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Characterization of block copolymers by size exclusion chromatography

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Summary

Poly(ethyl methacrylate-b-deuterated methyl methacrylate), poly(styrene-b-methyl methacrylate), and poly(styrene-b-dimethylsiloxane)diblock copolymers have been characterized by means of size exclusion chromatography (GPC) apparatus fitted with four detectors in series, viz continuous viscometer, UV spectrophotometer, low angle light scattering photometer, and differential refractometer. The continuous measurements of the scattered light intensity, the limiting viscosity number, the concentration, and the chemical composition permits complete determination of the molecular characteristics of block copolymers.

Introduction

During the past several years, there has been a growing commercial and academic interest in block copolymers, because of their unique properties in solution and in the solid state which can be related to their molecular structure. These properties are dependent upon the composition heterogeneity and the molecular weight distribution. Therefore, information of considerable importance can be obtained by determining for a copolymer the variation in composition as a function of molecular weight.

The aim of the present paper is to show that size exclusion chromatography coupled on line with viscometry, UV spectrophotometry, low angle laser light scattering, and refractometry is a convenient, rapid, and accurate technique for the characterization of block copolymers.

Experimental

Synthesis

Homopolymer and copolymer samples were synthesized via anionic polymerization techniques.

Poly(ethyl methacrylate-b-deuterated methyl methacrylate)diblock copolymers (PEMA-PMMAD) were synthesized in tetrahydrofuran at low temperature (- 70°C) using diphenylmethylsodium as the initiator (1). Homopolymers of deuterated methyl methacrylate were also prepared under the same conditions as the PMMAD blocks.

Poly(styrene-b-methyl methacrylate)diblock copolymers (PS-PMMA) were prepared according to the method developed by Rempp et al (2).

All reactions were conducted under high purity argon in glass vessels equipped with Teflon valves.

The synthesis of poly(styrene-b-dimethylsiloxane) samples (PS-PDMS) were

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*To whom offprint requests should be sent carried out by first polymerizing styrene with sec-butyllithium in benzene at room temperature. Upon completion of the first block, the copolymerization of hexamethylcyclotrisiloxane was performed in a benzene-diglyme or benzene-tetrahydrofuran mixture at 50°C. Polymerizations were carried out in a sealed vacuum apparatus using conventional break-seal techniques. More details on the synthesis procedure were described elsewhere (3).

Size exclusion chromatography (SEC)

Experimental data were obtained with a Waters 150C chromatograph coupled on line with four detectors. The first detector is a home-made continuous viscometer based on the measurement of the effluent pressure drop through a capillary tube (4). The second detector is a UV spectrophotometer Shimadzu SPD-6AV operating at 262 nm. The third detector is a low angle laser light scattering (LALLS) photometer Chromatix CMX 100. The last one is a standard Waters differential refractometer used as a concentration detector. Five columns in series packed with PL gel having upper permeability limits of : 10^6, 10^5, 10^4, 10^3 and 5.10^2 respectively were used. The mobile phase was tetrahydrofuran (THF) with a flow rate of 1ml/min.

Results and Discussion

The experimental results are given in Tables 1-5 and in Figures 1-4. We shall examine successively the case of PEMA-PMMAD, PS-PMMA and PS-PDMS block copolymers.

Poly(ethyl methacrylate-b-deuterated methyl methacrylate)

According to Bushuk and Benoît (5), the molecular weight measured from the light intensity scattered by a copolymer solution is an apparent molecular weight (M_{ap}) resulting from the fluctuations in composition inside the copolymer. Thus, M_{ap} depends on the refractive index increment of the sample and varies with the solvent used. However, if the indexes of refraction of the two blocks are nearly the same, as is the case for PEMA and PMMAD [$(dn/dc)_{PEMA/THF} = 0.084$; $(dn/dc)_{PMMAD/THF} = 0.079$], M_{ap} can be assimilated to the weight average molecular weight M_w whatever the refractive index of the solvent. As expected, for each copolymer sample we observe a very good agreement (Table 1) between the molecular weight determined by the multi-detector SEC apparatus and the theoretical molecular weight calculated from M_w of PEMA block and PEMA content. Moreover, the polydispersity indexes of copolymers and PEMA blocks are very close to one. This means that all samples exhibit a very narrow molecular weight distribution as revealed by the SEC chromatogram (Fig.1). It can also be seen that the agreement between the weight average molecular weights of PEMA blocks computed from SEC data and those measured by standard light scattering are in agreement within experimental error.

SEC data were used to obtain information about the conformation of copolymer chains in dilute solution in THF which is a good solvent for both blocks. For this purpose, the measured intrinsic viscosities of samples GL2, GL3 and GL4 were compared with the viscosities calculated assuming that this parameter is a weighted average of that of the corresponding homopolymers of identical molecular weight. The $[\eta]$ values for PEMA and PMMAD homopolymers were obtained using the relations :

$[\eta]_{PEMA} = 0.0225\ M^{0.66}$ and $[\eta]_{PMMAD} = 0.0143\ M^{0.68}$

that we have established from a standard series of monodisperse samples whose molecular weights ranged between 10000 and 500000 (Table 2). For each copolymer (Table 3), the fit between the experimental and calculated values of $[\eta]$ is satisfactory. This suggests that the intramolecular heterocontacts are very few (6), so that intramolecular phase separation occurs and copolymer molecules exhibit a segregated conformation in which chemically unlike blocks occupy different domains in space. (In the solid state, these copolymers adopt a segregated conformation, as revealed by DSC thermograms which exhibit two T_gs). The viscometric behavior of sample GL1 was not investigated, because of the low molecular weight of the copolymer giving small intrinsic viscosity value. Interpretation of this experimental value is inconclusive.

Table 1 : Experimental data on poly(ethyl methacrylate-b-deuterated methyl methacrylate) : PEMA-PMMAD diblock copolymers.

		SEC coupled with viscometry and LALLS							
		PEMA block			Copolymer				
Sample	[a] M_w	M_w	M_w/M_n	$[\eta]$ ($ml.g^{-1}$)	[b] wt% PEMA	[c] M_w^{th}	M_w	M_w/M_n	$[\eta]$ ($ml.g^{-1}$)
GL1	14000	14000	1.02	12.4	41.1	34000	34000	1.03	17.2
GL2	41000	41000	1.03	22.8	49.9	82100	83000	1.04	36.4
GL3	77000	76000	1.02	34.7	43.2	175900	176000	1.04	59.0
GL4	143000	144000	1.03	58.1	40.8	353000	360000	1.06	93.7

[a] measured by "static" light scattering in methylethylketone.
[b] measured by ^{13}C NMR.
[c] calculated from M_w of PEMA block and wt % PEMA.

Table 2 : Molecular characteristics of polyethyl methacrylate and deuterated polymethyl methacrylate samples determined by SEC coupled with viscometry and LALLS.

PEMA			PMMAD		
Sample	M_w	$[\eta]$ ($ml.g^{-1}$)	Sample	M_w	$[\eta]$ ($ml.g^{-1}$)
L1	14000	12.4	D1	18000	11.1
L2	41000	22.8	D2	38000	18.1
L3	76000	34.7	D3	120000	40.0
L4	144000	58.1	D4	173000	50.6
L5	370000	103.0	D5	359000	83.9
			D6	382000	86.2
			D7	400000	91.7
			D8	465000	98.0

Table 3 : Comparison between experimental and calculated values of [η] for PEMA-PMMAD copolymers.

Sample	$[\eta]_{exp}$ (ml.g^{-1})	$[\eta]_{calcd}$ (ml.g^{-1})	Δ [η]%
GL2	36.4	35.7	1.9
GL3	59.0	58.2	1.4
GL4	93.7	93.4	0.3

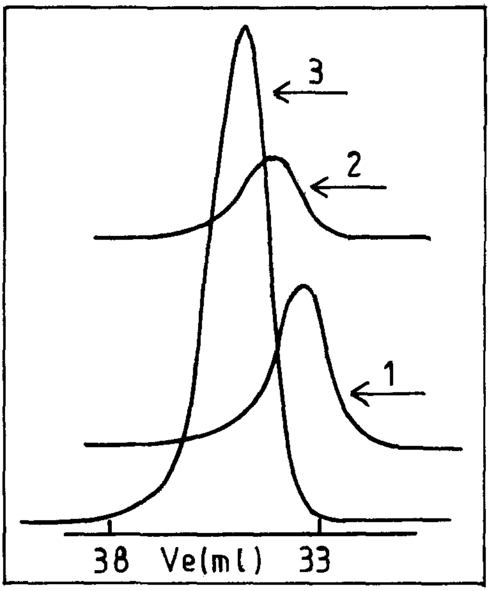


Figure 1 : Chromatogramm of sample GL3. Responses of : 1-viscometer, 2-LALLS photometer, 3-refractomer

Poly(styrene-b-methyl methacrylate)

The refractive indexes of PS and PMMA being different, SEC equipped with LALLS gives an apparent value of the molecular weight if the copolymer is heterogeneous in composition. The chemical composition has been determined for each fraction with the help of the UV detector, by using the method described by H.D. Adams (7). For this purpose, UV and refractive index (RI) detectors were calibrated in terms of amount of PS and PMMA. It was checked that PMMA did not adsorb at 262 nm. Thus, the UV detector is sensitive to only PS while the RI detector is sensitive to PS and PMMA. Then, for each fraction i the PS weight content can be obtained by the following relation :

$$(UV_{PS})_i = \frac{R_i K_{PMMA}}{K'_{PS} - (K_{PS} - K_{PMMA})R_i}$$

with $R_i = r_{uv}/r_{RI}$, where r_{uv} and r_{RI} are the responses of the UV and RI detectors, respectively. K'_{PS}, K_{PS} and K_{PMMA} are proportionality constants. The calibration was achieved by injecting various amounts of PS and PMMA.

The areas under the curves were determined by graphical integration and used to calculate the proportionality constants. The responses of UV and RI detectors were found to be linear with polymer concentration. The data for the two copolymers investigated are shown in Fig.2. Sample Z5 exhibits small composition fluctuations and is very narrow in molecular weight distribution (M_w/M_n = 1.05) (Fig.3). Moreover, the molecular weight measured with the LALLS detector corresponds to the theoretical molecular weight (Table 4). Therefore, M_{ap} can be taken as M_w. The situation is quite different for sample Z4. The chromatogram (Fig.4) presents a "shoulder" in the range of lower molecular weights, which is due to the presence of PS homopolymer. Thus, the polydispersity in molecular weight is relatively high : M_w/M_n = 1.27 and one observes an important increase in styrene content with decreasing molecular weight (Fig.2). It should be noted that the sensitivity of UV detector to detect the PS homopolymer is higher than that of the RI detector. This is explained by the fact that, as already mentioned, the UV detector is sensitive to only PS.

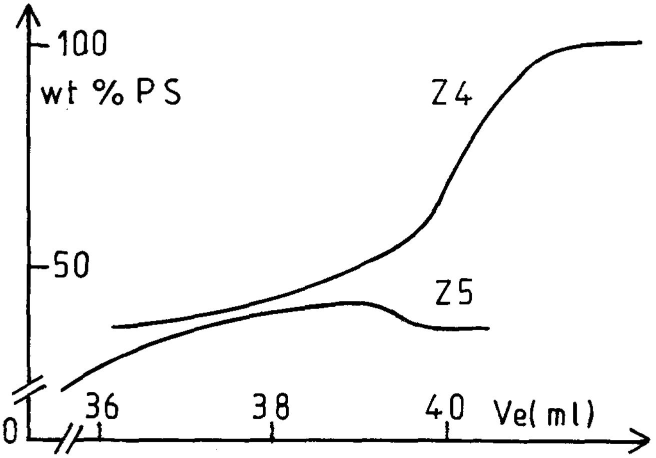
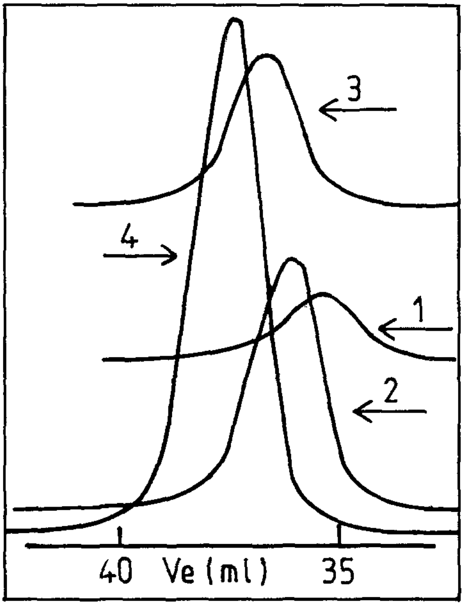


Figure 2 : Chemical composition (wt% PS) of samples Z4 and Z5 as a function of elution volume

Table 4 : Experimental data on poly(styrene-b-methyl methacrylate) : PS-PMMA diblock copolymers.

		SEC coupled with viscometry, UV spectrophotometry and LALLS							
		PS block			Copolymer				
Sample	[a] M_w	M_w	M_w/M_n	$[\eta]$ (ml.g^{-1})	[b] wt%PS	[c] M_w^{th}	M_{ap}	M_{ap}/M_n	$[\eta]$ (ml.g^{-1})
Z4	26000	26000	1.06	18.0	55.0	47000	51000	1.27	31.0
Z5					36.3	71600	73000	1.05	35.1

[a] measured by "static" light scattering in tetrahydrofuran.
[b] determined from UV adsorption data.
[c] calculated from M_w of PS block and wt% PS.



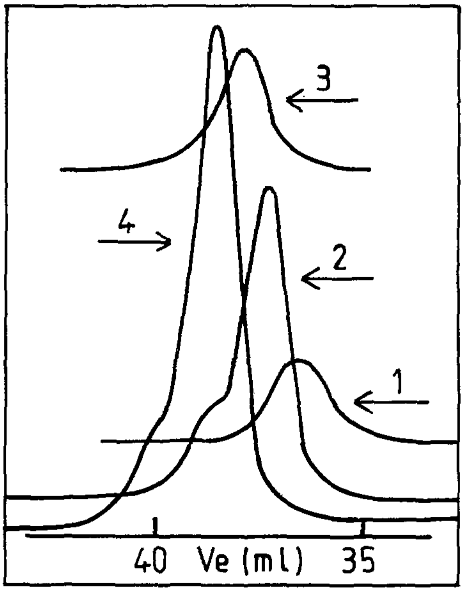


Figure 3 :
Chromatogram of sample Z5

Figure 4 :
Chromatogram of sample Z4

Responses of : 1-viscometer, 2-UV spectrophotometer, 3-LALLS photometer, 4-refractometer

Poly(styrene-b-dimethylsiloxane)

In THF these copolymers correspond to the particular case where one block (the PDMS sequence) has the same refractive index as the solvent. Then, the light scattered by copolymer molecules is due to the PS block. LALLS measurements still give an apparent molecular weight for the block copolymer (Table 5), but allow also the determination of the weight average molecular weight of the scattering part (PS part) of copolymer chains. For both copolymers, the fit between M_w of the PS part (M_w = 43000) and M_w of PS blocks (M_w = 42000) is excellent. It can be seen that for sample HE2 M_{ap} is much higher than M_w^{th}. This indicates that the copolymer, contrary to sample HE2-7, is heterogeneous in composition and molecular weight. This observation is to be related to the fact that sample HE2-7 is one of the fractions obtained by fractionation of the crude copolymer HE2.

Table 5 : Experimental data on poly(styrene-b-dimethylsiloxane) : PS-PDMS diblock copolymers.

		SEC coupled with viscometry and LALLS						
		PS block			Copolymer			
Sample	[a] M_w	M_w	M_w/M_n	$[\eta]$ $(ml.g^{-1})$	[b] wt% PS	[c] M_w^{th}	M_{ap}	M_{ap}/M_n
HE2	42700	42000	1.05	25.2	49.0	85700	100000	1.15
HE2-7					74.0	56800	57000	1.06

[a] measured by "static" light scattering in tetrahydrofuran.
[b] determined from UV adsorption data.
[c] calculated from M_w of PS block and wt% PS.

Conclusion

The four-detector GPC set-up is a powerful tool for the characterization of block copolymers. This technique allows one in particular to determine:

- the weight average molecular weight and polydispersity index of the first block (block A for a AB copolymer)
- the composition and molecular weight distributions of the copolymer
- the intrinsic viscosity which can yield information about the conformation of copolymer molecules.

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