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Discrimination of Poly(ethyl methacrylate)s According to Their Molar Mass and Tacticity by Coupling Size Exclusion Chromatography and Liquid Chromatography at the Critical Adsorption Point

Miroslav Janco,[†,‡] Tomohiro Hirano,[‡] Tatsuki Kitayama,*[,‡] Koichi Hatada,[‡] and Dusan Berek*[,§]

Department of Chemistry, Graduate School of Engineering Science, Osaka University,
Toyonaka, Osaka 560−8531, Japan; and Polymer Institute, Slovak Academy of Sciences,
Dubravska cesta 9, 842 36 Bratislava, Slovakia

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ABSTRACT: A coupling of size exclusion chromatography (SEC) and liquid chromatography at the critical adsorption point (LC CAP) has been applied to simultaneous discrimination of stereoregular poly(ethyl methacrylate)s (PEMAs) according to their molar mass and tacticity. The two-dimensional SEC/LC CAP separations were carried out with a chromatographic system which consisted of two analytical columns, one SEC column (polystyrene/divinylbenzene gel) and one LC CAP column (aminopropyl bonded silica gel) connected in series. Narrow fractions of PEMA samples eluted from the SEC column were on-line forwarded into the LC CAP column to be separated according to their tacticity. The column system was flushed with tetrahydrofuran (THF)/cyclohexane mixed eluents at compositions of 64/36 and 56/44 w/w, to attain the molar-mass-independent elution of either highly syndiotactic or highly isotactic PEMAs, respectively. In these eluents, the SEC column still separated PEMAs solely according to their molar masses, while the LC CAP column system discriminated PEMAs according to their tacticity. By use of the coupled SEC/LC CAP technique, the influence of molar mass distribution of analyzed sample on its separation according to tacticity in the LC CAP column was suppressed. For the first time the separation of stereoregular polymers over the entire tacticity range has been demonstrated.

Introduction

Molar mass and molar mass distribution (MMD) together with tacticity and its distribution determine many physical properties of stereoregular polymers. Therefore, determination of both of the distributions is of paramount importance. Molar mass and MMD of polymers are most often determined by size exclusion chromatography (SEC), and tacticity is determined solely by nuclear magnetic resonance (NMR) spectroscopy. On-line SEC/NMR hyphenation[1] is uniquely powerful to give information about both the distributions when tacticity varies together with molar mass in a defined way. When polymers of different tacticities have the same molar mass, however, the method will not give needed information, and a separation according to tacticity is required.

So far, there are a limited number of reports[2−10] describing chromatographic separation of stereoregular polymers according to their stereochemical structures. For example, Miyamoto et al. attempted to separate the mixtures of highly isotactic (it-) and highly syndiotactic (st-) poly(methyl methacrylate)s (PMMAs) by both thin-layer chromatography[2] and competitive adsorption method[3]. Sato et al. have discriminated it-, atactic (at-), and st-PMMAs by high performance liquid chromatography[4] applying eluent gradient technique. We have shown that the discrimination of highly stereoregular PMMAs is feasible also using supercritical fluid chromatography (SFC)[5,6] and liquid chromatography at limiting conditions of solubility/limiting condition of adsorption (LC LCS/LCA).[7] SFC was effective in separation of uniform it- and st-PMMAs[5] as well as uniform stereoblock PMMAs[6] while LC LCS/LCA has discriminated it- and st-PMMAs with narrow MMD.[7]

Recently, liquid chromatography at critical adsorption point (LC CAP), first introduced by Belenkii et al.,[11] has been proven to be a very promising separation technique for discrimination of stereoregular polymers according to their stereochemical structures.[8−10] In this method, particular chromatographic conditions (column packing, eluent composition, temperature, pressure, ...) are identified at which the critical adsorption point (CAP) for a certain constituent, e.g., st-one, is reached. At CAP all st-constituents elute from the column regardless of their molar masses in a particular elution volume that roughly corresponds to the total volume of liquid in the column. Under the same conditions, it-constituents still elute in an SEC mode and can be characterized on the molecular level in a conventional way. Similarly, the CAP for the it-component can be identified,[8,10] at which the st-constituents elute either in the SEC mode[8] or in the adsorption mode.[10] In this way, the highly stereoregular PMMAs[8] and PEMAs[9,10] with narrow MMD could be discriminated into it- and st-constituents mostly due to slight differences in their adsorption.[8−10]

Although all the above-mentioned results indicate dependence of chromatographic behavior of stereoregular polymers on their tacticity, the separation method applicable over the entire tacticity range is still missing. Moreover, the LC separation is usually affected by the MMD of polymers under study. To suppress the effect of MMD on tacticity separation, molar mass separation has to precede the tacticity separation. Therefore, in the

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* To whom correspondence should be addressed. E-mails: kitayama@chem.es.osaka-u.ac.jp and upoldber@savba.sk.

[†] On leave from Polymer Institute of Slovak Academy of Science, Bratislava, Slovakia.

[‡] Osaka University.

[§] Slovak Academy of Sciences.

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Table 1. Characteristics of Stereoregular Poly(ethyl methacrylate)s

sample code	polymerization conditions		$\bar{M}_w \times 10^{-3}$ (g/mol)[b]	$\bar{M}_w/\bar{M}_n$[b]	tacticity (%)[c]		
	initiator[a]	temp (°C)			mm	mr	rr
I−1	A	−60	4.9	1.08	96	4	0
I−2	A	−60	12.0	1.06	97	3	0
I−3	A	−60	18.9	1.06	91	5	4
I−4	A	−60	52.0	1.20	95	3	2
S−1	B	−78	6.8	1.08	0	9	91
S−2	B	−78	13.6	1.05	0	9	91
S−3	B	−78	18.7	1.05	2	9	89
S−4	B	−78	56.2	1.24	0	7	93
H−1	C	−95	9.8	1.04	7	92	1
H−2	C	−78	40.7	1.04	7	89	4
P−1	C	−60	8.8	1.11	4	61	35
P−2	C	−50	8.2	1.12	1	27	72
P−3	C	−60	16.7	1.06	4	63	33
P−4	C	−50	16.0	1.06	1	31	68

[a] Key: (A) *t*-BuMgBr/Me_3Al (1/1) in $CHCl_3$; (B) *t*-BuLi/R_3Al (1/3) in toluene; (C) *t*-BuLi/bis(2,6-di-*tert*-butylphenoxy)methylaluminum (1/5) in toluene. [b] Determined by SEC using a PL gel column (mixed D, 5 μm, 300 × 7.5 mm) in THF at 35 °C. [c] Determined from carbonyl carbon signals in ^{13}C NMR spectra measured in $CDCl_3$ at 55 °C at 125 MHz.

present work, SEC/LC CAP coupling has been applied to an on-line two-dimensional separation of the stereoregular PEMAs according to their molar mass and tacticity. The PEMAs have been selected for the investigations in this study since they could be prepared with a well-controlled level of stereoregularity and with a narrow MMD. Moreover, the chromatographic separation of PEMAs was not complicated by stereocomplex formation processes as in the case of PMMA samples where only one peak was eluted from the column in certain eluents[7] due to aggregation of it- and st-PMMAs.

Experimental Section

(a) Synthesis of Stereoregular PEMAs. A series of stereoregular PEMAs (Table 1) differing in both molar mass and tacticity were prepared by anionic living polymerizations at low temperatures by using highly stereospecific initiators.[12−14] Thus, highly isotactic (it-) PEMAs were prepared by the polymerization of EMA in chloroform ($CHCl_3$) at −60 °C with *t*-BuMgBr/Me_3Al (1/1 mol/mol) as initiator.[12] Highly syndiotactic (st-) and highly heterotactic (ht-) PEMAs[13,14] were obtained by the polymerizations of EMA in toluene at −78 °C that were initiated by *t*-BuLi/*n*-Bu_3Al[13] (Li/Al = 1:3) and *t*-BuLi/bis(2,6-di-*tert*-butylphenoxy)methylaluminum[14] ([MeAl(ODBP)$_2$], (1/5 mol/mol)), respectively. The predominantly syndiotactic PEMA samples (rr content 68−72%) and predominantly heterotactic PEMA samples (mr content 61−63%) of narrow MMD were obtained by changing the polymerization temperature.

The molar masses of PEMA samples were determined by using a PL-gel column (300 × 7.5 mm) packed with polystyrene/divinylbenzene gel (mixed D, particle size 5 μm) in tetrahydrofuran (THF) at 35 °C. The universal calibration method proposed by Grubisic and Benoit[15] was used for calculation of molar mass applying the already published Kuhn−Mark−Houwink−Sakurada constants $K = 1.164 \times 10^{-2}$ mL/g and $a = 0.73$ for PS in THF[16] and $K = 1.549 \times 10^{-2}$ mL/g and $a = 0.679$ for PEMA in THF[17] at 25 °C.

Tacticity data of PEMA samples were determined from ^{13}C NMR spectra measured in $CDCl_3$ at 55 °C on a Varian Unity 500 spectrometer operated at 125 MHz.

(b) Chromatographic Experiments. All liquid chromatographic measurements were carried out on an SEC/LC CAP coupling assembly (Figure 1) composed of an eluent container, a Jasco model PU-980 pump (Tokyo, Japan), a Rheodyne injector provided with a 20 μL sample loop, two Rheodyne switching valves (Cotati, CA), and a column system placed into a Jasco model CO 965 column oven (Tokyo, Japan) operated at 35 °C. A Model EMD-960 evaporative light scattering detector (Polymer Laboratories, Church Stretton, U.K.) monitored column effluent. The detector was operated by using compressed air as carrier gas from a Hitachi model 0.2LP-7S compressor (Tokyo, Japan). The carrier gas outlet pressure and flow rate were set at 0.2 MPa and 5 L/min, respectively. The temperature of the detector evaporative chamber was set at 65 °C. The detector signal was collected on-line by using a PC and Shimadzu model C-R7A Chromatopac data acquisition system (Kyoto, Japan).

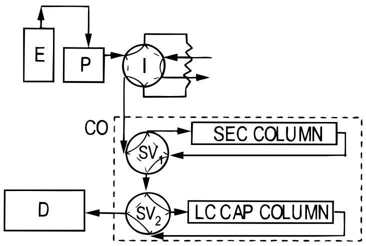

Figure 1. Diagram of the SEC/LC CAP assembly: E, eluent container; P, pump; I, injector; SV_1 and SV_2, switching valves; CO, column oven; D, detector. Valve position: “a” (solid line), “b” (dashed line).

The SEC/LC CAP separations were performed using a system composed of two columns connected in series. The first, SEC column (300 × 7.5 mm) packed with nonpolar polystyrene/divinylbenzene gel (PL-gel, mixed D, particle size 5 μm) was obtained from Polymer Laboratories (Church Stretton, U.K.). The second, LC CAP column (250 × 8 mm) packed with silica gel bonded with aminopropyl groups (Develosil SG−NH_2, pore size 12 nm, particle size 5 μm) was purchased from Nomura Chemical (Osaka, Japan).

Both surface chemistry and pore size of bare silica gel column packings were found to strongly influence the retentive characteristics of polymers eluted at CAP.[18] The heterogenity of LC CAP packing surface decreased sample recovery and caused peak broadening of samples eluted at CAP. Moreover, macromolecules excluded from packing pores did not follow LC CAP rules. Therefore, a silica gel bonded with aminopropyl groups, that was supposed to exhibit a more homogeneous surface, was used for LC CAP separation in this study. The pore size of LC CAP column packing was selected according to molar mass of PEMAs used for investigations. The linkage of both SEC and LC CAP columns into chromatographic system was realized by using a bypass capillary and two switching valves (SV1, SV2).

Individual PEMA samples (Table 1) and their model mixtures were used for SEC/LC CAP investigations. The sample solution concentrations were about 0.7−1.0 mg/mL for each constituent.

THF and mixtures of THF and cyclohexane were used as eluents and sample solvents. Analytical grade solvents were obtained from Nacalai Tesque (Kyoto, Japan) and were used as received. The presence of water in the eluent, in our case especially in THF, may affect the chromatographic behavior of the polymer under study. Therefore, the content of water in THF was checked by ^1H NMR. From the THF spectra measured in acetone-d_6 at 30 °C, it was determined that THF contained less than 0.05% of water. The THF/cyclohexane mixtures were prepared by weighing single components and therefore the compositions of the eluents are expressed in w/w ratio in all cases. The eluent flow rate was set at 1.0 mL/min.

(c) Procedural Description of the SEC/LC CAP Technique. The SEC/LC CAP measurements comprised the following steps (Figure 1):

1. Determination of the eluent composition which elutes a certain kind of stereoregular PEMA at a critical adsorption point (CAP) from a given LC CAP column (valve SV1 in position “b”, valve SV2 in position “a”).

2. Flushing SEC column with the eluent identified in the preceding step 1 and accomplishing SEC separation of the analyzed sample (SV1 in position “a”, SV2 in position “b”).

3. Introduction of narrow fractions eluted from the SEC column into the LC CAP column (both SV1, SV2 in position “a”).

4. Separation of each SEC fraction according to tacticity in the LC CAP column (SV1 in position “b”, SV2 in “a”).

Results and Discussion

Our preliminary experiments have shown that the tacticity of samples strongly influenced retention volumes of stereoregular PEMAs from chromatographic column packed with silica gel bonded with aminopropyl groups (SG$-$NH$_2$) in THF/cyclohexane mixed eluents. On the contrary, we have not observed any considerable changes of retention volumes for stereoregular PEMAs using chromatographic column packed with polystyrene/divinylbenzene (PS/DVB) gel in pure THF and THF/cyclohexane eluents with the cyclohexane content up to 44 wt %. In other words, the same calibration curves were obtained for it-, ht-, and st-PEMAs with PS/DVB -gel column in THF and THF/cyclohexane mixtures under study. This is somewhat surprising because the degree of stereoregularity was expected to influence values of limiting viscosity numbers of macromolecules in given solvent. If one accepts the validity of the universal calibration concept in SEC,[15] the corresponding retention volumes could be affected by sample tacticity, as well. This effect might be large in thermodynamically poor eluents.[19] Moreover, the calibration curves log M vs V_R for PS and PEMA obtained with the PS/DVB column in THF and THF/cyclohexane mixtures were identical. Since molar masses of PEMA samples were calculated from the universal calibration curve (see Experimental Section), this indicated that hydrodynamic volumes of PS and PEMA coils with the same molar mass were similar in the eluents used. This was an important prerequisite for application of the SEC/LC CAP procedure based on the conventional PS calibration instead on the universal calibration.

These experimental observations also indicated the applicability of appropriate SEC/LC CAP combination to an on-line separation of stereoregular PEMAs according to both molar mass and tacticity. The SEC preseparation of polymer sample was expected to suppress the influence of MMD of analyzed sample on tacticity separation in LC CAP column.

In the first series of experiments, the composition of THF/cyclohexane eluent was adjusted to elute highly st-PEMAs at CAP from a LC CAP column. To do so, the calibration curves of st-PEMAs were measured with single LC CAP column in THF/cyclohexane mixed eluents of different compositions (step 1) (Figure 2). It is clear that the addition of cyclohexane to THF expressively influenced the elution behavior of st-PEMA with eluents containing over 35 wt % of cyclohexane that is known to weakly interact with the polar bonded silica gel. Therefore, growing concentration of cyclohexane in eluent promoted adsorption of PEMA within column packing and an increase in retention volumes of the macromolecules. At the eluent composition of THF/cyclohexane = 64/36 w/w, st-PMMAs with different molar masses eluted from the column packing at the same retention volume, i.e., critical adsorption point was reached for st-PEMA on LC CAP column. Further addition of cyclohexane to the eluent caused the elution of st-PEMAs in the adsorption mode, that is polymer retention volumes increased with their molar masses. The sample recovery dropped with increasing molar mass of polymer and no elution was observed for the polymers with molar mass exceeding 5.6 × 10^3 g/mol.

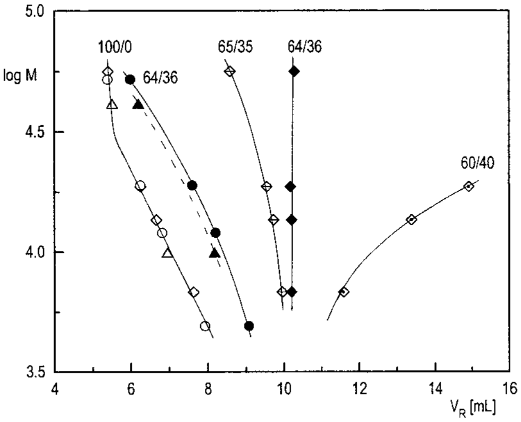

Figure 2. Calibration curves of st-PEMAs on a Develosil$-$NH$_2$ column (12 nm, 5 μm, 250 × 8 mm) in THF (◇ 100/0) and in THF/cyclohexane mixtures (◈ 65/35; ◆ 64/36, ⊡ 60/40) at 35 °C. Retention volumes for it-(○,●) and ht-PEMAs (△,▲) in THF (open symbols) and THF/cyclohexane (64/36) (solid symbols) are also plotted.

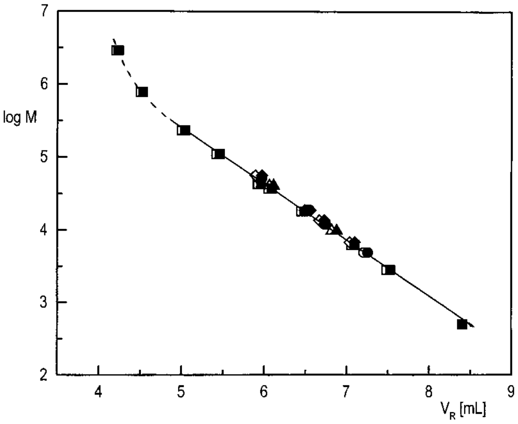

Figure 3. Calibration curves of polystyrene (PS) and PEMAs with different tacticities on a PL$-$gel column (mixed D, 5 μm, 300 × 7.8 mm) in THF (open symbols) and a THF/cyclohexane mixture (64/36 w/w) (solid symbols). Key: (□, ■) PS; (○,●) it-PEMA; (△,▲) ht-PEMA; (◇,◆) st-PEMA.

At the critical adsorption point for st-PEMAs, it- and ht- PEMAs still eluted in the SEC mode although their retention volumes were slightly larger than those measured in 100% THF (Figure 2). Nevertheless, the differences in the retention volumes between it- and st-PEMAs and also between ht- and st-PEMAs were sufficiently large for their discrimination. It is worth noting that the retention volumes of ht- and it-PEMAs were similar under these conditions and their separation could not be expected in this system.

Once the CAP for st-PEMA on LC CAP column was determined, the SEC column was flushed with the mixed THF/cyclohexane (64/36 w/w) eluent, and the calibration curves of PEMAs with different tacticities on the single SEC column were measured (step 2). The SEC column still separated PEMAs according to differences in their hydrodynamic volumes (Figure 3). We did not observe any important change in the course of calibration curves of stereoregular PEMA measured in THF and THF/cyclohexane (64/36 w/w) mixture. Under these circumstances, molar mass and MMD of any PEMA sample can be easily obtained by applying single SEC calibration dependence. However, this favorable

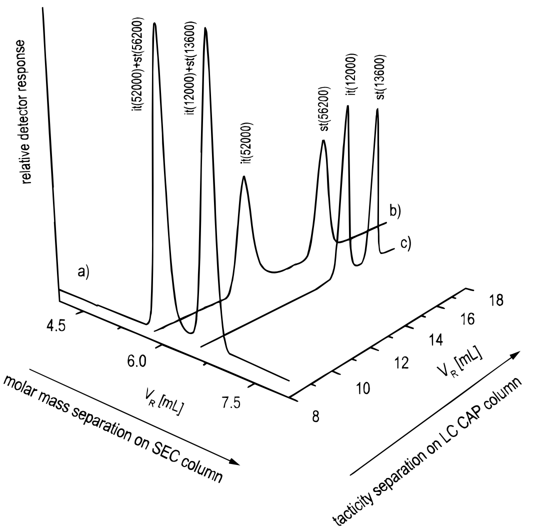

Figure 4. SEC/LC CAP separation of PEMA sample composed of two it-constituents with $\bar{M}_w = 12 \times 10^3$ and 52×10^3 g/mol and two st-constituents with $\bar{M}_w = 13.6 \times 10^3$ and 56.2×10^3 g/mol in a THF/cyclohexane mixture (64/36 w/w). Molar mass separation on a SEC column (a) and tacticity separation of first (b) and second (c) SEC fractions on LC CAP column are shown.

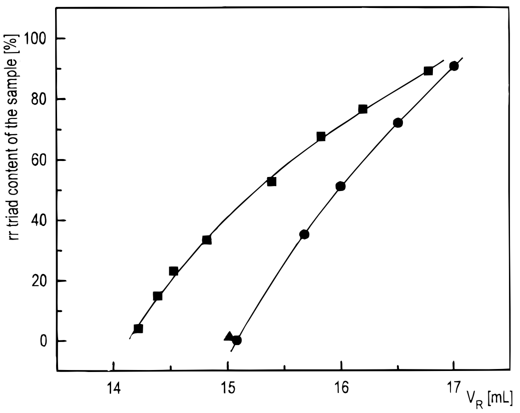

Figure 5. Tacticity calibration curves for two sets of stereoregular PEMAs (plots of sample rr triad content vs fraction retention volume) on a Develosil−NH$_2$ column (12 nm, 5 μm, 250 × 8 mm) in a THF/cyclohexane mixture (64/36% w). The fractions of PEMA samples eluted from the SEC column in the range 6.8−6.9 mL (for the first set) (●) and 6.55−6.65 mL (for the second set) (■) were forwarded into the LC CAP column for tacticity separation. Retention volume of a fraction of highly heterotactic PEMA eluted from the SEC column in the range 6.8−6.9 mL (▲) is also shown.

situation cannot be generalized, and for many systems additional SEC calibrations may be necessary.

The results shown so far indicate that PEMAs differing in both molar mass and tacticity can be separated according to their molar mass in the present SEC system. The SEC fractionated macromolecules are then forwarded into LC CAP column and separated according to tacticity differences.

An example of such separation is shown in Figure 4 for a model PEMA mixture composed of two highly it-PEMAs with $\bar{M}_w = 12.0$ and 52.0×10^3 g/mol and of two highly st-PEMAs with $\bar{M}_w = 13.6$ and 56.2×10^3 g/mol) by using the SEC/LC CAP on-line coupling. This PEMA model mixture was separated according to its molar mass into two peaks and each contained a mixture of it- and st-constituents with similar molar masses (step 3). The SEC fractions were successively forwarded into the LC CAP column where their separation into highly it- and highly st-constituents has been reached (step 4). The eluent flow within SEC column was interrupted during LC CAP elution. This stop-and-go approach did not affect in a pronounced way the width of the later eluted SEC peak.[20]

Similarly, the PEMA sample composed of two highly ht-PEMAs ($\bar{M}_w = 9.8 \times 10^3$ and 40.7×10^3 g/mol) and two highly st-PEMAs ($\bar{M}_w = 13.6 \times 10^3$ and 56.2×10^3 g/mol) was separated according to molar mass and tacticity by using the SEC/LC CAP coupled technique (result not shown). In both cases, the whole SEC fractions were forwarded into the LC CAP column for tacticity separation.

We have supposed that PEMAs with low tacticity should elute between retention volumes of highly it- and st-PEMAs. To check this assumption, two sets of PEMA samples with molar mass approximately (7.5−13.6) × 10^3 and (14.6−18.9) × 10^3 g/mol were used. The first set contained five PEMA samples with different tacticities (rr triad content 0, 35, 51, 72, 91%), and the second one contained eight PEMA samples with corresponding rr triad content (0, 15, 23, 33, 53, 68, 76, 89%). Each sample was injected separately into SEC/LC CAP assembly flushed with THF/cyclohexane (64/36 w/w) eluent. Their 100 μL fractions eluted from SEC column at elution volumes of 6.8−6.9 mL ($\bar{M}_w$ = (7.5−13.6) × 10^4) and 6.55−6.65 ($\bar{M}_w$ = (14.6−18.9) × 10^4) for the first and second sets, respectively, were forwarded into LC CAP column. Peak retention volumes of these fractions leaving LC CAP column were plotted against rr triad content of the sample. In this way the "tacticity calibration curves" were constructed (Figure 5). The plots of rr triad content vs retention time showed nonlinear dependence. Many factors can be responsible for this course of tacticity calibration curves. The influence of the mr triad was excluded since retention volumes of the same SEC fractions of it- and ht-PEMA were similar (Figure 5). However, we assumed that the slight molar mass dependence of tacticity[21] in samples used and/or the "polymer chain−column packing" interaction that occurred on a higher level than chain segment level and even higher than the triad level could be responsible for this behavior. To give an exact explanation of this phenomenon, further SEC/NMR experiments have been carried out.

By using a tacticity plot and the retention volume of the unknown sample, its rr triad content can be roughly estimated. However, the content of mm and mr triads in the analyzed sample remains unknown. Such tacticity calibration curves can be constructed for any molar masses if proper standards are available.

It was also of interest to investigate if a mixture of PEMAs exhibiting broad tacticity distribution can be discriminated by LC CAP: in other words, if a separation of stereoregular polymers over the entire tacticity range is possible by this technique. For this purpose, the PEMA sample composed of four constituents with similar molar masses ($\bar{M}_w$ = (8.2−13.6) × 10^3 g/mol) but differing in their tacticity (rr triad content = 0, 35, 72, and 91%) was injected into the SEC/ LC CAP assembly. Only one peak that corresponded to the mixture of four particular components was observed in SEC while separation into four peaks according to tacticity differences (rr triad content) has been achieved with the LC CAP column (Figure 6). According to our knowledge, this is the first two-dimensional separation

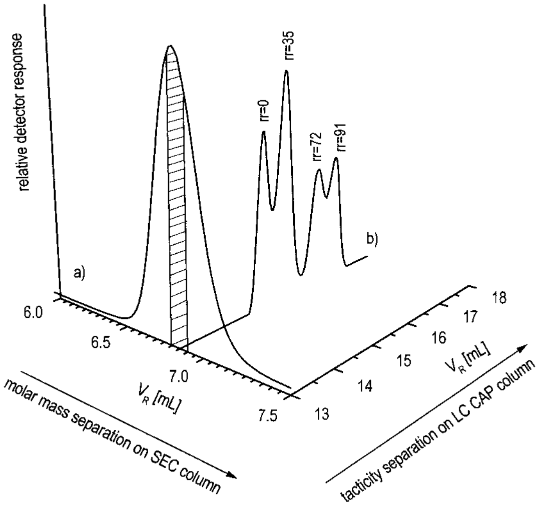

Figure 6. SEC/LC CAP separation of PEMA sample composed of four constituents with similar molar mass ($\bar{M}_w$ = 12, 8.2, 8.8, and 13.6 g/mol) but differing in their tacticity (rr content 0, 35, 72, 91%) in a THF/cyclohexane mixture (64/36 w/w). A 100 μL sample of the SEC fraction (eluted in the range 6.8−6.9 mL) was subjected into the LC CAP column for tacticity separation.

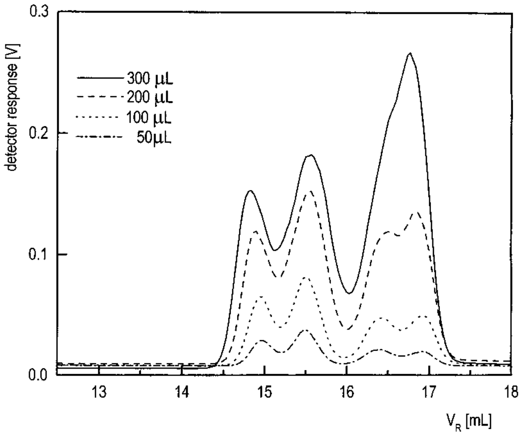

Figure 7. Influence of SEC fraction volume on efficiency of separation according to tacticity in the LC CAP column. The PEMA sample used was composed of four constituents with similar molar masses but differing in their tacticity (rr content 0, 35, 72, 91%).

of macromolecules according to their molar mass and tacticity in its entire range. To give the conclusive proof of tacticity composition of each peak eluted from LC CAP column, the hyphenation of NMR and LC CAP techniques is required. The determination of tacticity of macromolecules within each peak eluted from LC CAP column by NMR is a subject of further work.[22]

We also examined the influence of the SEC effluent volume injected into LC CAP column on the efficiency of the tacticity separation (Figure 7). The PEMA sample composed of four constituents with similar molar masses ($\bar{M}_w$ = (8.2−13.6) × 10^3 g/mol) but differing in their tacticity (rr triad content = 0, 35, 72, and 91%) was injected into the SEC column. Different volume fractions (50, 100, 200, and 300 μL) from SEC were forwarded into the LC CAP column. The separation efficiency of the LC CAP column decreased with increasing reinjected volume, and the resolution of the st-components (rr triad content 72 and 91%) of analyzed mixture was lost entirely when a 300 μL volume was treated. Evidently, the size of SEC fraction forwarded into the LC CAP column must be minimized in order to suppress these adverse effects. The reduction of SEC fraction volume is, however, limited by detector sensitivity and the experimental feasibility of switching valve operation. As a compromise, 100 μL slices of samples eluted from the SEC column have been successively forwarded into the LC CAP column.

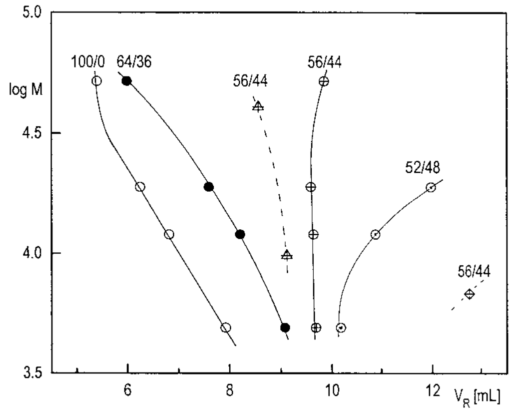

Figure 8. Calibration curves of it-PEMAs on a Develosil−NH_2 column (12 nm, 5 μm, 250 × 8 mm) in THF (○ 100/0) and in THF/cyclohexane mixtures (● 64/36; ⊕ 56/44 and ⊙ 52/48) at 35 °C. Retention volumes of ht- (cross in the middle of a triangle) and st-PEMAs (cross in the middle of a tilted square open) in THF/cyclohexane (56/44 w/w) mixture (CAP for it-PEMA) are also shown.

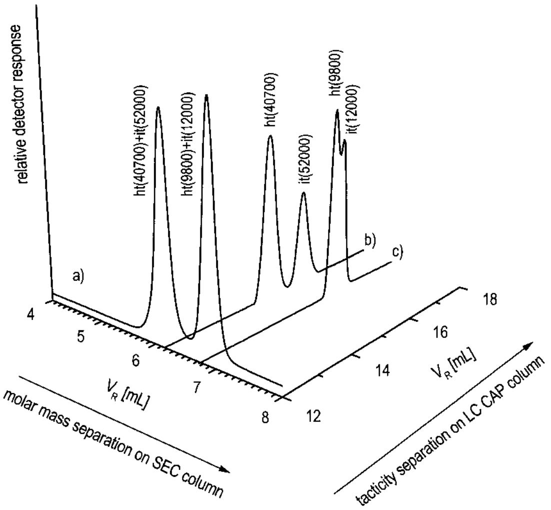

Figure 9. SEC/LC CAP separation of a PEMA sample composed of two ht-constituents with $\bar{M}_w$ = 9.8 × 10^3 and 40.7 × 10^3 g/mol and two it-constituents with $\bar{M}_w$ = 12 × 10^3 and 52 × 10^3 g/mol in a THF/cyclohexane (56/44 w/w) eluent. Molar mass separation on SEC column (a) and tacticity separation of first (b) and second (c) SEC fractions on LC CAP column are shown. Then 100 μL samples of each SEC fraction were injected into LC CAP column for tacticity separation.

In the next set of experiments, more cyclohexane was added to the eluent. The calibration curves of stereoregular PEMAs were shifted to the higher retention volumes. At the THF/cyclohexane composition of 56/44 w/w, it-PEMAs eluted from the LC CAP column in a single retention volume; that is, the critical adsorption point for it-PEMA was reached (Figure 8). At the same eluent composition, high molar mass st-PEMAs were fully retained within the LC CAP column packing and only low molar mass PEMA fractions were eluted in the adsorption mode (Figure 8). On the other hand, highly ht-PEMA samples still eluted in the SEC mode (Figure 9), although their retention volumes were strongly affected by adsorption processes. Using THF/cyclohexane eluent with composition 56/44 w/w, that is, the CAP for it-PEMAs, the SEC/LC CAP separation of a PEMA sample composed of two highly ht-PEMAs with $\bar{M}_w = 9.8 \times 10^3$ and 40.7×10^3 g/mol and two highly it-PEMAs with $\bar{M}_w = 12 \times 10^3$ and 52×10^3 g/mol was achieved (Figure 9). Unfortunately, the retention volumes of ht- and it-PEMAs, at least for low molar masses, did not differ significantly in this system (Figure 8). We assume that the use of optimized eluent or/and column packing could improve tacticity separation by increasing differences in retention volumes of particular stereoisomers. Surprisingly, the courses of calibration curves of stereoregular PEMAs on the PS/DVB column do not differ even in this mixed eluent. Therefore, it was interesting to examine the eluent composition in which the differences in elution behavior of highly stereoregular PEMAs on PS/DVB column appear. The first measurable difference in elution of stereoregular PEMAs on the SEC column was observed in THF/cyclohexane eluent with composition 40/60 w/w.

Conclusions

Poly(ethyl methacrylate)s (PEMAs) of different tacticities eluted from both nonpolar (polystyrene/divinylbenzene gel) and polar (aminopropyl modified silica gel) column packings in a pure SEC mode if tetrahydrofuran (THF) was used as eluent. The elution behavior of PEMAs differing in tacticity was not affected on the polystyrene/divinylbenzene column packing even with decreasing desorption strength and thermodynamic quality of eluent toward PEMA by adding 44 wt % of cyclohexane into THF. On the contrary, tacticity differences strongly influenced elution of stereoregular PEMAs from the polar column packing when the eluent desorption strength decreased, that is, when the amount of cyclohexane in mixed eluent increased. The stereoregular PEMAs eluted from the aminopropyl-bonded silica gel with THF/cyclohexane mixtures in the order of heterotactic, isotactic and syndiotactic PEMA. It means that the interactions of stereoregular PEMAs with this polar column packing in various THF/cyclohexane mixed eluent were the lowest for heterotactic and the highest for syndiotactic PEMA. However, the extent of adsorption of particular stereoisomers cannot be generally predicted. In a certain mixed eluent, syndiotactic polymers are more readily adsorbed on the column packing while in another one the adsorption of isotactic polymers is stronger.[8]

On-line size exclusion chromatography/liquid chromatography at the critical adsorption point (SEC/LC CAP) coupling was applied to the simultaneous two-dimensional discrimination of stereoregular PEMAs according to their both molar mass and tacticity. Thus, the SEC/LC CAP coupling allowed one to suppress the influence of molar mass distribution on tacticity separation and to construct two-dimensional plots reflecting molar mass and tacticity of polymers under study. The separation of stereoregular PEMAs over the entire tacticity range was achieved for the first time.

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