Separation of Poly(methyl methacrylate)s According to Their Tacticity II. Chromatographic Investigations of Poly(methyl methacrylate)s with Different Tacticity at the Critical Adsorption Point

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ABSTRACT: The poly(methyl methacrylate)s (PMMA)s differing in their tacticity were investigated by liquid chromatography at the critical adsorption point (LC CAP). The set of chromatographic conditions (eluent composition determining its adsorption strength, column packing nature and temperature) was identified for given highly stereoregular PMMA)s, under which the exclusion of polymer chain from the pores (entropic effect) was just compensated by the adsorption of the polymer chain on the column packing surface (enthalpic effect). The result was that no separation according to the solute molar mass took place. Using bare silica gel column packing and tetrahydrofuran (THF)/*n*-hexane mixture as eluent at 30°C, syndiotactic (st-) PMMA)s were more readily adsorbed on the column packing surface than isotactic (it-) PMMA)s. The critical adsorption point (CAP) for st-PMMA)s was reached with the eluent composition THF/*n*-hexane (83.2/16.8, w/w). Under the same conditions, however, it-PMMA)s were eluted in the size exclusion chromatography (SEC) mode and the separation was achieved for mixtures of it-PMMA and st-PMMA of lower molar mass. With the same bare silica gel as the stationary phase and chloroform (CHCl₃)/ethanol or CHCl₃/THF mixtures as eluents at 30°C, st-PMMA)s were less adsorbed on column packing and they eluted in the SEC mode while the CAP was reached for it-PMMA)s, *i.e.*, CHCl₃/ethanol (97.2/2.8, w/w) or CHCl₃/THF (87.7/12.3, w/w). By using latter non-aggregating mixed eluents containing chloroform, the satisfactory separation of st- plus it-PMMA mixtures were achieved even for polymers with molar masses exceeding 100000 g mol⁻¹. The results indicate the potential of liquid chromatographic procedures that combine exclusion and adsorption mechanisms in separation of macromolecules according to their stereoregularity. Further, the advantages of the LC CAP mixed eluents is demonstrated that are composed solely of the solvents for polymers under study.

KEY WORDS Poly(methyl methacrylate) / Tacticity / Isotactic Poly(methyl methacrylate) / Syndiotactic Poly(methyl methacrylate) / Liquid Chromatography at Critical Adsorption Point / Separation /

The characteristic feature of stereoregular polymers is the distribution of not only molar mass but also stereoregularity. The average molecular weight (*M*) and its distribution (MWD), together with stereo regularity and its distribution, determine the macroscopic properties of these polymers.

An on-line size exclusion chromatography/nuclear magnetic resonance hyphenation¹ is a powerful tool for characterization of stereoregular polymers when their tacticity varies with molar mass. However, it is impossible to independently assess both the above-mentioned distributions by a liquid chromatographic method that is based on single separation mechanism, *e.g.*, by size exclusion chromatography (SEC). At least, the combination of two different separation mechanisms has to be used. The discrimination is feasible for polymers with narrow MWD, differing in their degree of stereoregularity, by combining SEC mechanism of separation with the processes dependent on the differences in the solubility of particular stereoisomers, *i.e.*, by applying the liquid chromatography under limiting conditions of solubility.²

Another new and modern coupled liquid chromatographic procedure that allows separation and characterization of complicated polymer systems is liquid chromatography at critical adsorption point (LC CAP).³ LC CAP presents a combination of size exclusion (entropic) separation mechanism with adsorption (enthalpic) separation mechanism. A set of the chromatographic con-

ditions is identified for a given homopolymer, *i.e.*, column packing, eluent strength, temperature, pressure, under which the two above counteractive separation mechanisms mutually compensate so that no separation according to the molar mass takes place. This behavior can be utilized in the characterization of block⁴ or graft copolymers,⁵ functional oligomers,⁶ and polymer mixtures⁴ which constituents exhibit different adsorption characteristics, including mixtures of block copolymers and their parent homopolymers.⁷ The experimental conditions are chosen usually in such a way that one constituent is set at its critical adsorption point while another constituent is normally separated in the SEC mode.

In the present work we have tested the potentiality of the LC CAP in separation of poly(methyl methacrylate)s (PMMA)s with different tacticity.

EXPERIMENTAL

All chromatographic measurements were carried out using a liquid chromatograph, composed of a Waters Model 510 pump (Milford, MA, U.S.A.), a Knauer six-port three-way injection valve provided with a 20 μ L sample loop, a Knauer column oven (all from Knauer, Berlin, Germany), and a Model DDL-21 evaporative light scattering detector (Eurosep Instruments, Cergy-St. Christophe, France). The column 250 $\times$ 4 mm was packed with Nucleosil (bare silica gel), pore size 12 nm, particle

Table I. Characteristic of syndiotactic and isotactic poly(methyl methacrylate)s²

Sample	Polymerization conditions ^a	$\bar{M}_w^b$	$\bar{M}_n^b$	$\bar{M}_w/\bar{M}_n^b$	Tacticity/% ^c		
		10 ³ g mol ⁻¹	10 ³ g mol ⁻¹		<i>mm</i>	<i>mr</i>	<i>rr</i>
SG-33-200	A	12.7	10.6	1.20	0	11	89
DPI-1	A	28.6	22.7	1.26	0	11	89
EM357	A	100.7	73.0	1.38	2	7	91
NF714-1000	A	153.3	111.9	1.37	0	12	88
MA-35-2	B	12.3	9.8	1.25	97	2	1
ON72C	B	27.4	21.8	1.26	97	2	1
NF678	B	86.9	63.0	1.38	97	2	1
NF712	B	157.1	100.0	1.57	98	1	1

^aA, prepared with *t*-C₄H₉Li-(C₂H₅)Al(1/3) in toluene at -78°C; B, prepared with *t*-C₄H₉MgBr in toluene at -60°C. ^bDetermined by SEC. ^cDetermined by ¹H NMR.

size 5 μ m. Alternatively, a column set consisting of three columns Nucleosil (bare silica gel) 12 + 30 + 100 nm, 5 μ m, 3 $\times$ 250 $\times$ 4 mm was applied. The detector signal was collected on-line by using a PC and Waters Baseline data acquisition system (Milford, MA, U.S.A.).

The highly isotactic (it-) and highly syndiotactic (st-) PMMAs with narrow MWD were prepared by the stereospecific living polymerizations.^{8,9} More detailed information related to their synthesis and tacticity determination is given in the Table I and also in the first paper of this series.² The predominantly syndiotactic PMMA samples (*rr* content from 44.7 to 51.6%) of narrow MWD in the range of M from 2.7×10^3 to 570.0×10^3 g mol⁻¹ were obtained from PSS Co. (Mainz, Germany). One set of the eight PMMA samples of moderately broad MWD with *rr* content of 49–69% and M from 16×10^3 up to 613×10^3 g mol⁻¹ was obtained from Rohm Co. (Darmstadt, Germany).

Twenty microliters of polymer solution in eluent used (0.5 mg mL⁻¹) were injected into analytical column at 30°C.

Tetrahydrofuran (THF), chloroform (CHCl₃), ethanol (EtOH), *n*-hexane, and their mixtures were used as eluents and sample solvents. Mixed eluents were prepared by weighing particular components so that the compositions of the eluents are expressed in w/w ratio. Chloroform contained 0.8% of ethanol as a stabilizer. The amounts of EtOH in eluent given in this paper represent EtOH stabilizer plus EtOH added. The eluent flow rate was 1.0 mL min⁻¹ in all cases.

RESULTS AND DISCUSSION

Both the highly stereoregular PMMAs and the PMMAs of low tacticity eluted from chromatographic column packed with bare silica gel in SEC mode using pure THF as eluent (Figure 1). The courses of particular calibration curves were very similar and the full discrimination of PMMAs according to their tacticity is not possible using this chromatographic system.

The calibration curves for st-PMMAs in THF/*n*-hexane mixtures are shown in Figure 2. The addition of *n*-hexane to THF expressively influenced the elution behavior of st-PMMA. With increasing percentage of *n*-hexane in eluent, the retention volumes of st-PMMAs were shifted to higher retention volumes, and at eluent composition of THF/*n*-hexane = 83.2/16.8% all st-

Figure 1. Calibration curves for PMMA with different tacticity in THF (open symbols) and in THF/*n*-hexane (83.2/16.8 w/w) (solid symbols). Column: Nucleosil (bare silica gel), 12 nm, 5 μ m, 250 $\times$ 4 mm. $\square$, $\blacksquare$, PMMA (Rohm GmbH); $\circ$, $\bullet$, PMMA (PSS Co.); $\triangle$, $\blacktriangle$, it-PMMA; $\diamond$, $\blacklozenge$, st-PMMA.

Figure 2. Calibration curves for st-PMMA in THF and in THF/*n*-hexane mixtures at 30°C. Column: Nucleosil (bare silica gel), 12 nm, 5 μ m, 250 $\times$ 4 mm. Weight% of *n*-hexane in eluent: $\square$, 0; $\circ$, 10; $\triangle$, 15; ∇ , 16.5; $\blacklozenge$, 16.8; $+$, 17.2; $\times$, 18.3.

PMMAs eluted from the column packing at similar retention volumes more or less independently of their molar masses. This retention volume was, however, a

Figure 3. Chromatograms of mixtures of it- and st-PMMAs. Column: Nucleosil (bare silica gel), 12 nm, 5 μ m, 250 $\times$ 4 mm. Eluent, THF/*n*-hexane = 83.2/16.8 w/w.

Figure 4. "Calibration curves" for it-PMMAs in $\text{CHCl}_3/\text{EtOH}$ mixtures at 30°C. Column set: Nucleosil (bare silica gels), 12 + 30 + 100 nm, 5 μ m, 3 $\times$ 250 $\times$ 4 mm. Weight% of EtOH in eluent: $\blacktriangle$, 2.8; +, 2.9; $\square$, 3; $\circ$, 10.8; *, 20.8; $\triangle$, 30.8.

little higher than the total volume of liquid in the column. The CAP was shown to be very sensitive to the slight changes in eluent composition. Further addition of *n*-hexane to eluent caused the elution of st-PMMAs according to the liquid adsorption chromatographic mode, i.e., their retention volumes rose with their molar mass.

The retention behavior for samples with different stereoregularities in mixed eluent THF/*n*-hexane 83.2/16.8% is also shown in Figure 1. The retention of PMMAs evidently depended on the degree of their tacticity. This indicates the possibility to separate PMMAs according to their tacticity by applying the combination of exclusion and adsorption mechanisms in liquid chromatography.

An example of separation of it-PMMAs that elute in size exclusion mode from st-PMMAs that elute at their critical adsorption point is shown in Figure 3. Lower molar mass polymers ($M = 12000$ and 28000 g mol^{-1}) which did not yet aggregate in THF/*n*-hexane "critical mixture" could be fairly well separated. In the case of

Figure 5. Calibration curves for st- and it-PMMAs in a mixture of $\text{CHCl}_3/\text{EtOH}$ (97.2/2.8, w/w) at 30°C. The chromatogram of st-PMMA ($153300 \text{ g mol}^{-1}$) and it-PMMA ($157100 \text{ g mol}^{-1}$) polymer mixture is also plotted. Column set: Nucleosil (bare silica gels), 12 + 30 + 100 nm, 5 μ m, 3 $\times$ 250 $\times$ 4 mm.

higher molar mass polymer mixtures, however, only one peak appeared on chromatogram in the area of the column interstitial volume. This peak might correspond to the aggregates of st- and it-PMMAs. The discussion of this point will require further experimental data.

In the next step the non-aggregating solvent chloroform was used. Since PMMAs is fully adsorbed on bare silica gel using CHCl_3 as eluent, a polar additive was chosen to promote the polymer elution. Chloroform already contained a small amount of ethanol as stabilizer. Therefore, further EtOH was added to eluent as desorption promoting liquid in some experiments. Mori *et al.* have found that small amount of EtOH added to CHCl_3 effectively reduced adsorption of acrylic copolymers on bare silica gel.¹⁰ We have found the similar effect for it-PMMA when the extent of its adsorption can be easily controlled by the addition of ethanol (Figure 4). Unfortunately, this system was extremely sensitive to the small changes in the eluent composition, too. The CAP lay at very low ethanol content (2.8%).

Figure 5 shows that at the CAP for it-PMMAs, the st-PMMAs were eluted according to the SEC mode. The discrimination of it- and st-PMMAs with similar molar masses was well possible. In contrast to THF/*n*-hexane system, $\text{CHCl}_3/\text{EtOH}$ system could be used also with higher molar mass samples since the aggregation was suppressed. However, the recovery of polymers decreased quite drastically with increasing molar mass. Instead of $\text{CHCl}_3/\text{EtOH}$ mixture that is composed of a solvent and nonsolvent for PMMA, we decided to use a CAP eluent containing two solvents for PMMAs; chloroform was chosen as a non-aggregating, adsorption-promoting solvent, and THF as an adsorption suppressing liquid.

Critical adsorption point for it-PMMAs in CHCl_3/THF mixture was well defined as seen in Figure 6. The CAP was still rather sensitive to the small variations not only in eluent composition but also in temperature. Thus, in this particular experiment, the temperature change was used for fine tuning of CAP of it-PMMA. The adsorption of it-PMMAs within the column packing was stronger than that of st-PMMAs. Consequently,

Figure 6. Calibration curves for it-PMMA in CHCl_3/THF mixtures at 30°C . Column set: Nucleosil (bare silica gels), $12 + 30 + 100\text{nm}$, $5\ \mu\text{m}$, $3 \times 250 \times 4\text{mm}$. Weight% of CHCl_3 in eluent: $\triangle$, 86.5; $\circ$, 87.6; $\square$, 87.7; $\times$, 88; $\blacktriangle$, 87.7; (at 35°C).

Figure 7. Calibration curves for st- and it-PMMA in CHCl_3/THF (87.7/12.3, w/w). The chromatograms of it-PMMA and st-PMMA polymer mixtures are also plotted: $\cdots$, 157100 + 153300; $-\cdot-, 27400 + 28600; $—$, 12300 + 12700 g mol^{-1} . Column set: Nucleosil (bare silica gels), $12 + 30 + 100\text{nm}$, $5\ \mu\text{m}$, $3 \times 250 \times 4\text{mm}$.$

st-PMMA were still eluted in the SEC mode when the critical adsorption point for it-PMMA was reached and satisfactory discrimination of mixtures of it-PMMA and st-PMMA was achieved even for polymers with molar mass exceeding 10^5 g mol^{-1} (Figure 7).

Peak broadening and even splitting is sometimes observed in the course of LC CAP of high polymers.^{11,12} This phenomenon is evidenced in Figure 7. It is shown that the peaks monitored at the critical adsorption point were rather broad and the peak broadening increased with increasing molar mass.

Our observations show that the adsorption of macromolecules on solid surfaces depends under otherwise identical conditions not only on the polymer chemical nature and molar mass but also on its stereochemical structure. This conforms with results obtained by Sato *et al.*¹³ who investigated the elution characteristics of it- and st-PMMA by both normal phase and reversed phase high performance liquid chromatography (HPLC).

Using a cross-linked polyacrylonitrile gel as the column packing, and various two component aggregation-preventing eluents, he achieved the separation of it-PMMA from either st-PMMA or atactic PMMA. Sato *et al.*¹³ also observed a change in the elution order when varying the column packing and the eluent. A single peak appeared when the polymer mixtures were injected into the chromatographic column flushed with some stereo-complex-forming solvents such as THF, methyl acetate, and ethyl acetate.

CONCLUSIONS

PMMA of different tacticities give similar courses of the SEC calibration curves using the non-adsorbing, good solvent, THF and silica gel column packing. Tacticity differences, however, influence the adsorption of PMMA when the eluent strength decreases. Consequently, liquid chromatography at the critical adsorption point (LC CAP) can be applied to the discrimination of mixtures of highly stereoregular PMMA. The extent of adsorption of particular stereoisomers cannot be generally predicted: In one eluent st-PMMA are more strongly adsorbed while in another one the adsorption of it-PMMA is stronger. Our results demonstrate not only the potential of LC CAP method but also its general limitations, namely

- High sensitivity of CAP to the experimental conditions, such as eluent composition and temperature.
- Limited recovery of polymers that rapidly decreased with increasing molar mass of samples investigated namely when the solvent-nonsolvent mixed eluents are used. The solvent plus solvent mixed eluents show experimental advantages over eluents composed of a solvent and a nonsolvent in the LC CAP of high molar mass polymers.
- Sensitivity of CAP to the polymer structure. Consequently, it is necessary to identify the critical adsorption point with polymer standards having the same stereochemical structure as the macromolecules that will be later characterized by the LC CAP method.
- Extensive peak broadening at CAP that increases with increasing polymer molar mass.

Considering above limitations, the liquid chromatographic procedures that combine exclusion and adsorption separation mechanisms can be used for discrimination and characterization of stereoregular PMMA and possibly also of other polymers such as stereoblock copolymers.

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