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Chromatographic investigations of macromolecules in the critical range of liquid chromatography: 11. Polymer blend separation using a reversed stationary phase†

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The separation of blends of polymethacrylates was accomplished by liquid chromatography at the critical point of adsorption. Using a non-polar stationary phase and tetrahydrofuran-acetonitrile as the eluent, separations were conducted under chromatographic conditions, corresponding to the critical point of adsorption of the least polar component of the blend. After the separation step the blend components were precisely detected by an on-line capillary viscometer. The molar masses of the components were calculated from the viscometer signal via the corresponding Mark–Houwink relationship. At critical conditions for polydecyl methacrylate not only blends with a second homopolymer could be separated, but also blends where the second component was a blend itself.

(Keywords: chromatography; macromolecules; polymer blend)

INTRODUCTION

Polymer blends are mixtures of two or more high molar mass components of different chemical structures. These components may be homopolymers or copolymers and, accordingly, the identification and quantitative determination of blend components is a demanding analytical task. The quantitative determination of the chemical composition of a polymer blend is possible by n.m.r. and *FT*i.r. spectroscopy[1–4]. For the determination of the molar masses of the blend components, however, in most cases a separation step is required. Size exclusion chromatography (SEC) may be used for the determination of the total molar mass of the polymer blend. As for the blend components, SEC is limited to blends containing components of sufficiently different molar masses[5,6]. A separation of polymer blends with respect to chemical structure may be obtained by adsorption or gradient elution chromatography[7,8]; however, the molar masses of the components must then be determined by separate SEC experiments.

Recently, it was shown by us that polymer blends can be analysed by liquid chromatography at the critical point of adsorption (LCCC)[9,10]. LCCC has been established as a third mode in liquid chromatography of polymers, in addition to SEC and liquid adsorption chromatography (LAC). At the critical point of adsorption the entropic and enthalpic effects of the polymer-adsorbent interactions compensate each other, and chromatographic separation is not accomplished with respect to the length of the polymer chain but to its heterogeneity. Accordingly, the chain length does not contribute to retention and behaves chromatographically 'invisible'[11–14].

For a polymer blend $A_n + B_m$, the free Gibbs energy (ΔG), which is a function of the entropic (ΔS) and the enthalpic interactions (ΔH) in the chromatographic system, comprises a contribution of each blend component.

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_d$$

$$\Delta G = \Sigma n \Delta G_A + \Sigma m \Delta G_B$$

These contributions reflect the chain length effects of each component on the distribution coefficient K_d. If now a chromatographic experiment is conducted under conditions corresponding to the critical point of component A, ΔG_A becomes 0, and all molecules of A elute at $K_d^A = 1$, irrespective of their molar mass. The free Gibbs energy is then only a function of the chain length of B.

$$\Delta G = \Sigma m \Delta G_B$$

Vice versa, at the critical point of B all molecules of B elute at $K_d^B = 1$ and separation is accomplished with respect to the chain length of A.

$$\Delta G = \Sigma n \Delta G_A$$

Accordingly, at the critical point of adsorption of A, the molar mass distribution of B is determined, whereas at the critical point of B, component A is analysed[15].

Recently, we reported on the separation of polymethacrylate blends using a polar stationary phase and methyl ethyl ketone-cyclohexane as the eluent. As the detector an on-line viscometer was used[16].

The present paper is dedicated to the separation of polymer blends by LCCC using a reversed phase chromatographic system. For model blends it will be demonstrated that, after the chromatographic separation, the molar masses of the components can be determined from the viscometer signal via the corresponding Mark–Houwink relationships.

EXPERIMENTAL

The separations were carried out on a modular chromatographic apparatus, comprising a Waters model 510 pump, a

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† Part 10: cf. Pasch and Rode[16]

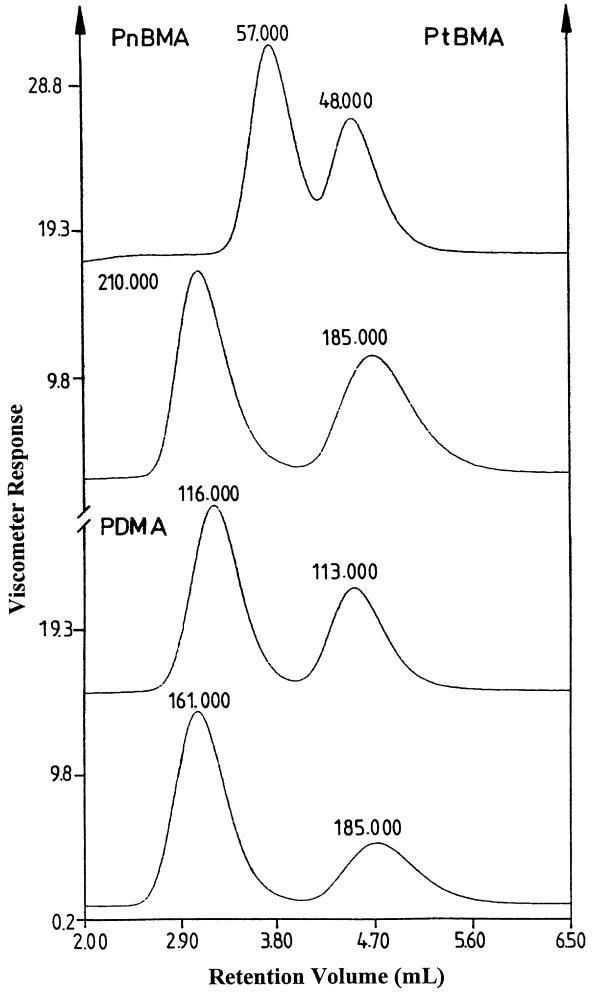

Figure 1 Chromatographic separation of PnBMA–PtBMA and PDMA–PtBMA blends at the critical point of PtBMA, stationary phase: LiChrospher Si-300 + Si-1000, mobile phase: MEK–cyclohexane 18.8:81.2% (v/v), assignments of the peaks indicate nominal molar masses

Viscotek 200 dual refractive index-viscosity detector, a Rheodyne six-port injection valve and a Waters column oven. The columns were either Merck LiChrospher Si-300 and Si-1000, 10 μm average particle size, 200 × 4 mm i.d., self-packed columns, or Macherey–Nagel Nucleosil $5C_{18}$, 300 and 1000 Å, 250 × 4 mm i.d., prepacked columns.

All solvents were h.p.l.c. grade.

The polymethacrylate blends were either technical products of Röhm GmbH, Darmstadt, Germany, or prepared by dissolving the components in a common solvent and evaporating the solvent in a film-forming procedure. The given molar masses are manufacturers' values.

RESULTS AND DISCUSSION

The high selectivity of chromatography at the critical point of adsorption (LCCC) has been demonstrated recently for the separation of macrocyclic polystyrenes[17]. In addition to separation according to architecture (cyclics *versus* linears), a functionality-type separation of the linear precursors was obtained.

With a similar high selectivity polymer blends can be separated. This is shown for the separation of blends of poly-*t*-butyl methacrylate (PtBMA) and poly-*n*-butyl methacrylate (PnBMA) in *Figure 1*. Using a normal phase chromatographic system, PnBMA is completely separated from PtBMA even when their molar masses are similar. This type of separation is achieved using chromatographic conditions corresponding to the critical point of PtBMA. As stationary phase silica gel is used, the mobile phase composition is methyl ethyl ketone-cyclohexane 18.8:81.2% (v/v), see also Pasch *et al.*[15,16] for other applications.

As has been shown previously[15], blend separations on polar silica gel afford elution of the components in the order of increasing polarity. For proper elution of all components, chromatographic conditions are used corresponding to the critical conditions of the most polar component. The less polar components are then eluted in the SEC mode.

Elution in the order of decreasing polarity (i.e. increasing hydrophobicity) can be achieved when a reversed phase system is used. In this case the least polar species are most strongly retained. In terms of LCCC separations, chromatographic conditions are established corresponding to the critical conditions of the most hydrophobic component. The less hydrophobic species elute earlier from the stationary phase and regardless of the molar mass of the blend components, separate component peaks are obtained.

To prove the validity of this approach, model blends of different polymethacrylates are prepared and separated by LCCC. The separation of blends comprising polydecyl methacrylate (PDMA) and polymethyl methacrylate (PMMA) under critical conditions of PDMA is shown in *Figure 2*. As the stationary phase a C_{18}-modified silica gel (RP-18), which is very common in reversed phase chromatography, and a mobile phase of THF-acetonitrile (ACN) 78.5:21.5% (v/v) is selected. The procedure for determining the critical conditions for a particular polymer is described in detail in Entelis *et al.*[11] and Pasch *et al.*[14,16]. In agreement with the theory, all PDMA fractions elute at one retention volume regardless of their molar mass. The more polar PMMA elutes in the SEC mode, i.e. elution takes place in the order of decreasing molar mass. Using a conventional PMMA calibration curve, the molar mass distribution of the PMMA fractions could be calculated from a concentration detector signal.

In the present case, instead of a concentration detector, an on-line viscometer is used. The signal intensity for this detector is proportional to $[\eta]c$, where $[\eta]$ is the intrinsic viscosity and c is the concentration. For the model blends under investigation the concentrations of the components are known and, accordingly, $[\eta]$ can be calculated by dividing the peak area by the concentration[18]. For unknown samples, the viscometer must be coupled to a concentration detector, preferably an evaporative light scattering detector, for determining c of the fractions.

The intrinsic viscosity is connected to the molar mass via the Kuhn–Mark–Houwink–Sakurada equation $[\eta] = K M^a$. For a given $[\eta]$ the molar mass M can be calculated, provided that the Mark–Houwink coefficients K and a are known. To determine K and a experimentally, $[\eta]$ of a set of calibration standards of known molar mass must be determined. Plotting log M *versus* log $[\eta]$, the coefficients K and a are determined from the slope and the intercept, respectively. The calibration curves molar mass *versus* retention volume and the Mark–Houwink plots for PMMA and PDMA are given in *Figure 3a* and *b*. *Figure 3a* clearly indicates that, regardless of the molar masses of the components, a separation of the elution zones is achieved. From the experimentally determined $[\eta]$ of the components the respective molar masses are calculated via *Figure 3b*. A comparison between the nominal molar masses and the

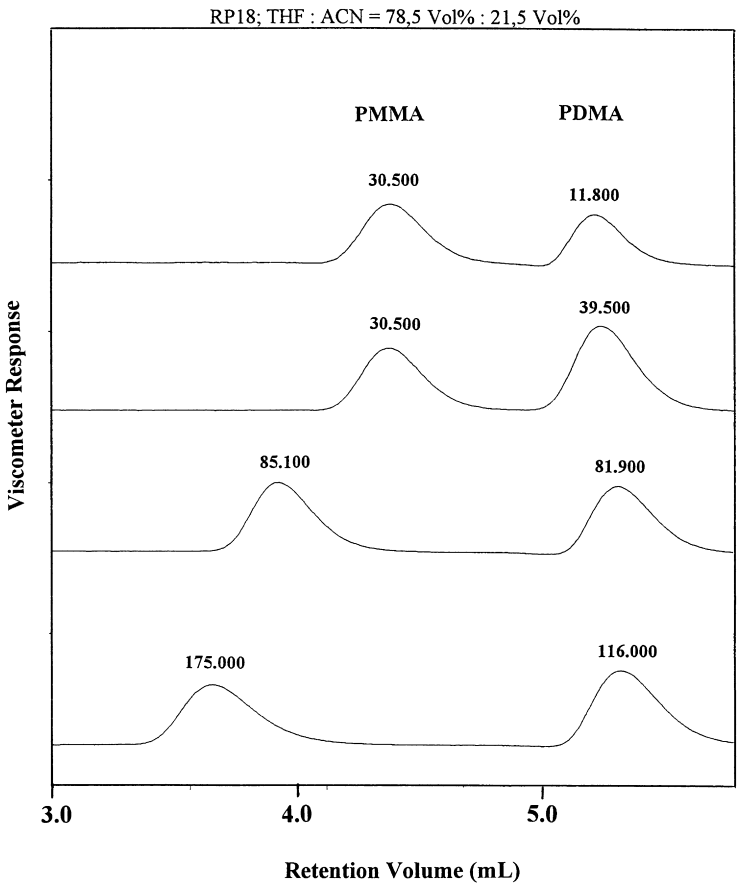

Figure 2 Chromatographic separation of PMMA–PDMA blends at the critical point of PDMA, stationary phase: Nucleosil RP-18 300 + 1000 Å, mobile phase: THF–ACN 78.5:21.5% (v/v)

Table 1 Average molar masses of blend components determined by LCCC and viscometric detection

Sample	Nominal		Experimental		
	c (mg mL^{-1})	M_w (g mol^{-1})	V_R (mL)	$[\eta]$ (dL g^{-1})	M_w (g mol^{-1})
1					
PDMA	2.595	11.800	5.165	0.083	11.600
PMMA	1.469	30.500	4.325	0.211	30.800
2					
PDMA	2.685	39.500	5.185	0.161	37.400
PMMA	1.495	30.500	4.325	0.211	30.800
3					
PDMA	2.642	81.900	5.31	0.249	80.700
PMMA	1.424	85.100	3.925	0.500	81.400
4					
PDMA	2.558	116.000	5.335	0.31	118.700
PMMA	0.963	175.000	3.665	0.774	155.000
5					
PDMA	2.545	116.000	5.355	0.307	116.700
Blend A (25:75)	2.154	104.300	3.79	0.514	109.700[a]
6					
PDMA	2.525	116.000	5.39	0.306	116.000
Blend A (50:50)	2.415	97.400	3.825	0.512	102.800[a]
7					
PDMA	2.654	81.900	5.355	0.246	79.000
Blend A (75:25)	2.294	107.300	3.84	0.516	94.600[a]
8					
PDMA	2.601	81.900	5.13	0.245	78.400
Blend B (25:75)	2.128	78.700	3.90	0.474	82.200[a]
9					
PDMA	2.797	81.900	5.125	0.251	81.800
Blend B (75:25)	2.346	81.000	3.885	0.496	84.700[a]

Blend A: PMMA + PnBMA, Blend B: PMMA + P(MMA-*co*-nBMA)
[a]Conventional PMMA calibration

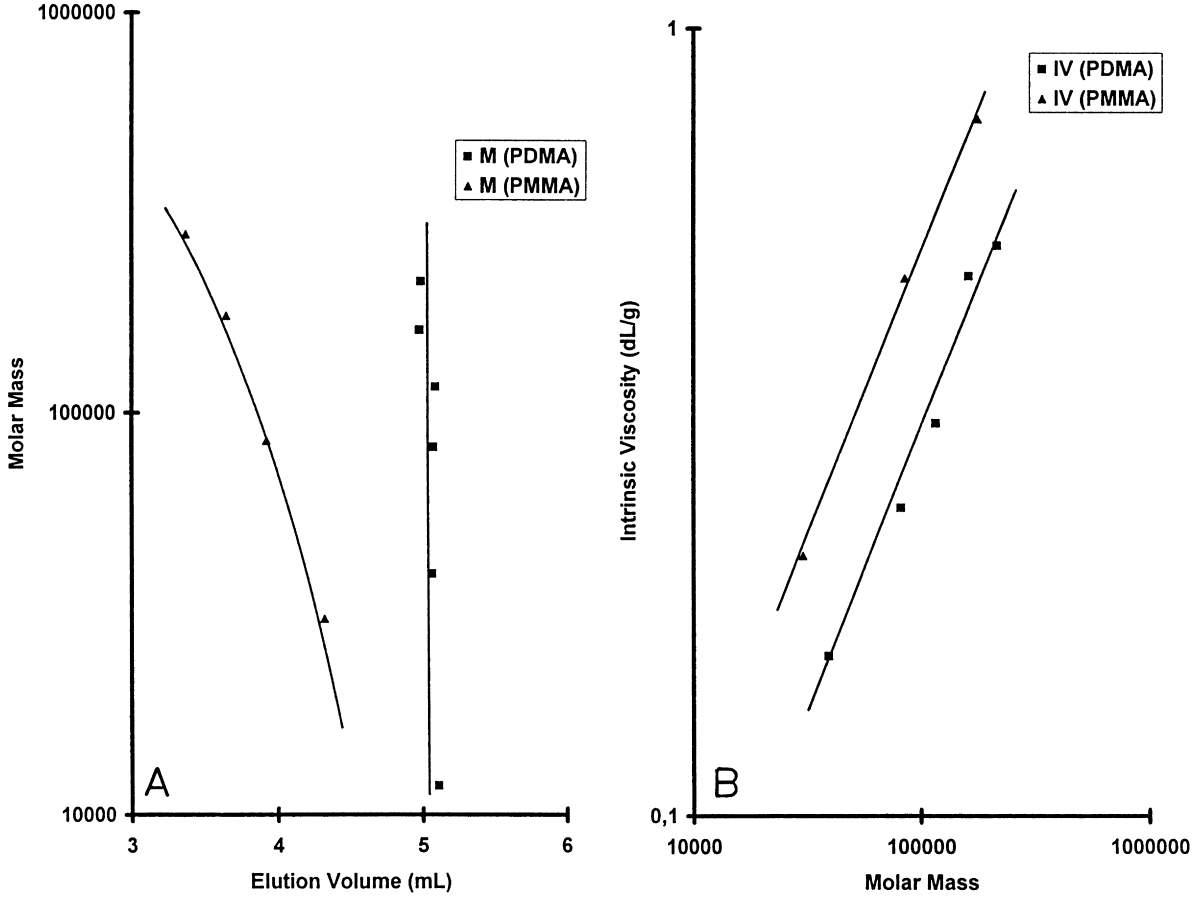

Figure 3 Calibration curves molar mass *versus* retention volume: (A) and Mark–Houwink plots, (B) for PMMA and PDMA at the critical point of PDMA, stationary phase: Nucleosil RP-18 300 + 1000 Å, mobile phase: THF–ACN 78.5:21.5% (v/v)

Table 2 Eluent compositions and Mark–Houwink coefficients, corresponding to the critical point of adsorption of polymethacrylates, stationary phase: Nucleosil RP-18 300 Å + 1000 Å, mobile phase: THF–ACN; Mark–Houwink coefficients at the critical point of adsorption are written in bold

Polymer	Mobile phase composition *THF*–ACN							
	78.5%		53.1%		49.6%		49.4%	
	log *K*	*a*	log *K*	*a*	log *K*	*a*	log *K*	*a*
PMMA	−4.236	0.793	−4.254	0.791	−4.260	0.790	−4.176	0.771
PS	−3.702	0.690	−3.400	0.598	−2.977	0.504	**−2.972**	**0.503**
PtBMA	−4.644	0.843	−4.492	0.799	**−4.136**	**0.725**		
PnBMA	−4.093	0.748	**−3.879**	**0.690**				
PDMA	**−3.388**	**0.567**						

molar masses determined by LCCC-viscometry gives an excellent agreement, see *Table 1*.

Under the same chromatographic conditions PDMA blends can be separated of which the second blend component is a blend itself. This is shown for blends of PDMA and technical blends of PMMA + PnBMA and PMMA + P(MMA-*co*-nBMA), respectively (see *Figure 4*). PMMA + PnBMA stands for blends of PMMA and PnBMA, while PMMA + P(MMA-*co*-nBMA) corresponds to blends of PMMA and a methyl methacrylate-*n*-butyl methacrylate copolymer. These blend components elute in the SEC mode and, since their molar masses are of the same magnitude, separation into PMMA and PnBMA or P(MMA-*co*-nBMA), respectively, is not achieved. The molar masses of these multicomponent fractions are determined via a conventional SEC procedure using a PMMA calibration curve. The calculated values agree well with the nominal molar masses (see *Table 1*).

In a similar way to the separation of PDMA blends under chromatographic conditions corresponding to the critical point of PDMA, other polymethacrylates can be separated at the respective critical points. The chromatographic conditions are always selected such that they correspond to the critical point of the least polar component. The critical conditions for different polymethacrylates and polystyrene (PS) together with the corresponding Mark–Houwink coefficients are summarized in *Table 2*. Complementary to *Figure 1*, where separation of PnBMA and PtBMA is conducted at the critical point of PtBMA, *Figure 5* shows a similar separation under chromatographic conditions corresponding to the critical point of PnBMA. Resolution is equally good and, therefore, depending on the available columns and eluents, both separations can be conducted with the same success.

Unfortunately, the critical eluent compositions of PS and PtBMA differ only by 0.2% by volume of THF in the eluent.

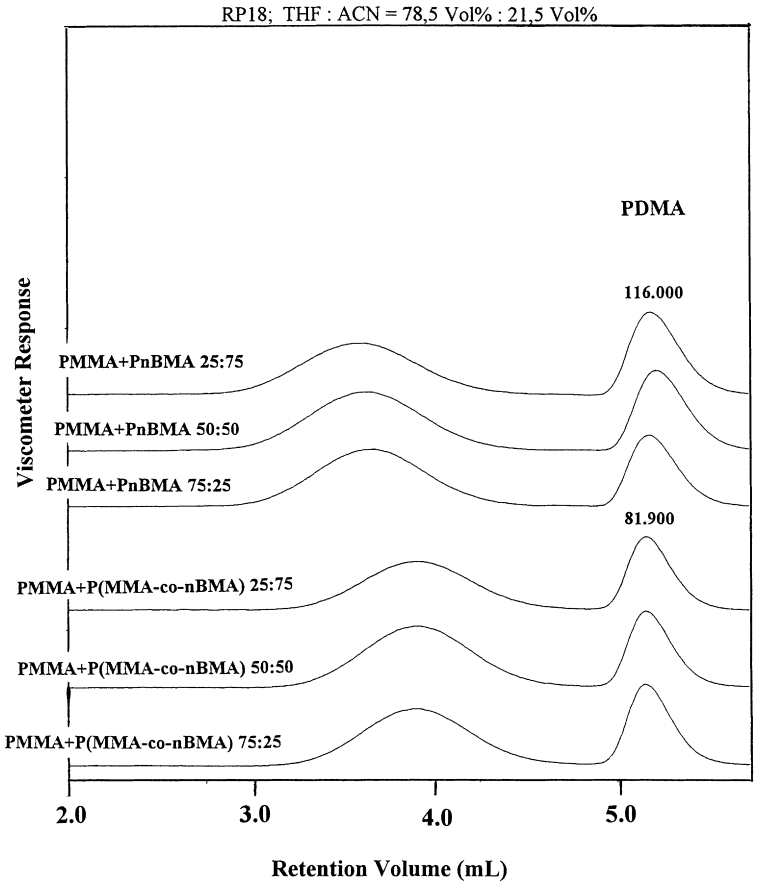

Figure 4 Chromatographic separation of blends of PDMA with PMMA + PnBMA and PMMA + P(MMA-*co*-nBMA), respectively, at the critical point of PDMA, stationary phase: Nucleosil RP-18 300 + 1000 Å, mobile phase: THF–ACN 78.5:21.5% (v/v)

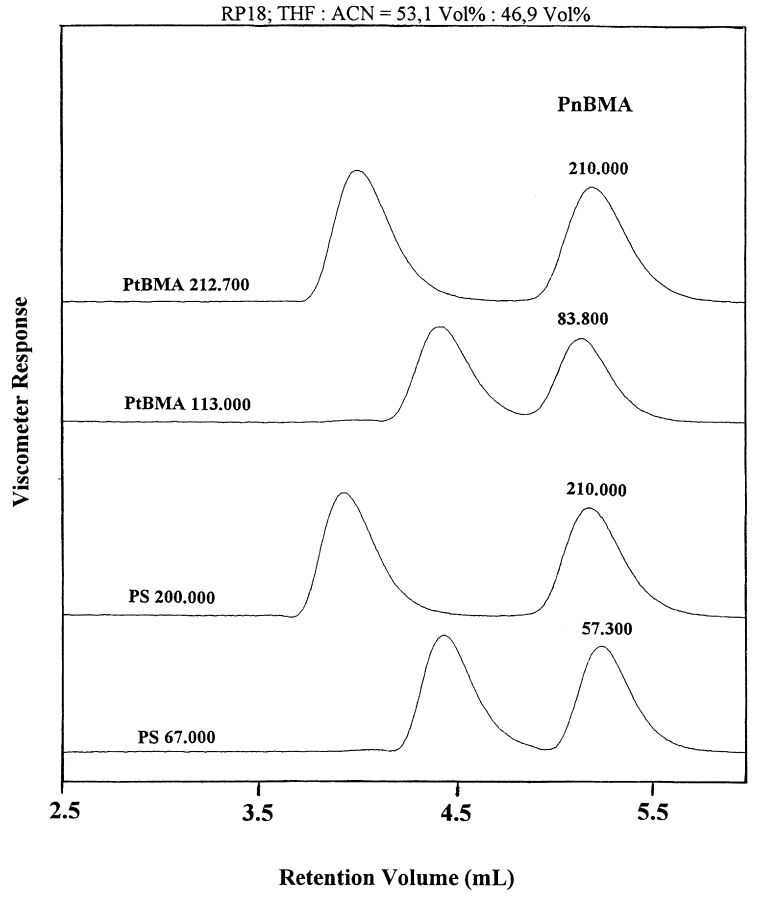

Figure 5 Chromatographic separation of PtBMA–PnBMA and PS–PnBMA blends at the critical point of PnBMA, stationary phase: Nucleosil RP-18 300 + 1000 Å, mobile phase: THF–ACN 53.1:46.9% (v/v)

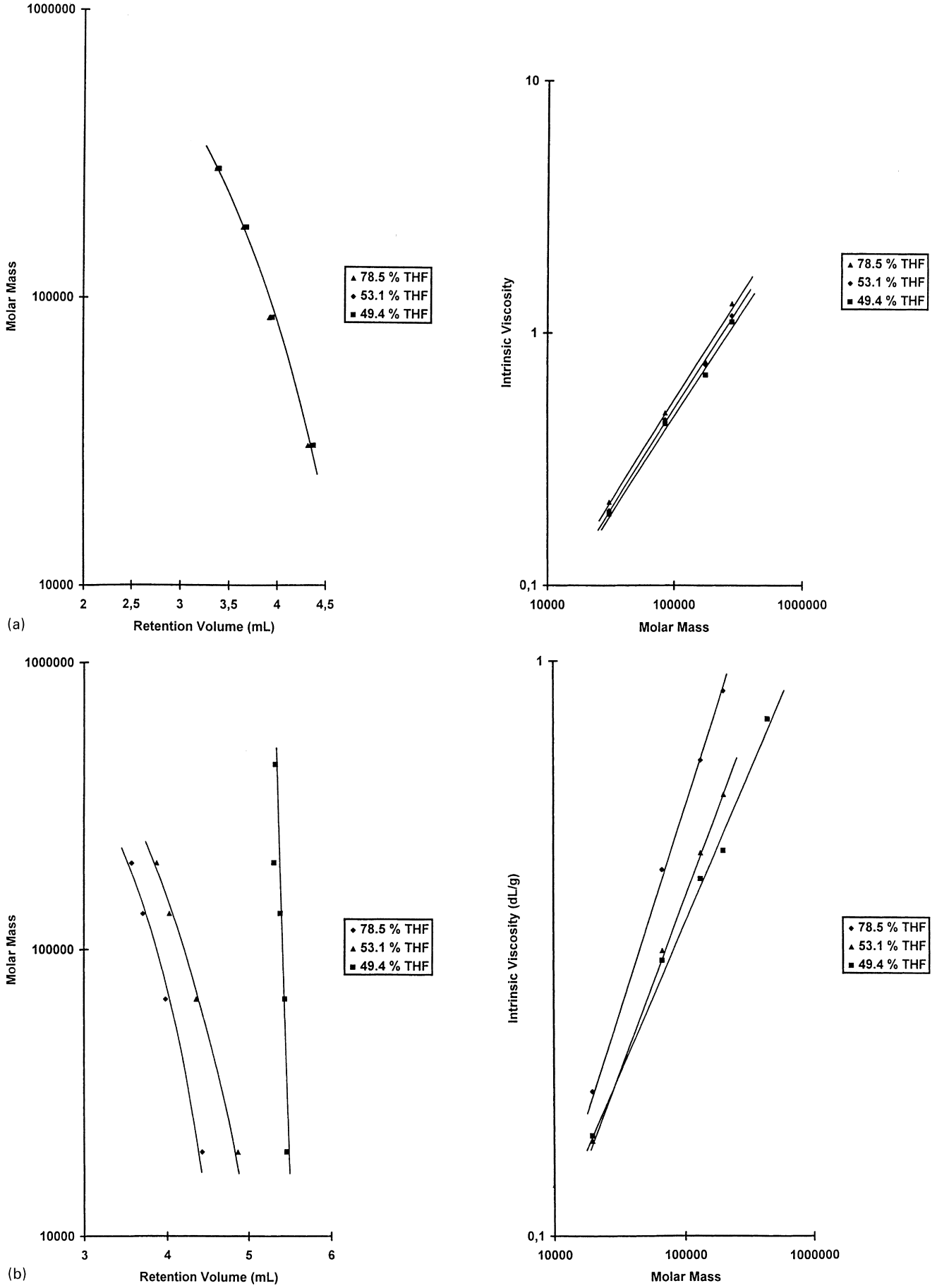

Figure 6 Calibration curves molar mass *versus* retention volume and Mark–Houwink plots for PMMA (a) and PS (b), stationary phase: Nucleosil RP-18 300 + 1000 Å, mobile phase: THF–ACN

This difference is too small to furnish separation and, therefore, PS and PtBMA cannot be separated by LCCC.

The most important feature of using a viscometer detector in liquid chromatography of polymers including LCCC is, that while completely changing the elution behaviour of different polymer species by changing the mobile phase composition, their hydrodynamic properties remain nearly unchanged. The change of the eluent composition from a thermodynamically good solvent to a solvent of lower thermodynamic quality does not change the elution behaviour and the hydrodynamic volume as long as the critical point of adsorption is not approached. This is shown for PMMA in *Figure 6a*, where going from 78.5% to 49.4% by volume of THF in the eluent does not affect the calibration curve and the Mark–Houwink plot. The behaviour of polystyrene under similar chromatographic conditions is given in *Figure 6b*. Approaching the critical eluent composition, the calibration curve molar mass *versus* retention volume changes from SEC to the completely different critical behaviour. At the same time there is only a small change in the hydrodynamic properties. The Mark–Houwink exponent a decreases by about 25% due to a certain contraction of the polymer coils in the eluent. In all cases, however, the linear relationship of log M *versus* log $[\eta]$ is kept and can be used for molar mass determinations.

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