# Chromatographic investigations of macromolecules in the critical range of liquid chromatography: 3. Analysis of polymer blends

**H. Pasch**
*Deutsches Kunststoff-Institut, Schlossgartenstrasse 6, 6100 Darmstadt, Germany*
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Polymer blends of various compositions were analysed by liquid chromatography at the critical point of adsorption. 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 blend component. In addition, the molar mass and the molar-mass distribution of the second blend component may be determined via a conventional size exclusion chromatography procedure. It is shown that, in addition to homopolymer blends, blends comprising a copolymer as one component may be separated.

**(Keywords: liquid chromatography; critical point of adsorption; blends; separation; analysis)**

## INTRODUCTION

Multicomponent systems (blends) are an important part of commercial polymeric materials. An advantage of these materials is the useful combination of the properties of the components without creating chemically new polymers. This approach in many cases is more feasible than developing new tailor-made polymer structures. The applications of polymer mixtures or blends range from construction materials to paints and adhesives.

The identification and quantitative determination of blend components is a demanding analytical task and universal methods do not exist. In addition to spectroscopic methods, such as infra-red spectroscopy and nuclear magnetic resonance, which may help to identify blend components, a separation step is often required.

One way to separate polymer blends is selective extraction with appropriate solvents. It has been shown, however, that in many cases, even after prolonged extraction periods, quantitative separation was not achieved[1]. A second way to separate the components of a polymer blend is the application of a solution-precipitation system, where the blend is completely dissolved in an appropriate solvent and one component is selectively precipitated by adding a non-solvent for this particular polymer[2,3]. An important limitation of this approach is the overlapping of the effects of the chemical structure and the molar mass in the precipitation step.

In conclusion, size exclusion chromatography may be used for the separation of polymer blends[4,5]. As s.e.c. separates according to the hydrodynamic volume of the macromolecule, this method is limited to blends containing components of different molar mass.

The present paper is aimed at analysing polymer blends using a new chromatographic technique—liquid chromatography at the critical point of adsorption.

## EXPERIMENTAL

The chromatographic investigations were carried out on a modular h.p.l.c. system, comprising a Waters model 510 pump, a Waters differential *RI* detector R401, a Knauer u.v./vis. filter photometer, a Rheodyne six-port injection valve and a Waters column oven. The columns were either a Macherey-Nagel Nucleosil Si-100, 5 $\mu$m average particle size, 200 × 4 mm i.d., prepacked column or Merck LiChrospher Si-300 and Si-1000, 10 $\mu$m average particle size, 200 × 4 mm i.d., self-packed columns.

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

The polymer blends were prepared either by dissolving the components in a common solvent and evaporating the solvent in a film-forming procedure or by mixing the components in a Brabender Plasticorder.

## RESULTS AND DISCUSSION

It is established that there are three modes of liquid chromatography of macromolecules — size exclusion, adsorption and critical. Size exclusion chromatography (s.e.c.) is based on changes of entropy of the macromolecule when passing into the pores of the stationary phase. It separates macromolecules according to their hydrodynamic volume. With increasing molar mass the distribution coefficient $K_d$ changes from 1 to 0. Adsorption chromatography is based on enthalpic interactions and $K_d$ grows exponentially with increasing molar mass. The critical mode corresponds to the case where the entropy losses of the bond between two successive monomer units close to the pore wall are compensated by the interaction energy with the wall[6]. At this point $K_d = 1$ regardless of the molar mass of the macromolecule. Accordingly, the chain length of the macromolecule does not contribute to retention and behaves chromatographically 'invisible'[7,8].

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It was shown in previous investigations that, at the critical point of adsorption, functional polymers may be characterized with respect to their functionality-type distribution[9,10]. Using this 'invisibility' concept, block copolymers may be characterized as well. Taking a block copolymer $A_nB_m$ the block $A_n$ may be characterized at the critical point of $B_m$ and vice versa[11].

In a similar way it is expected to be possible to separate blends consisting of polymers of different polarity. In all cases, selecting the critical conditions of one blend component, the other blend component may be analysed with respect to its molar-mass distribution. Under critical conditions, different from size exclusion and adsorption, an overlapping of the elution zones of the blend components is avoided (see *Figure 1*).

To explain the separation procedure of polymer blends using chromatography at the critical point of adsorption, the behaviour of blends of polystyrene (PS) and poly(methyl methacrylate) (PMMA) in different chromatographic modes is shown in *Figure 2*. With silica gel Si-100 as the stationary phase, the mobile phase comprised mixtures of methyl ethyl ketone (MEK) and cyclohexane. At a composition of the mobile phase of 100 vol% MEK, a size exclusion mode is operating for both components. Under these conditions PMMA and PS may be separated only if their molar masses are quite different. For low-molar-mass compounds (PS, PMMA 30000) the two components of the blend may be identified, but separation is poor. For higher molar masses (PS, PMMA 150000), however, one symmetric elution peak, similar to the elution profile of a homopolymer, is obtained.

When cyclohexane is added to MEK the elution behaviour of PMMA changes dramatically, whereas for PS it remains nearly constant. The slope of the calibration curve of log $M$ vs. $RT$ increases (see *Figure 2*, upper right corner) and at 73 vol% MEK/27 vol% cyclohexane a vertical line is obtained. This corresponds to the critical conditions of PMMA where molar mass does not contribute to retention. As can be seen in *Figure 2*, in the near-critical region (75 vol% MEK) separation of blend components of equal molar mass is improved, compared to the size exclusion mode. Blends of higher-molar-mass PMMA and lower-molar-mass PS, however, may not be separated, because the elution zone of PMMA is shifted towards higher retention times and therefore overlaps with the elution zone of the PS.

At the critical point of PMMA (73 vol% MEK/27 vol% cyclohexane) a complete separation of the elution zones of PMMA and PS is achieved. *Figure 3* demonstrates clearly that for PMMA regardless of its molar mass one retention time is obtained corresponding to $K_d = 1$ for all molar masses. Since these conditions correspond to a size exclusion mode for PS, the retention time of this component decreases with increasing molar mass. Accordingly, the molar mass and the polydispersity of

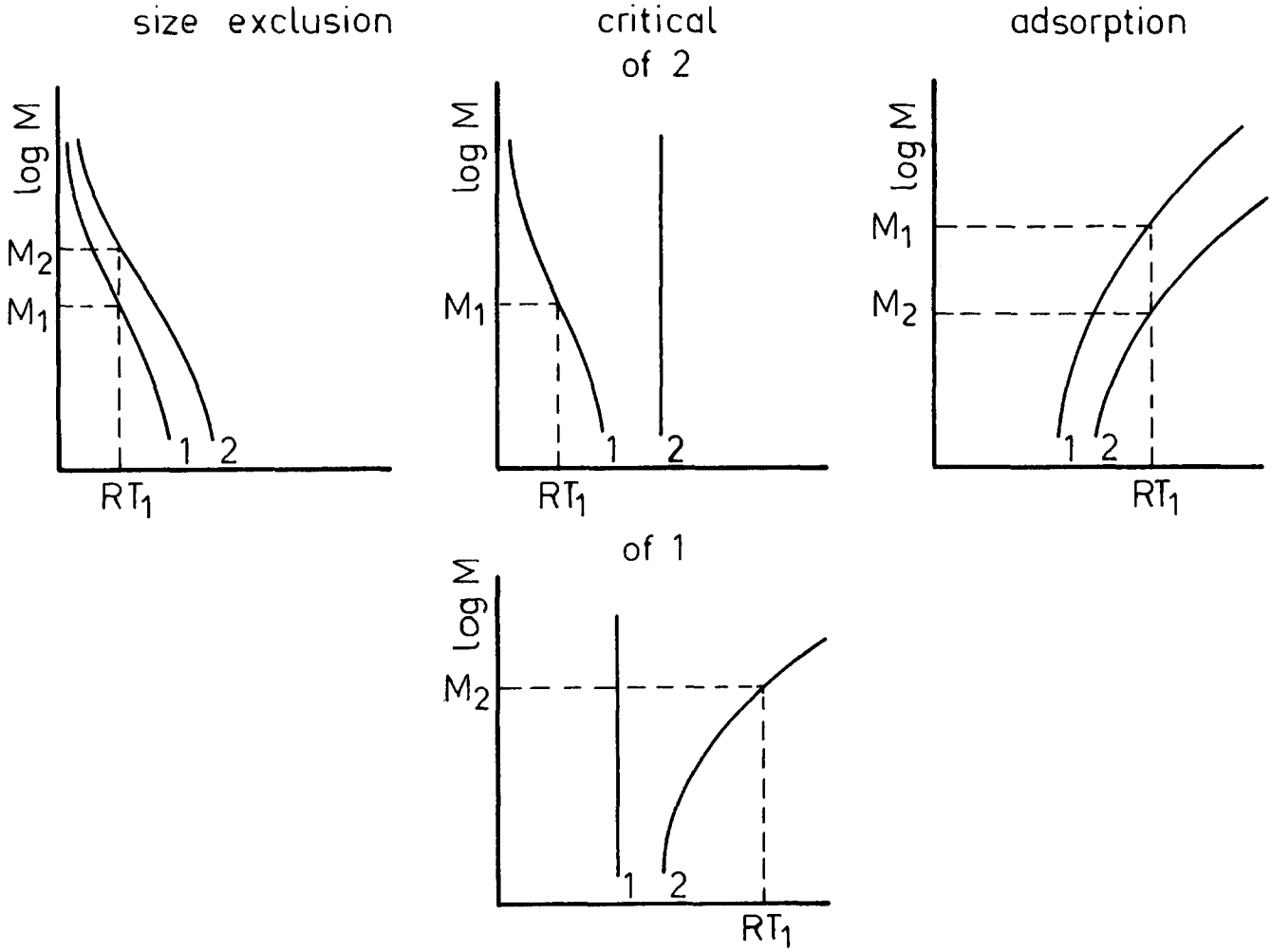


**Figure 1** Behaviour of the calibration curves of a two-component polymer blend in the three chromatographic modes

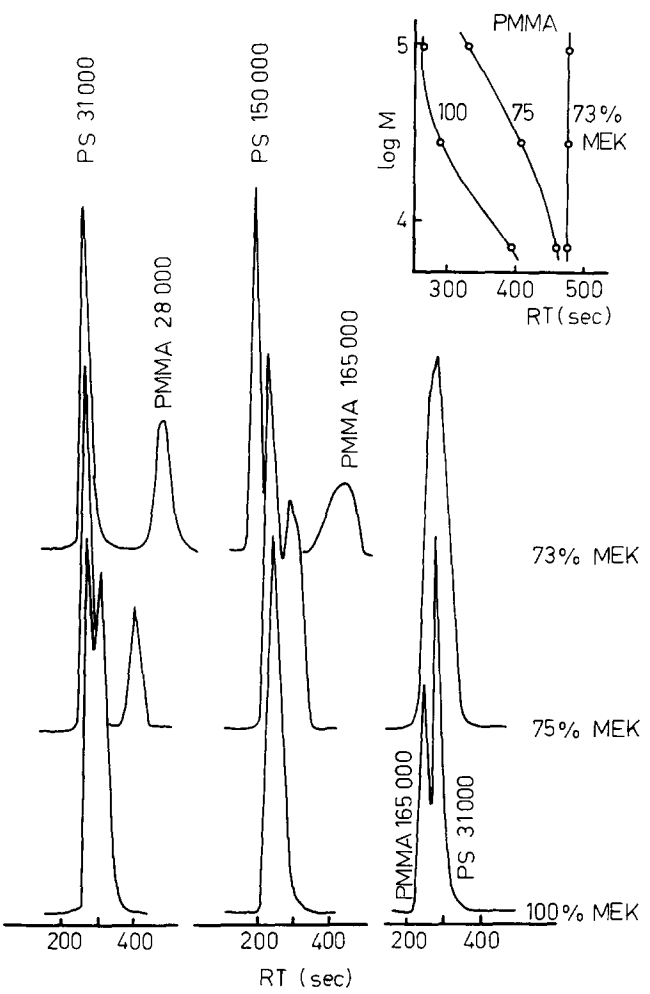


**Figure 2** Critical diagram of PMMA and chromatograms of PS–PMMA blends in different chromatographic modes. Stationary phase, Nucleosil Si-100; mobile phase, methyl ethyl ketone–cyclohexane

the PS blend component may be determined via an appropriate calibration.

At the critical point of PMMA, other polymer blends comprising PMMA as one component may be separated as well. *Figure 4* shows the behaviour of poly(vinyl chloride) (PVC)–PMMA blends in the size exclusion mode for both components (100 vol% MEK) and in the critical mode for PMMA (73 vol% MEK/27 vol% cyclohexane). Again, in the first case the blend components are only separated when both are of relatively low molar mass. In all other cases only a certain tailing of the elution profiles indicates an inhomogeneity of the sample. A completely different picture is obtained when the blends are separated at the critical point of PMMA. In this case, similar to the PS–PMMA blends, baseline-separated peaks are obtained for the blend components.

As was shown in the previous chapter, at the critical point of PMMA the second blend component is eluted in a size exclusion mode. In order to determine the molar mass and polydispersity of this component correctly, the pore size and pore size distribution of the stationary phase must correspond to the hydrodynamic volume of the component to be analysed. As for silica gel Si-100, higher-molar-mass samples are eluted in the vicinity of the exclusion limit. In this case it is necessary to increase the pore size of the stationary phase.

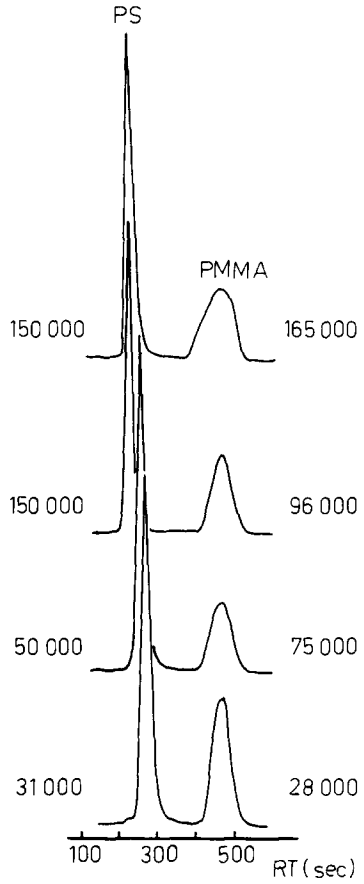


**Figure 3** Chromatograms of PS–PMMA blends at the critical point of PMMA. Stationary phase, Nucleosil Si-100; mobile phase, methyl ethyl ketone–cyclohexane 73:27 vol%

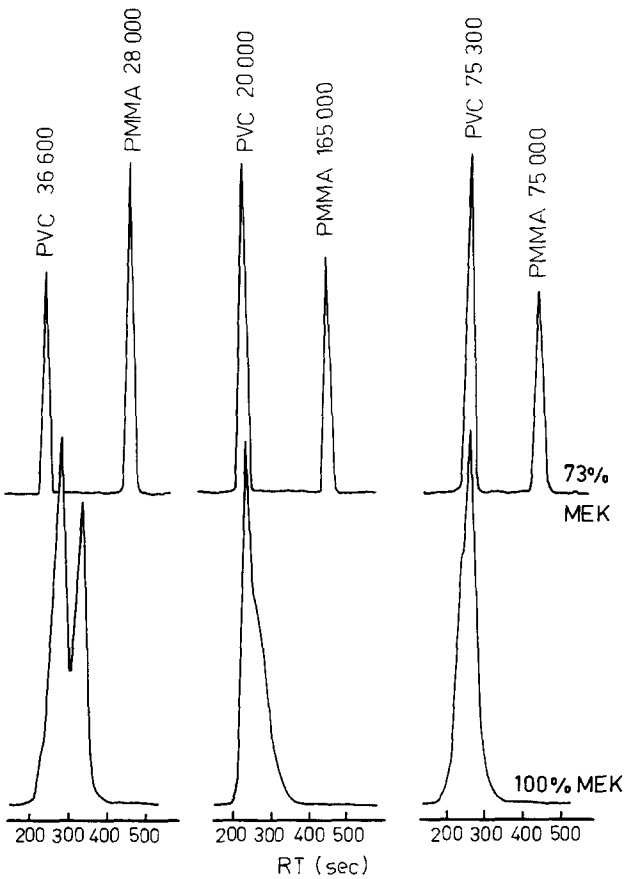


**Figure 4** Chromatograms of PVC–PMMA blends in size exclusion and critical modes; for conditions, see *Figure 2*

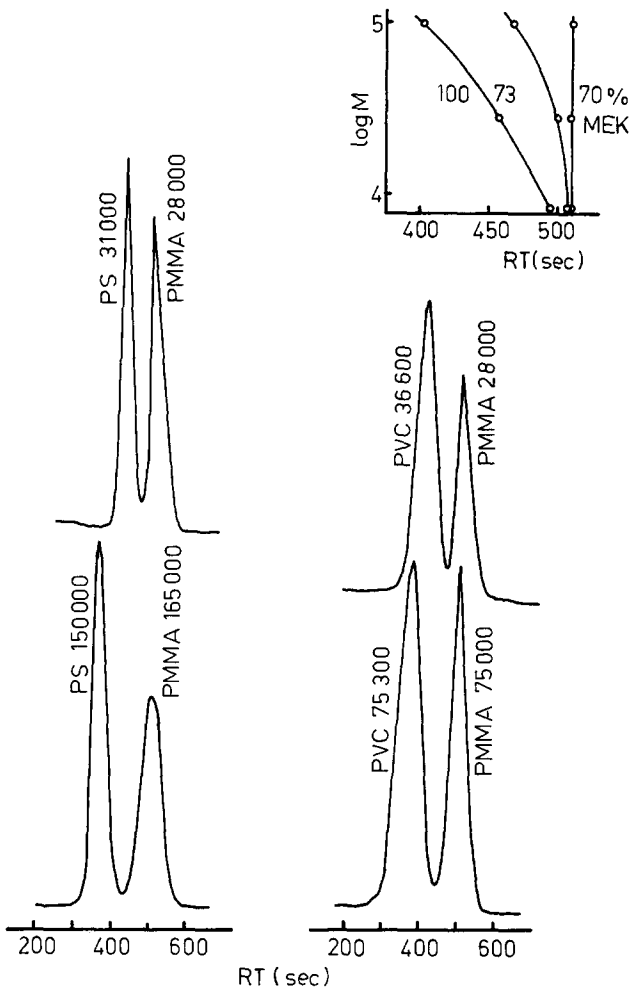


**Figure 5** Critical diagram of PMMA and chromatograms of PS–PMMA and PVC—PMMA blends at the critical point of PMMA. Stationary phase, LiChrospher Si-300 and Si-1000; mobile phase, methyl ethyl ketone–cyclohexane 70:30 vol%

The separation of polymer blends on a two-column system of silica gel Si-300 and Si-1000 is shown in *Figure 5*. For this column system, which has slightly different silica surface characteristics, the mobile phase composition has to be adjusted accordingly. As can be seen, the critical point of PMMA is shifted to a mobile phase composition of 70 vol% MEK/30 vol% cyclohexane (*Figure 5*, upper right corner). At this point PS–PMMA and PVC–PMMA blends may be separated into their components. However, compared to the separation on Si-100, the resolution of the new column system is lower. This is mainly due to the average particle size of 10 $\mu$m compared to 5 $\mu$m for the Si-100 stationary phase. It is expected that the resolution may be improved by decreasing the particle size of the stationary phase.

Since PMMA is always eluted at $K_d = 1$ regardless of its molar mass, all different types of polymer blends comprising PMMA as one component may be separated. This is demonstrated for a few more examples in *Figure 6*. Even chemically very similar blend components, such as poly(cyclohexyl methacrylate) (PCHMA) and PMMA are separated. In addition, not only blends of homopolymers but also blends of copolymers and PMMA may be investigated. Similar to the homopolymers, poly(styrene-*co*-acrylonitrile) and poly(styrene-*co*-methyl methacrylate) are eluted in a size exclusion mode.

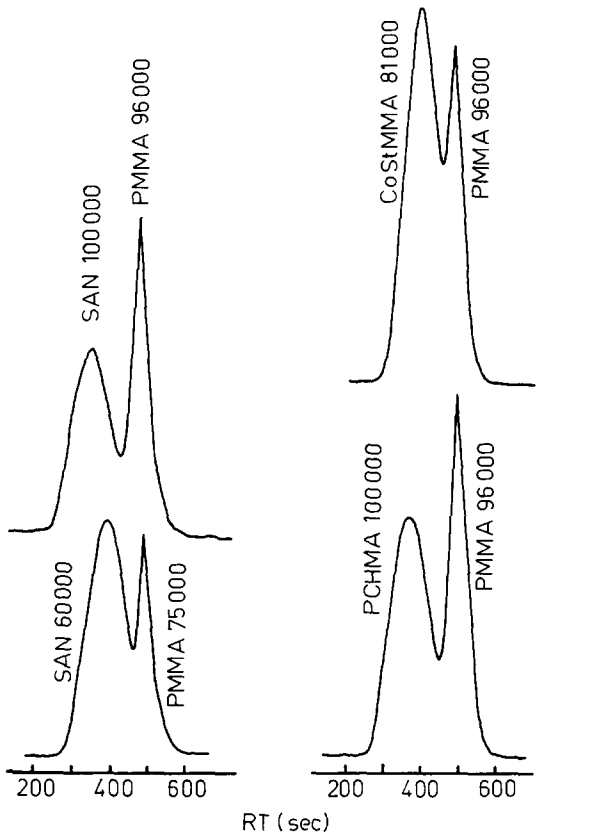


**Figure 6** Chromatograms of blends of PMMA and copolymers at the critical point of PMMA; for conditions, see *Figure 5*

**Table 1** Molar-mass determination of PS in PS–PMMA blends and PVC in PVC–PMMA blends

| Nominal $M_w$ | | Determined PS molar mass | | |
|---|---|---|---|---|
| PS | PMMA | $M_w$ | $M_n$ | $U = M_w/M_n$ |
| 31000 | 28000 | 28400 | 24100 | 1.18 |
| 150000 | 165000 | 147400 | 138900 | 1.06 |
| Nominal $M_w$ | | Determined PVC molar mass | | |
| PVC | PMMA | $M_w$ | $M_n$ | $U = M_w/M_n$ |
| 75300 | 75000 | 79000 | 65800 | 1.20 |
| 36600 | 28000 | 38400 | 31500 | 1.22 |

Finally, the quantitative determination of the molar mass and the polydispersity of PS in PS–PMMA blends and PVC in PVC–PMMA blends may be carried out using a conventional s.e.c. calibration procedure; see *Table 1* for two samples each. As was expected, the agreement between the nominal molar mass and the determined value is very good.

## CONCLUSION

Liquid chromatography at the critical point of adsorption has proved to be a useful method for the separation of polymer blends. By operating at the critical point of one blend component, the other component may be eluted in a size exclusion mode. Via an appropriate s.e.c. calibration procedure, the molar mass and polydispersity

may be determined. It was demonstrated that not only blends comprising homopolymers, but also blends containing a copolymer as one component, may be analysed.

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