Separation of poly(methyl methacrylate)s according to their tacticity

1. Preliminary studies on the tacticity dependence of chromatographic behavior of stereoregular PMMAs

Dušan Berek[1,*], Miroslav Jančo[1], Tatsuki Kitayama[2], and Koichi Hatada[2]

[1]Polymer Institute, Slovak Academy of Sciences, Dúbravská Cesta 9, 84236 Bratislava, Slovakia
[2]Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Summary

The unconventional liquid chromatography of polymers under limiting conditions of their solubility was applied to poly(methyl methacrylate)s differing in their tacticity. The polymers were dissolved in thermodynamically good solvents and injected into an appropriate size exclusion chromatographic (SEC) column flushed with matched, moderately strong nonsolvents. The set of (limiting) conditions was found under which less soluble syndiotactic poly(methyl methacrylate) moved along the column together with the zone of its initial solvent while better soluble isotactic poly(methyl methacrylate) was eluted according to the SEC mechanism. This indicates the potential of liquid chromatography under limiting conditions to characterize the tacticity of poly(methyl methacrylate)s.

Introduction

The anionic, stereospecific polymerization of methacrylates often encounters simultaneous distributions of molecular weight and of stereoregularity of polymers (1), while only a limited number of polymerizations afford highly stereoregular polymethacrylates with narrow molecular weight distribution (2-5). The information on both of these distributions is of prime importance for the understanding of polymerization mechanism. When the tacticity of the polymer varies with molecular weight, an on-line GPC/NMR is uniquely powerful to give information on the molecular weight dependence of tacticity (6-9). When the polymers of different tacticities have a similar molecular weight distribution, however, the method will not give further information and a chromatographic separation in regard to tacticity is required.

Isotactic (it-) and syndiotactic (st-) poly(methyl methacrylate)s (PMMAs) are known to form stereocomplexes (10). There have been several attempts that utilize this stereospecific interaction between stereoregular PMMAs for enhancing the separation selectivity with regard to the stereoregularity of macromolecules. Polystyrene gel (11) or silica gel (12) grafted with isotactic PMMA branches have been used as column packing materials for the separation of PMMA with regard to tacticity.

Another approach towards this end is to utilize the tacticity dependence of chromatographic behavior of stereoregular PMMA on usual chromatographic adsorbents such as silica gel. In the present work, the liquid chromatographic elution behavior was studied for PMMAs with

---

*Corresponding author

different tacticities under limiting conditions of their solubility (13). The basic idea behind this approach is as follows: The polymer is dissolved in a thermodynamically good solvent and injected into a size exclusion chromatographic (SEC) column which is flushed with a nonsolvent for the sample. For given column the precipitation strength of eluent is finely tuned by the amount of nonsolvent added or by temperature variation. The sets of limiting conditions can be found (13,14) under which macromolecules travel through the column independently of their molecular weights, accopanying the zone of the initial solvent. In other words, the retention volume of macromolecules of different sizes is nearly constant and lies in the area of the total volume of liquid within the column. In fact, macromolecules tend to move faster than small molecules of the initial solvent due to the exclusion effects. However, they are prevented from leaving the zone of their solvent due to the repulsive interactions with eluent. If macromolecules leave the solvent zone, they start precipitating, which results in a decrease of their movement velocity. Consequently, macromolecules are catched up with the zone of sample solvent and redissolved so that the process may be repeated. As a result, macromolecules move just within the front of the solvent zone. However, if the precipitating power of eluent is too high or if the macromolecules undergoing phase separation / precipitation are strongly adsorbed on the column packing, no elution occurs.

The described procedure can be used to separate constituents of polymer mixtures that differ in their solubility. This approach was tested with binary mixtures of polystyrenes and PMMAs (15). By an appropriate choice of the eluent and the sample solvent, i.e. by applying the limiting conditions for one polymer constituent (A) the latter elutes within the solvent zone not interfering with the second constituent (B) in the mixture which behaves according to the SEC mechanism. Consequently, the molecular weight and molecular weight distribution of the B polymer can be independently determined by the conventional SEC procedure within the same run.

It was of interest to check if the differences in solubility between PMMAs of different tacticities can sufficiently manifest themselves in their LC elution behavior, i.e. if the limiting conditions for generally less soluble st-PMMA can be found that would be still SEC conditions for better soluble it-PMMA.

Experimental

A size exclusion chromatography system used comprised a Waters Model 501 pump, a Model PK-1 injection valve provided with a 12 μl loop (Institute of Chemical Process Fundamentals, Academy of Sciences of Czech Republic, Prague), and a Cunow Model DDL-21 evaporative light scattering detector (Cergy-Pointoise, France). The detector signal was recorded on a Type TZ two-pen chart recorder (Laboratory Instruments Co., Prague, Czech Republic). The data were also on-line collected using a PC Based Data Acquisition System (Waters, Milford, USA).

Chromatographic measurements were made on bare silica gel sorbents SGX-500 and SGX-1000 with the pore diameters of 50 and 100 nm, respectively (Tessek Co., Prague, Czech Republic). About 3.5 g of material was packed in a 250 mm stainless steel column with ID of 6 mm by means of a Knauer pneumatic pump (Berlin, Germany) at 30 MPa using methanol as both the slurry and the transporting liquid.

Twelve μl of polymer solution in a good solvent (tetrahydrofuran) was injected. The sample concentration was 0.5 mg/mL.

Analytical grade solvents tetrahydrofuran (THF) and hexane were obtained from Merck (Darmstadt, Germany) and toluene and methanol from Lachema (Brno, Czech Republic). The above organic solvents were used without further purification together with bidistilled water. The mixed mobile phases were prepared on the weight basis of particular components. The eluents were degassed for five minutes in an ultrasonic bath just before use. The flow rate was 1 mL/min.

Isotactic and syndiotactic PMMAs were prepared by the stereospecific living polymerizations with $t-C_4H_9MgBr$ (2,3) at $-60^\circ C$ and $t-C_4H_9Li-(n-C_4H_9)_3Al$ (4,5) at $-78^\circ C$, respectively, in toluene. Polymerizations were carried out in glass ampoules filled with dried nitrogen, and terminated by the addition of methanol containing a small amount of HCl. The reaction mixture was poured into a large amount of hexane to precipitate the polymeric product. The precipitate was collected by filtration, washed successively with hexane, dilute HCl and water, and dried under vacuum at 50° C. Triad tacticity of the PMMAs was determined by ^{1}H NMR measurements of the polymer solutions in $CDCl_3$ at 55° C on a JNM-GSX270 NMR spectrometer at 270 MHz. Molecular weights were determined on a Jasco 880-PU chromatograph equipped with Shodex GPC columns KF-80M and KF-802.5 (30cm x 0.80 cm i.d.) with maximum porosities of $2x10^7$ and $2x10^4$, respectively, using tetrahydrofran (THF) as eluent. The chromatograms were calibrated with standard polystyrene samples. The results of characterization are given in Table 1.

Table 1.

Characteristics of st- and it- PMMAs used in this paper

Sample	Initiator	$\bar{M}_w$ [a]	$\bar{M}_n$ [a]	$\bar{M}_w/\bar{M}_n$ [a]	Tacticity (%) [b]		
					mm	mr	rr
SG-33-200	A	12 700	10 600	1.20	0	11	89
DPI-1	A	28 600	22 700	1.26	0	11	89
EM357	A	100 700	73 000	1.38	2	7	91
NF714-1000	A	153 300	111 900	1.37	0	12	88
MA-35-2	B	12 300	9 800	1.25	97	2	1
ON72C	B	27 400	21 780	1.26	97	2	1
NF678	B	86 900	62 960	1.38	97	2	1
NF712	B	157 100	100 050	1.57	98	1	1

A-prepared with $t-C_4H_9Li-(C_2H_5)Al(1/3)$ in toluene at -78° C

B-prepared with $t-C_4H_9MgBr$ in toluene at -60° C

a-Determined by size exclusion chromatography; b-Determined by ^{1}H NMR;

Table 2.

Tacticity of the PMMAs of low stereoregularity

$\bar{M}_w/10^3$ [a]	$\bar{M}_w/10^3$ [b]	$\bar{M}_w/\bar{M}_n$ [a]	Tacticity (%) [c]		
			mm	mr	rr
16	17	1.14	6	45	49
31	34	1.24	7	42	51
65	65	1.22	4	33	63
103	88	1.27	3	33	64
169	165	1.21	2	32	66
294	290	1.28	2	29	69
461	460	1.75	2	29	69
613	597	1.85	3	33	64

a - Determined by size exclusion chromatography;

b - Determined by light scattering; c - Determined by ^{1}H NMR

A series of of PMMA samples with narrow molecular weight distributions was a gift from Rohm Co., (Darmstadt, Germany) who provided also their molecular weight data. We determined their tacticities by ^{1}H NMR spectroscopy. As shown in Table 2 these PMMAs are less stereoregular and are referred in this text as PMMAs of low stereoregularity.

Results and discussion

The narrow PSs and PMMAs of low stereoregularity, as well as st- and it-PMMAs were successively injected into columns packed with wide pore silica gels using pure THF as eluent. The corresponding calibration curves are shown in Figs. 1 and 2. The polymers behave regularly. Small shifts of calibration curves obtained for PS and PMMA can be explained by differences in their hydrodynamic volumes in THF. As known, macromolecules of PMMA have smaller hydrodynamic volume in THF than PS. The difference of hydrodynamic volumes of st- and it-PMMA in THF is difficult to detect in this experiment, although it has been known that it-PMMA coils are more extended than st-PMMA coils in the unperturbed state i.e. in θ - solvents and also in several good solvents [16]. For example, it has been demonstrated by SEC
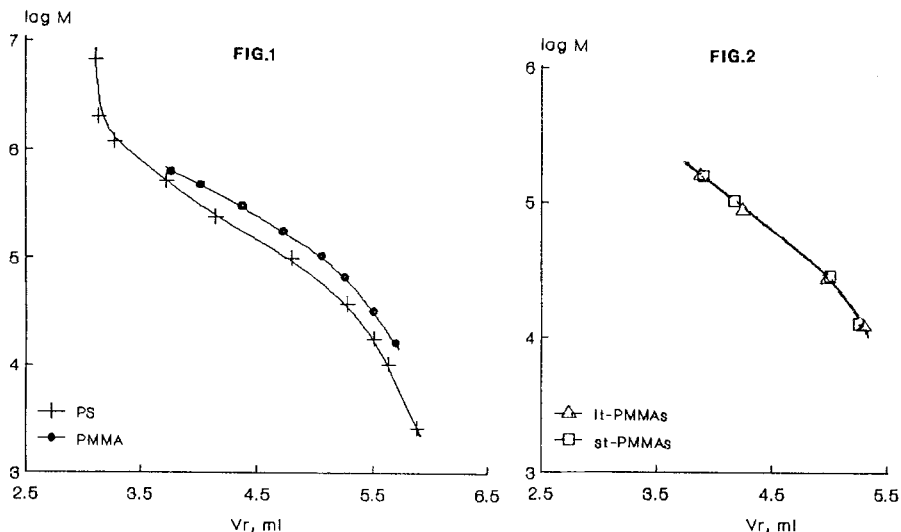
Fig.1 Calibration curves for narrow polystyrenes and poly(methyl methacrylate)s of low stereoregularity injected into silica gel column with pore size 100 nm. Eluent THF.

Fig.2 Calibration curves for syndiotactic and isotactic PMMAs injected into silica gel column with pore size 50 nm. Eluent THF.

experiments that it-PMMA has larger hydrodynamic volume than st-PMMA in chloroform [17] and in THF [18].

Next, we determined the calibration curves of st- and it-PMMAs in the mixed eluents THF plus water and toluene plus methanol of different compositions. We found that both st- and it-PMMAs with already rather low molar masses were fully retained within the columns when the content of nonsolvent in eluent was high. Consequently, it would be impossible to work with these mixed eluents. In the above experiments, nonsolvents for injected polymers, i.e. methanol and water are more polar than solvent constituents of the mixed eluents, i.e. toluene and THF. Therefore, the preferential sorption of nonsolvent molecules can be anticipated on the polar surface of bare silica gel. This fact is probably responsible for retainment of PMMAs within silica gel. The nonsolvent "layer" on the silica surface may enhance the precipitation of macromolecules and their trapping within the column packing.

In the next series of experiments, we applied a nonpolar nonsolvent for PMMA viz. hexane so that the solvent, THF was preferentially sorbed on the silica gel surface. Mixed eluents toluene plus hexane were not used as no elution of PMMAs can be expected in these mixtures. Typical examples of the calibration curves obtained with THF plus hexane eluents are shown in Fig. 3 and 4. It is evident that the difference in solubility of it- and st-PMMA samples is large enough to find the eluent composition which is limiting for the less soluble syndiotactic polymer while more soluble it-PMMA can be analyzed in the SEC mode. The behavior of the PMMA samples of low stereoregularity indicates the possibility to apply the LC under limiting conditions to estimate the tacticity of PMMA.
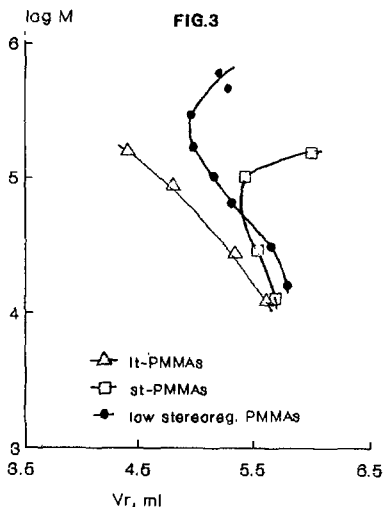
Fig.3 Calibration curves for narrow PMMAs of low stereoregularity, syndiotactic and isotactic PMMAs injected into silica gel column with pore size 50 nm. Eluent THF / Hexane = 75:25 % wt. Sample solvent THF.
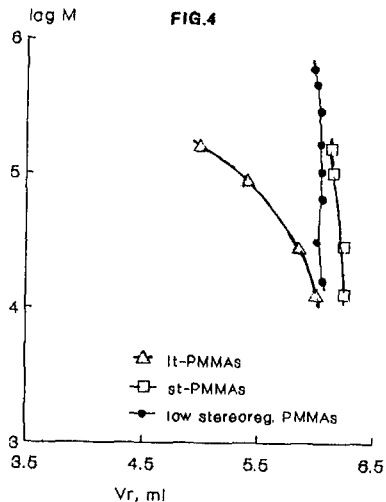
Fig.4 Calibration curves for narrow PMMAs of low stereoregularity, syndiotactic and isotactic PMMAs injected into silica gel column with pore size 100 nm. Eluent: THF / Hexane = 82:18 % wt. for stereoregular PMMAs and THF / Hexane = 81:19% wt. for PMMAs of low stereoregularity. Sample solvent THF in both cases.

The result of experiments with mixtures of st- and it-PMMAs injected together into the column under limiting conditions can be explained by the complexation of PMMAs with different tacticities (10); no separation was obtained because the complexes of st- and it-PMMAs in THF are rather stable. Increasing temperature and using solvents which suppress the PMMA complexation will probably help in this situation.

Conclusions

Applying a thermodynamically good sample solvent and an appropriate nonsolvent as eluent in the liquid chromatography of polymers, one can produce fairly distinguished elution patterns for the polymer samples differing in their chemical composition or physical structure. The "limiting conditions" can be found for given polymer viz. the specific eluent precipitating strength, under which macromolecules elute from an SEC column together with the zone of their initial, thermodynamically good solvent. The limiting conditions depend on the column properties. The above phenomenon can be used for discrimination of components of complex polymer systems such as polymer mixtures and random, block or graft copolymers. We demonstrated that even small difference in solubilities of syndiotactic and isotactic poly(methyl methacrylate)s can afford a basis for such discrimination.

References

1. Hatada K, Kitayama T, Ute K (1988) Prog Polym Sci 13: 189
2. Hatada K, Ute K, Tanaka K, Kitayama T, Okamoto Y (1985) Polym J 17: 977
3. Hatada K, Ute K, Tanaka K, Okamoto Y, Kitayama T (1986) Polym J 18: 1037
4. Kitayama T, Shinazaki T, Masuda E, Yamamoto M, Hatada K (1988) Polym Bull 20: 565
5. Kitayama T, Shinozaki T, Sakamoto T, Yamamoto M, Hatada K (1989) Makromol Chem Supplement 15: 167
6. Hatada K, Ute K, Kashiyama M, Imanari M (1990) Polym J 22: 218
7. Hatada K, Ute K, Kitayama T, Yamamoto M, Nishimura T, Kashiyama M (1989) Pollym Bull 21: 489
8. Hatada K, Ute K, Nishimura, T, Kashiyama M, Fujimoto N (1990) Polym Bull 23: 549
9. Ute K, Kashiyama M, Oka K, Hatada K, Vogl O (1990) Makromol Chem Rapid Commun 11: 31
10. Liquori AM, Anzuino G, Corio VM, D'Alagni M, de Santis P (1965) Nature (Loodon), 206: 358
11. Hatada K, Okamoto Y, Kitayama T, Sasaki S (1983) Polym Prep Jpn 32: 1215
12. Okamoto Y, Yanagida M, Hatada K (1989) Polym J 21: 795 and (1988) Polym Prep Jpn 37: 562
13. Hunkeler D, Macko T, Berek D, (1991) Polym Mat Sci Eng 65: 101 and (1993) In: Powder T (ed) Chromatography of polymers. ACS Symp Series 521: 90
14. Hunkeler D, Jančo M, Guryanova VV, Berek D In: Powder T (ed) Chromatography of polymers. ACS Symp Series, in press
15. Jančo M, Berek D in preparation
16. Cowie JMG (1972) Solutions of Stereoregular Polymers. In Huglin MB (ed) Light Scattering form Polymer Solutions. Academic Press London p 605
17. Hatada K, Kitayama T Stereoreguar Macromonomers with Respect to Main Chain and/or Side Chain. In: Mishra MK (ed) Macromolecular Design: Concept and Practice (Macromonomers, Macroinitiators, Macroiniferters, Macroinimers, Macroiniters and Macroinifers) Polymer Frontiers Int'l Inc New York in press
18. Ute K, Miyatake N, Osugi Y, Hatada K (1993) Polym J 25: 1153