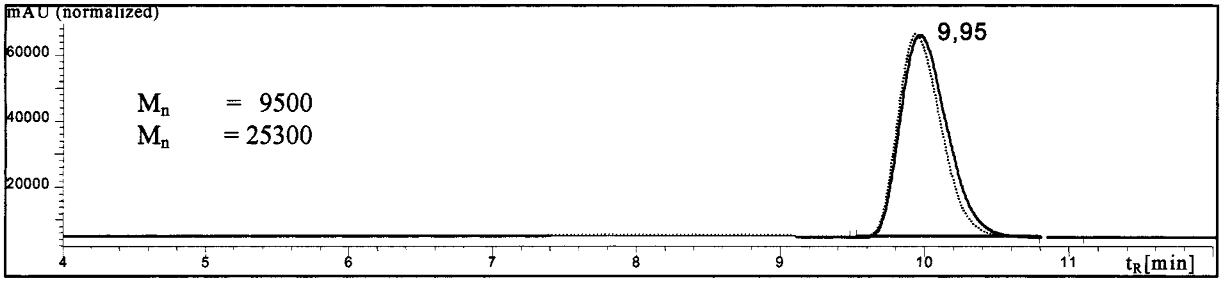

Figure 5. Chromatograms of PtBMA standards at critical conditions of PtBMA.

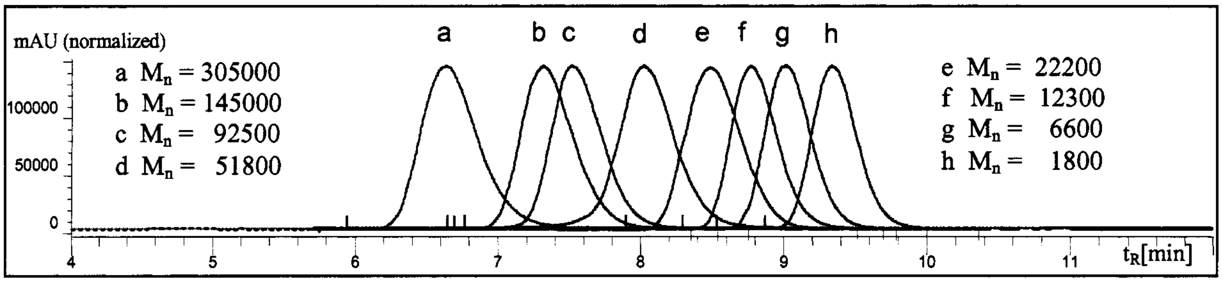

Figure 6. Chromatograms of PMMA standards at critical conditions of PtBMA.

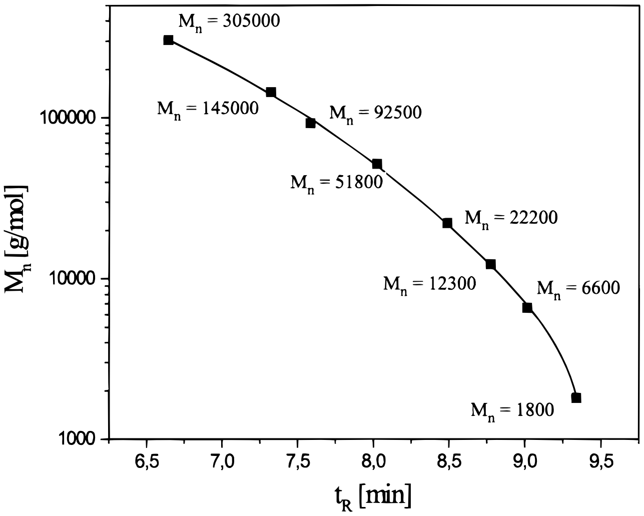

Figure 7. Calibration curve for PMMA in LACCC at critical conditions of PtBMA (reversed phase).

block copolymers with PtBMA precursor and different PMMA block lengths were investigated (Figure 8). It was found that all block copolymers contain precursor, even sample **2**, where no precursor was visible in SEC. In contrast to SEC, LACCC allows the quantitative determination of the content of precursor. Block copolymers **2**, **3**, and **4** elute according to the molar mass of the PMMA block. The next step was to clarify experimentally whether the assumption of “invisibility” of the PtBMA block at critical conditions of PtBMA is really fulfilled. Therefore, it was necessary to synthesize copolymers with identical block lengths of PMMA and different block lengths of PtBMA. The retention behavior of these copolymers at critical conditions of PtBMA is shown in Figure 9. The varied block length of PtBMA result no differences in retention times. The retention time of the copolymers only depends on the PMMA block length which is the same in both copolymers. This is a very important finding: it demonstrates that the increase in hydrodynamic volume due to the second block (and the expected lower retention time) is exactly compensated for by the adsorption of that block onto the stationary phase, at least up to a block length ration of 1:5. Deviations may occur if the block which elutes in the critical mode is much greater than the block which has to be determined.

2D Chromatography. Two-dimensional chromatography allows to separate block copolymer and precursor and then to estimate the molar masses of the LACCC fractions by SEC (Figure 10). The LACCC ordinate in the two-dimensional plot indicates the chemical composition and the SEC abscissa the total molecular weight. After calibration of SEC, it is possible to determine the molar mass of the PtBMA precursor and of the complete copolymer (weighted PMMA/PtBMA calibration curve). The difference of the M_n‘s of the copolymer and of the PTBMA precursor gives informa-

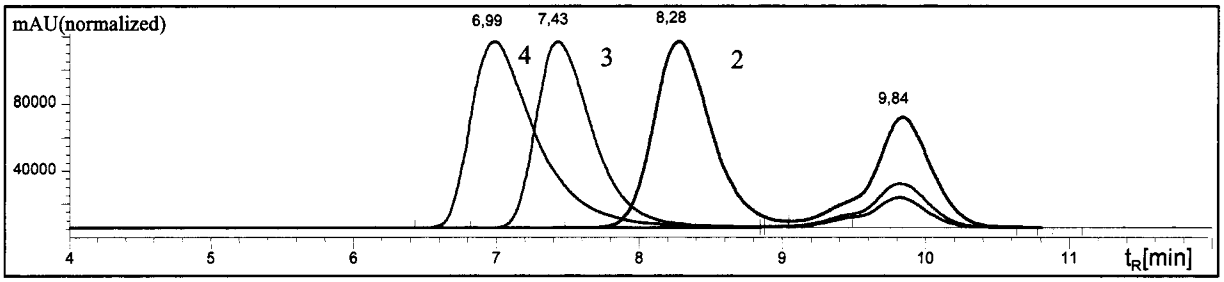

Figure 8. LACCC chromatograms of PtBMA-*b*-PMMA **2**, **3**, and **4**. (precursor PtBMA, M_n = 73 000 g/mol) with different PMMA block lengths at critical conditions of PtBMA.

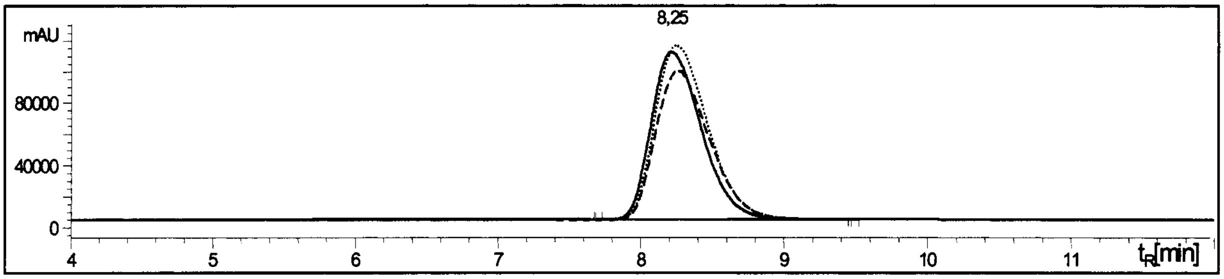

Figure 9. LACCC chromatograms of PtBMA-*b*-PMMA **5**, **6**, and **7**. (Precursor PMMA, $M_n = 31\,000$ g/mol) with different PtBMA block lengths at critical conditions of PtBMA.

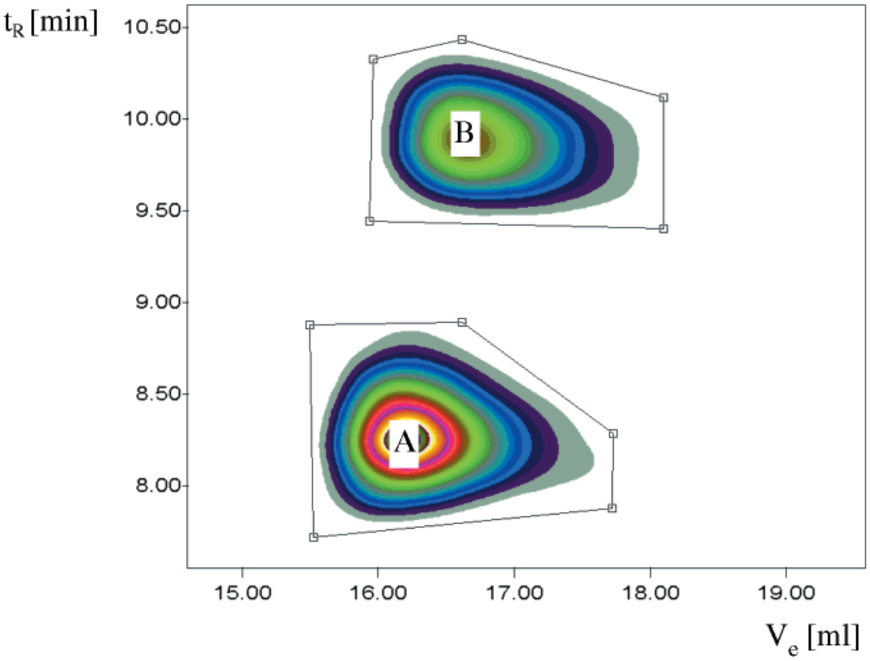

Figure 10. 2D contour plot of reaction product **2** (reversed phase, csc for PtBMA): (A) PtBMA-*b*-PMMA; (B) PtBMA **1**. LACCC at critical conditions of PtBMA.

Table 1. Molar Masses of PMMA Blocks, As Determined by SEC (Two-Dimensional Experiment) and by LACCC at Critical Conditions of PtBMA (RP System)

sample	$M_{n,PtBMA}$ (by SEC)	$M_{n,PMMA}$ (by SEC; $M_{n,block} - M_{n,PtBMA}$)	$M_{n,PMMA}$ (by LACCC)	$M_{n,block}$ (by SEC, 2D)
1, PtBMA (precursor of **2**, **3**, **4**)	73 000			
2, PtBMA-*b*-PMMA		29 600	30 200	102 600
3, PtBMA-*b*-PMMA		108 100	113 300	181 100
4, PtBMA-*b*-PMMA		167 500	174 900	240 500

Table 2. Molar Masses of PtBMA Blocks, As Determined by SEC (Two-Dimensional Experiment) and by LACCC at Critical Conditions of PMMA (Normal Phase System)

sample	$M_{n,PMMA}$ (by SEC)	$M_{n,PtBMA}$ (by SEC; $M_{n,Block} - M_{n,PMMA}$)	$M_{n,PtBMA}$ (by LACCC)	$M_{n,block}$ (by SEC, 2D)
5, PMMA (precursor of **6**, **7**)	31 000			
6, PMMA-*b*-PtBMA		46 300	41 800	77 300
7, PMMA-*b*-PtBMA		85 300	86 700	116 300

tion on the M_n of the PMMA block (Tables 1 and 2). No information on the precursor is needed here. However, the problem of linear interpolation of calibration curves still pertains. In Table 1 the PMMA block lengths determined by SEC (two-dimensional experiment) and LACCC are compared. The average molar masses estimated by LACCC agree very well with values from SEC obtained by subtracting the molar mass of the PtBMA precursor from that of the block (deviation 2−4%).

LACCC Experiments: Normal Phase. Similar to measurements carried out at critical conditions of PtBMA, it is possible to determine the PtBMA block length in the copolymer at critical conditions of PMMA. After changing the polarity of stationary phase from reversed to normal phase (porous silicagel) and using mixtures of THF/*n*-hexane as mobile phase, critical conditions of PMMA and PtBMA were determined as shown in Figure 11. In the same way as described above it is now possible to characterize the PtBMA block

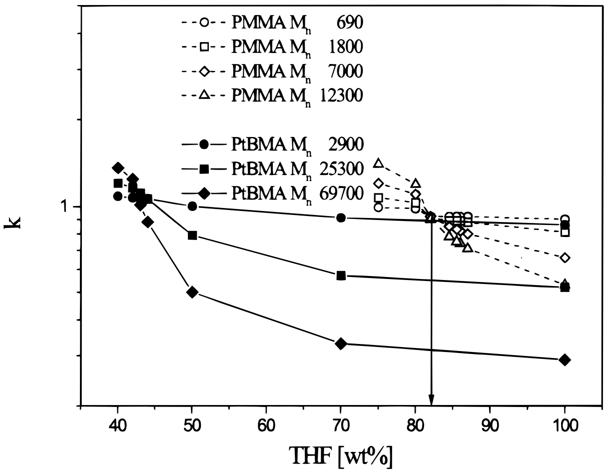

Figure 11. Determination of critical conditions of adsorption for PtBMA and PMMA in mixtures of tetrahydrofuran/*n*-hexane (normal phase).

length in PtBMA-*b*-PMMA. The chromatograms for PtBMA-*b*-PMMA with different block lengths of PtBMA are shown in Figure 12. The determined average molar masses only differ by 4–6% (Table 2). In the next decisive experiment just inverse to that made in the reversed phase system, copolymers with identical block lengths of PtBMA and different block lengths of PMMA are investigated. They all elute at the same retention time characteristic for the block length of PtBMA in this chromatographic system (Figure 13). A more detailed description can be found in ref 13.

Conclusions

It has been shown that liquid chromatography at critical conditions of adsorption is a versatile method for the complete characterization of diblock copolymers such as PtBMA-*b*-PMMA up to a ratio of block lengths of 1:5. No knowledge about the precursors is necessary. We believe that it can be generalized to other types of block copolymers also it has to be checked whether there are limitations for strongly differing polarities of the single blocks. Phase reversal enables the characterization of both blocks of a diblock copolymer in the presence of both kinds of homopolymer. The characterization of each block was realized in size exclusion mode of LACCC: for the PtBMA block in a normal phase system and for the PMMA block in a reversed phase system. Molar mass and polydispersity of blocks were determined via calibration with homopolymers. The analysis of results of block A under critical conditions of block B results in the same parameters as two-dimensional chromatography but with significantly less effort. This principle also holds for ABA triblock copolymers[14] and even for graft copolymers.[15]

For further investigations the following remarks should be made: In general, the elution of block- or homopolymers in SEC mode is not problematic because the solution in a thermodynamically good solvent prevents precipitation occurring in the case of poor solubility. The reversed elution of both homopolymers A and B can be reached on a reversed phase separation column. For such a system a solvent/nonsolvent combination has to be found which can be used without precipitation of the sample. For $K_{D,B} < K_{D,A}$ the elution of block B or homopolymers then again follows the retention law of SEC.

Adsorption mode for the noncritically eluting block will be preferred, if the difference $K_{D,B} - K_{D,A}$ is small. Then the required resolution will be much better than in SEC mode. At this point again two cases have to be distinguished: (i) If the difference of csc's for blocks A and B is small the elution should take place at isocratic conditions. The exponential increase of the retention takes place at lower retention times, typical for adsorption. (ii) If the difference of csc's is larger, gradient elution should be used by raising the amount of the good solvent or by raising the elution temperature in order

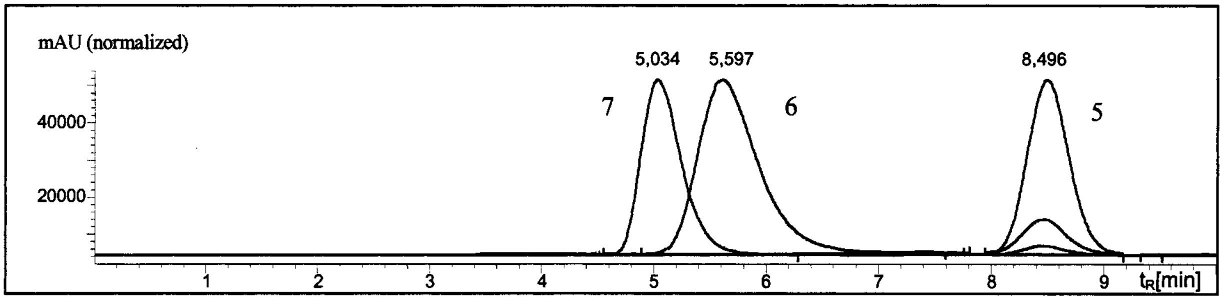

Figure 12. LACCC chromatograms of PMMA-*b*-PtBMA **5**, **6**, and **7** (precursor PMMA, M_n = 31 000 g/mol) with different PtBMA block lengths at critical conditions of PMMA.

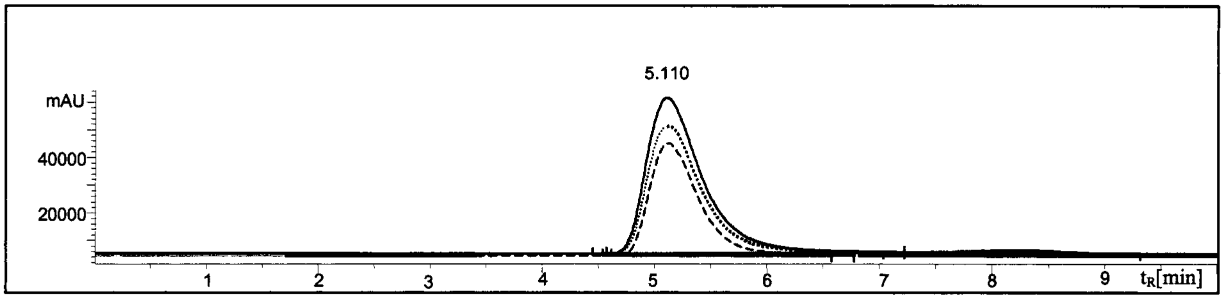

Figure 13. LACCC chromatograms of PMMA-*b*-PtBMA **2**, **3**, and **4** (precursor PtBMA M_n = 73 000 g/mol) with different PMMA block lengths at critical conditions of PMMA.

to suppress an irreversible adsorption or to elute precipitated molecules from the column.

Acknowledgment. The authors gratefully acknowledge financial support by the German Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie and by BASF AG, Ludwigshafen, Germany (Grant No. 03 N 3006), and by the Deutsche Forschungsgemeinschaft.

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