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Chromatographic investigations of macromolecules in the critical range of liquid chromatography: 9. Separation of methacrylate-based polymer blends

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Binary polymer blends of polymethacrylates were separated by liquid chromatography at the critical point of adsorption. By operating at chromatographic conditions corresponding to the critical point of one blend component, the blends were separated regardless of the molar-mass distributions of the components. It was shown that, depending on the polarity of the components, polar or non-polar stationary phases must be used. Operating at the critical point of poly(methyl methacrylate), less polar methacrylates can be analysed using silica gel as the stationary phase and methyl ethyl ketone–cyclohexane as the eluent. For the analysis of polar polymethacrylates at the critical point of poly(decyl methacrylate), a reversed stationary phase and tetrahydrofuran–acetonitrile are a useful combination. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid chromatography; polymethacrylates; critical point of adsorption)

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, a technical polymer blend may be composed of homopolymers, of homo- and copolymers, or of copolymers. An advantage of these materials is the useful combination of the properties of the components without creating chemically new polymers. This approach often is more feasible than developing new tailor-made polymer structures. The application of blends ranges from construction materials to paints and adhesives.

The identification and quantitative determination of blend components is a demanding analytical task. In order to describe fully the chemical structure of a polymer blend, information must be obtained on the chemical structure of the components, their molar masses, the quantitative blend composition and the total molar mass. 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. This can principally be done by selective extraction or precipitation, but it was shown by a number of authors that the overlapping effects of chemical structure and molar mass disturb the quantitative separation[5,6].

Size exclusion chromatography (s.e.c.) may be used for the determination of the total molar mass of the polymer blend. As for the blend components, s.e.c. is limited to blends containing components of sufficiently different molar masses[7,8]. A separation of polymer blends with respect to chemical structure may be obtained by adsorption or gradient elution chromatography[9,10]. The molar masses of the components must then be determined by separate s.e.c. experiments for the fractions.

Recently it was shown by us that polymer blends can be analysed by liquid chromatography at the critical point of adsorption[11,12]. By operating at the critical point of one blend component, it is possible to separate the blend regardless of the chemical structure and the molar mass of the second component. Since in this experiment the second component is eluted in a size-exclusion mode, its molar-mass distribution can be determined.

The present paper is aimed at analysing polymer blends comprising polymethacrylates. The high resolving power of liquid chromatography at the critical point of adsorption will be demonstrated and solvent effects will be discussed.

EXPERIMENTAL

The separations were carried out on a modular chromatographic apparatus, comprising a Waters model 510 pump, a Waters differential refractometer R 401, 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 × 4mm i.d., self-packed columns) or Macherey-Nagel Nucleosil $5C_{18}$ (300 and 1000 Å, 250 × 4mm 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

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solvent and evaporating the solvent in a film-forming procedure. The given molar masses are manufacturers' values.

RESULTS AND DISCUSSION

Liquid chromatography at the critical point of adsorption has been established as a third mode in liquid chromatography of polymers, in addition to s.e.c. and liquid adsorption chromatography (l.a.c.). 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 its heterogeneity. Accordingly, the chain length does not contribute to retention and behaves chromatographically 'invisible'[13–16].

For a polymer blend $A_n + B_m$, the Gibbs free 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:

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

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

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 Gibbs free energy is then only a function of the chain length of B:

$$\Delta G = \sum m\Delta G_B$$

On the other hand, 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:

$$\Delta G = \sum n\Delta G_A$$

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.

As has been shown previously, the critical point of a particular polymer on a certain stationary phase can be obtained by optimizing the mobile phase composition. The present investigations were carried out on a two-column set of silica gel LiChrospher with average pore sizes of 300 and 1000 Å. When pure methyl ethyl ketone (MEK) is used as the eluent, different polymethacrylates elute in the conventional s.e.c. mode. The calibration curves of elution volume (V_e) *versus* molar mass, given in *Figure 1* for poly(methyl methacrylate) (PMMA), poly(t-butyl methacrylate) (PtBMA), poly(n-butyl methacrylate) (PnBMA) and poly(decyl methacrylate) (PDMA), reflect the inability of the system to separate different polymethacrylates of similar molar mass. Samples of molar mass of about 100 000 g mol^{-1} would elute at elution volumes of 3.08 ml (PnBMA), 3.21 ml (PtBMA), 3.32 ml (PDMA) and 3.43 ml (PMMA). Since the peak width of a narrow disperse sample is about 0.5 ml, even PnBMA and PMMA could not be separated into two individual peaks.

If now the mobile phase is changed from MEK to MEK–cyclohexane, the elution behaviour of the polymethacrylates changes depending on their polarity. For the most polar PMMA the elution volume increases with decreasing MEK/cyclohexane ratio. At a mobile phase composition of MEK/cyclohexane 70/30 per cent by volume, the calibration curve becomes a straight line parallel to the molar-mass axis, indicating critical conditions for PMMA (cf. investigations in ref. 11). At this mobile phase composition, the calibration curves of the less polar PtBMA, PnBMA and PDMA remain unchanged.

Further decreasing the MEK/cyclohexane ratio shifts the calibration curve of PMMA into the adsorption separation range. At the same time the PtBMA, which is next in polarity, starts to elute at higher elution volumes. For PtBMA the critical point is obtained at a mobile phase composition of MEK/cyclohexane 18.8/81.2 per cent by volume (see *Figure 2*). By further decreasing the MEK/cyclohexane ratio, the critical points of PnBMA and PDMA can be approached as well. The eluent compositions, corresponding to the critical point of the polymethacrylates, are summarized in *Table 1*. These experimental data can be used to develop optimum conditions for the separation of binary blends of polymethacrylates.

The separation of a binary blend of PnBMA (83 800 g mol^{-1}) and PMMA (96 000 g mol^{-1}) using different mobile phase compositions is demonstrated in

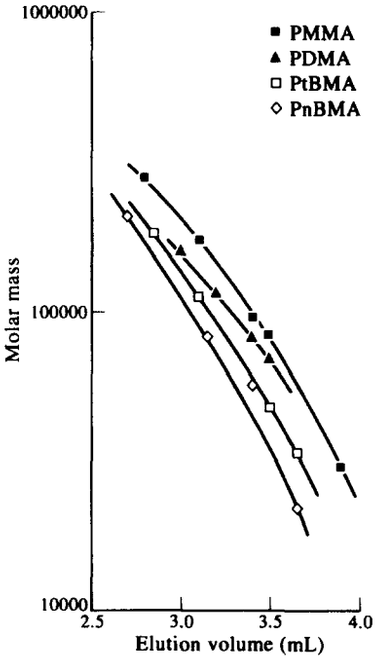


Figure 1 S.e.c. calibration curves of molar mass vs. elution volume for different polymethacrylates. Stationary phase, LiChrospher 300+1000 Å; eluent, methy ethyl ketone

Table 1 Eluent compositions corresponding to the critical point of adsorption of polymethacrylates. Stationary phase, LiChrospher 300 Å+1000 Å

Polymer	MEK/cyclohexane (vol%)
PMMA	70.0/30.0
PtBMA	18.8/81.2
PnBMA	14.3/85.7
PDMA	3.34/96.66

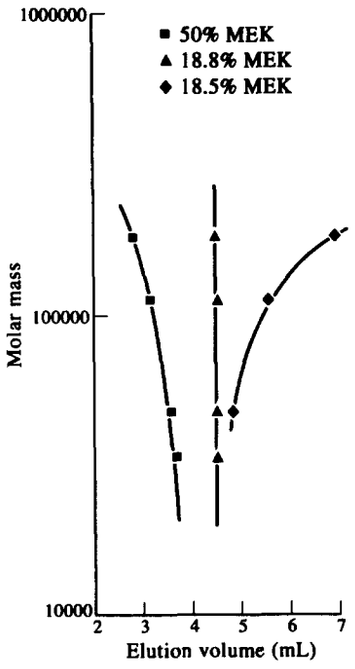


Figure 2 Critical diagram of molar mass vs. elution volume for poly(t-butyl methacrylate). Stationary phase, LiChrospher 300 + 1000 Å; eluent, methyl ethyl ketone/cyclohexane

Figure 3. When the experiment is carried out in pure MEK, a separation into components is not achieved because both components elute in the size-exclusion mode and the corresponding calibration curves are very similar (see *Figure 1*). A different behaviour is obtained when changing the mobile phase to MEK/cyclohexane 70/30 vol%. In this case a well resolved elution peak for the PnBMA is formed, whereas the elution peak for PMMA partially overlaps with a pronounced negative solvent peak. This solvent peak appears at $K_d = 1$ due to preferential adsorption of MEK. Depending on the concentration and the polarity of the blend components, the solvent peak may completely overlap with one of the component peaks. Since the position of the solvent peak is very stable, it can be separated from the PMMA peak by changing the mobile phase composition to MEK/cyclohexane 68/32 vol%. At these experimental conditions, the PnBMA elutes in the s.e.c. mode, whereas the PMMA is slightly shifted into the adsorption mode (see calibration curves *Figure 4a*). The solvent peak appears between both components and does not interfere with the component peaks. Using these experimental conditions, any binary blend comprising PMMA as the most polar component may be separated (see *Figure 4b*).

For the separation of polymer blends with PtBMA, the corresponding critical conditions for this component must be used. In order to avoid interference with the solvent peak, the separations are preferably carried out in a slight l.a.c. mode using a mobile phase of MEK/

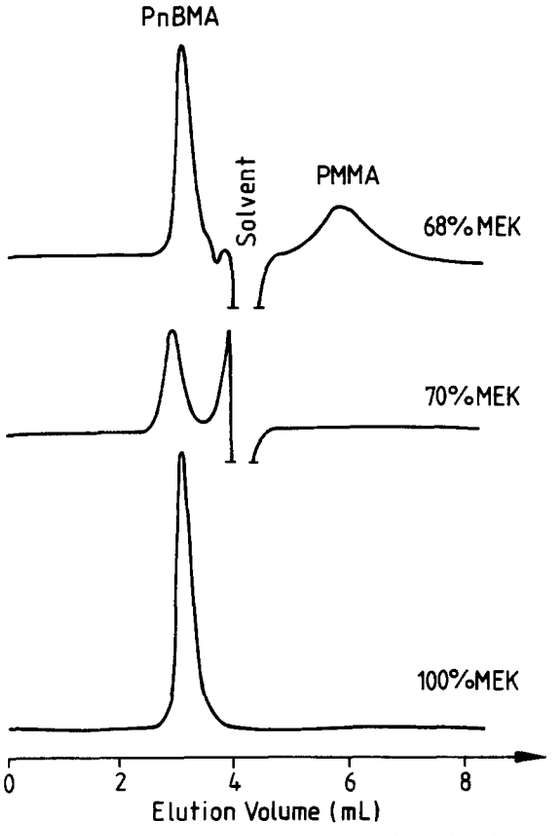


Figure 3 Chromatographic separations of a binary blend of poly(methyl methacrylate) (96 000 g mol^{-1}) and poly(n-butyl methacrylate) (83 800 g mol^{-1}) in different modes of separation. Stationary phase, LiChrospher 300 + 1000 Å; eluent, methyl ethyl ketone/cyclohexane

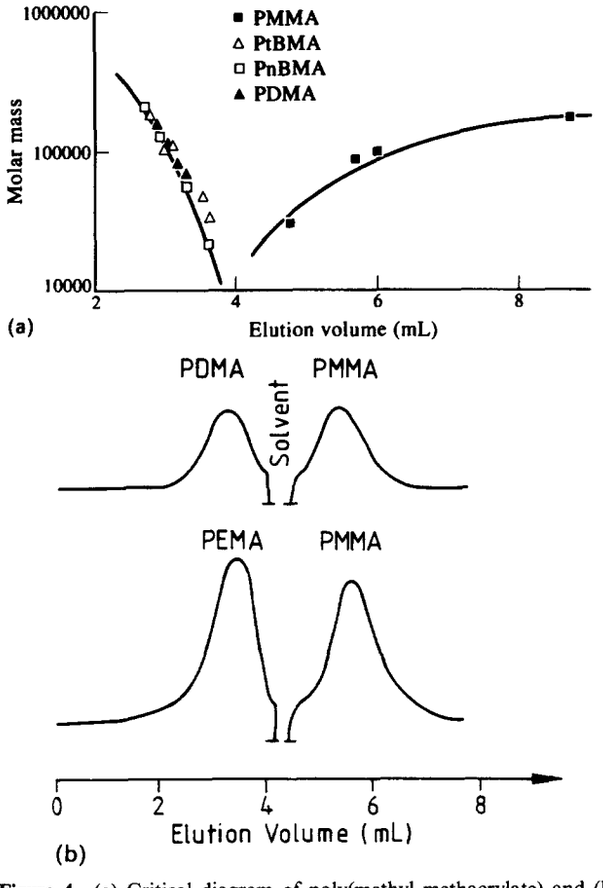


Figure 4 (a) Critical diagram of poly(methyl methacrylate) and (b) chromatographic separations of binary blends containing poly(methyl methacrylate). Stationary phase, LiChrospher 300 + 1000 Å; eluent, methyl ethyl ketone/cyclohexane 68/32 vol%

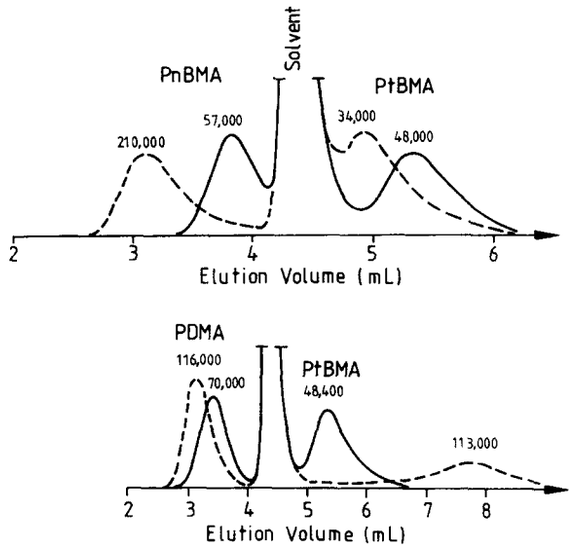


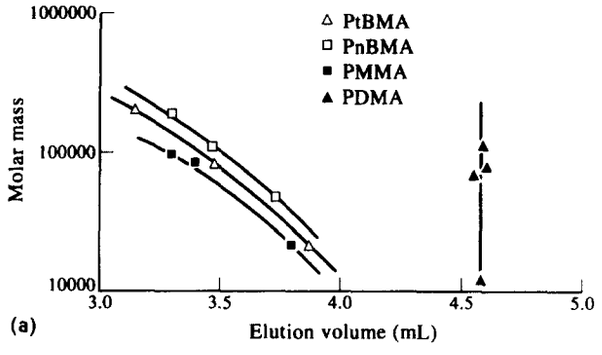
Figure 5 Chromatographic separations of binary blends containing poly(t-butyl methacrylate). Stationary phase, LiChrospher 300 + 1000 Å; eluent, methyl ethyl ketone/cyclohexane 18.6/81.4 vol%

cyclohexane 18.6/81.4 vol%. The separation of different blends containing PtBMA is shown in *Figure 5*. Because of the lower polarity of PtBMA compared to PMMA, cyclohexane is preferably adsorbed and a positive solvent peak is formed. The remarkable feature of these separations is the fact that even such similar components like PtBMA and PnBMA may be separated completely.

The experiments described so far are based on the separation of polymethacrylates on a polar stationary phase of silica gel. On silica gel, separation is accomplished with respect to increasing polarity. The higher the polarity of the polymethacrylate, the stronger is the adsorption on the stationary phase. As a consequence, the separation of two polymethacrylates of different polarity must be carried out at the critical point of the more polar component. The less polar component then elutes in the s.e.c. mode and may be analysed with respect to molar-mass distribution. If the separation were conducted at the critical point of the less polar compound, the more polar component would elute in the l.a.c. mode. Since in l.a.c. adsorption increases exponentially with the chain length, irreversible adsorption would be likely to occur for high-molar-mass samples. Therefore, in order to conduct blend separations at the critical point of the less polar component, a different stationary phase must be selected.

Polymer components may be separated according to decreasing polarity on non-polar stationary phase. Very common in h.p.l.c. are hydrophobic surface-modified silica gels, so called 'reversed phases', such as octadecyl- (RP-18) or octyl-modified (RP-8) silica. These stationary phases separate with respect to hydrophobicity, and at the critical point of the less polar polymethacrylate the more polar polymethacrylate elutes in the s.e.c. mode. Such a separation regime is the best choice for the separation of polymer blends containing PDMA as the least polar component.

Using a set of two columns of Nucleosil RP-18 with average pore sizes of 300 and 1000 Å, critical conditions for PDMA can be established with a mobile phase of tetrahydrofuran–acetonitrile (THF–ACN) (see *Figure 6a*). The critical point of adsorption corresponds to a mobile phase composition of THF/ACN 79/21 vol%. Since under these conditions a positive solvent peak interferes with the PDMA elution peak, separation is carried out at THF/ACN 77/23 vol% (see *Figure 6b*). Under these conditions well separated peaks for both components are obtained which may be quantified.



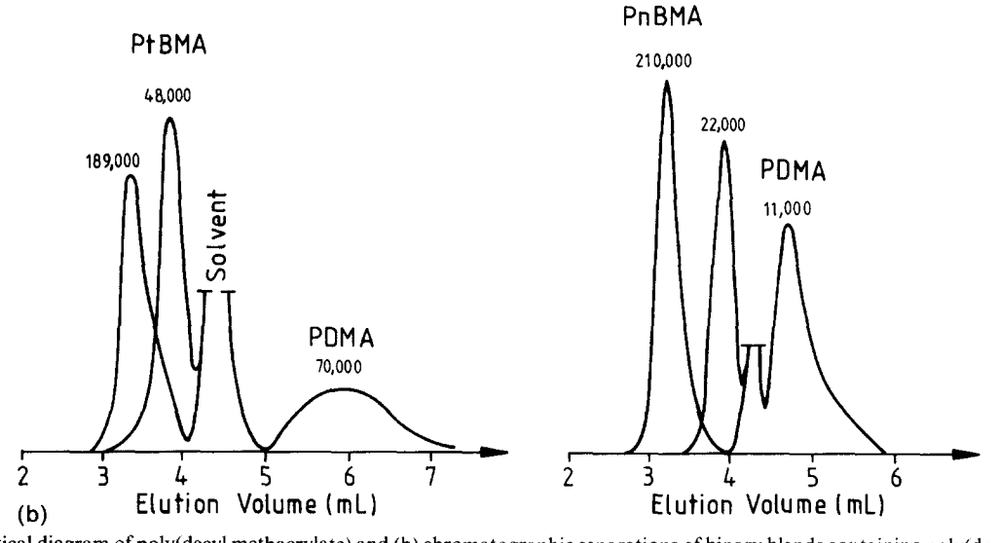


Figure 6 (a) Critical diagram of poly(decyl methacrylate) and (b) chromatographic separations of binary blends containing poly(decyl methacrylate). Stationary phase, Nucleosil RP-18 300 + 1000 Å; eluent, tetrahydrofuran/acetonitrile 77/23 vol%

As has been shown, blends of polymethacrylates can be separated regardless of the molar masses of the components by liquid chromatography at the critical point of adsorption. The composition of the blend may then be calculated from the relative areas of the elution peaks considering the different response factors of the components. For the component eluting in the s.e.c. mode, the molar-mass distribution can be determined using conventional s.e.c. calibration procedures. The limiting factor of these separations is the adverse effect of the solvent peak. In forthcoming investigations this problem will be addressed and alternative detection methods will be evaluated.

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