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Inhibition of anomalous exclusion of styrene–maleic anhydride copolymers

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The average molar masses of styrene–maleic anhydride (SMA) copolymers, calculated from data obtained by size exclusion chromatography (s.e.c.), are often lower (by a factor of two) or higher (by a factor of eight) than the values expected from light scattering and viscometry. However, the polystyrene samples which are used as reference materials exhibit no such deviations. Therefore, the exclusion mechanism during the elution of SMA is significantly interfered with by certain adsorption and repulsion mechanisms, with these being dependent on the set of columns used, the comonomer content and the molar mass. This interference can be attributed to the existence of active polar sites on the packing and to partial ring opening of the maleic anhydride ring, thus resulting in the formation of a dicarboxylic acid species. Ring opening might also be followed by protolysis. This anomalous behaviour can be suppressed by the addition of 5 wt% acetic acid to the solvent used, i.e. tetrahydrofuran (THF). The presence of the acetic acid does not influence the intrinsic viscosity. Thus the coil dimensions (hydrodynamic volume) do not change and the universal calibration remains valid. Copyright © 1996 Elsevier Science Ltd.

(Keywords: size exclusion chromatography; styrene copolymers; elution mechanism)

INTRODUCTION

Styrene–maleic anhydride is a copolymer with a wide variety of applications[1]. This is attributable to the functionality of the anhydride ring[2] and to the high glass transition temperature, which increases with increasing maleic anhydride content. Evaluation of the molar mass distribution (*MMD*) of the copolymers is important from two points of view: the process kinetics determines the molecular structure, which in turn determines the properties of the copolymers. Therefore, fundamental knowledge about the *MMD* may not only supply information about the kinetics but may also contribute to a better understanding of the relationship between structure and properties. A fast and reliable method to determine the *MMD* of polymers is size exclusion chromatography (s.e.c.). According to Chow[3] it should be possible to characterize copolymers of SMA having molar masses ranging from 20 to 700 kg mol^{-1} and compositions ranging from 5 to 50 mol% maleic anhydride (MA). This author concluded that successful characterization of SMA in THF by using styrene–divinylbenzene columns could be achieved in this way.

Unfortunately, during our investigations it appeared that the results obtained were dependent on the set of styrene–divinylbenzene columns that were used and on the number of SMA copolymers being eluted on the columns. Curiously, the polystyrene samples used for calibration purposes showed no such anomalies and behaved as expected, i.e. independent of the set of columns being used. Therefore, the discrepancies in chromatographic behaviour must be attributed to a strong interaction between the copolymer and the packing material. Anomalous effects during the exclusion of SMA were also reported by Tacx *et al.*[4] and Segudovic *et al.*[5]. The aim of this present investigation is to identify these interfering mechanisms and to suppress them during the exclusion process.

EXPERIMENTAL

Dissolution and filtration

The polymers were dissolved in THF (Aldrich, h.p.l.c. grade) (0.1 wt% for s.e.c. and 1 wt% for light scattering measurements) over a period of 3 h at 20°C, and stabilized with di-tert-butylparacresol (DBPC) (0.05 wt%). The solutions were filtered (1.2 μ Millipore filter) and then injected.

Size exclusion chromatography (s.e.c.)

Size exclusion chromatography was performed on a Hewlett–Packard chromatograph (HP 1090) equipped with a diode array detector and a refractive index detector (HP 1037A). Various sets of s.e.c. (micro-Styragel) columns were used (details are given in *Table 1*). Calibration was carried out by using 10 different polystyrene standards having narrow distributions and known average molar masses ranging from 580 to 2000 kg mol^{-1}. The calibration curve for polystyrene was transformed into a calibration curve for SMA by using the Mark–Houwink equations for SMA and PS, as referred to by Chow[3]. The solvent flowrate was 1.0 ml min^{-1}, with THF being used as the eluent. All data were processed by using a HP-300 computer equipped with a HP software package.

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Light scattering

Light scattering experiments were carried out by using a SOFICA apparatus (FICA 50). The intensity of scattered light was measured at 5 different concentrations and at 11 angles ranging from 30 to 150°. The apparatus was calibrated by using benzene.

Viscometry

Intrinsic viscosity measurements were carried out by using an Ubbelohde capillary viscometer having an internal diameter of 0.5 mm and a length of 15 cm. The flow times were measured by using a viscotimer (Lauda). Because the flow times were relatively long ($t_0 > 100$ s), the correction for kinetic energy could be ignored. The samples were dissolved in the viscometer reservoir at 25°C and the solutions were then diluted by adding fresh solvent.

Electron spectroscopy for chemical analysis (e.s.c.a.)

The e.s.c.a. experiments were performed by using a Leybold LHS-10 apparatus, employing MgKα radiation. The base pressure was 10^{-10} mbar, and the X-ray tube operated at 13 kV and 20 mA. The data were processed by using a Leybold DS-5 software package running on a HP-1000 computer.

RESULTS AND DISCUSSION

Interference with the exclusion of SMA by repulsion and adsorption

Various SMA copolymers having molar masses ranging from 100 to 160 kg mol^{-1} and compositions ranging from 12 to 28 wt% maleic anhydride (MA) were characterized by s.e.c. using column set 1. At the same time, this set was also used for the characterization of other types of polymers. Reliable results were obtained, as shown in *Table 2* (column set 1 (good result)). Over a period of time, the number of polymers other than SMA was decreased, while the number of SMA copolymers characterized by using this set was increased. Unfortunately, the results obtained for SMA changed with time: after a long period of time the results given in *Table 2* (column set 1 (bad result)) were obtained. This urged us to install various sets of new columns as detailed in *Table 1*, with the results being summarized in *Table 2*. From these results it appears that the intrinsic viscosities calculated from the *MMD* and determined by an independent off-line measurement are in agreement only in the case of the column set 1 (good result) data. Furthermore, the polydispersity of the distributions are in agreement with the polydispersity expected for copolymers prepared by solution radical copolymerization. It can be inferred that the discrepancies between the intrinsic viscosities and molar masses calculated from the *MMD* and determined by viscometry and light scattering measurements increase with increasing comonomer (MA) content and molar mass. The polydispersities of the distributions also exhibit increasing deviations with increasing comonomer content and increasing molar mass. In *Figure 1* three distributions are represented which were obtained by using column set 1 (good result and bad result) data and column set 3 data for a copolymer having $M_w = 160$ kg mol^{-1} and 28 wt% MA. In all of these cases a reference sample of polystyrene having a molar mass of 180 kg mol^{-1} and the polystyrene calibration standards exhibited no anomalies. Inter- and intramolecular aggregation of the SMA coils is not a plausible explanation for this behaviour since light scattering and viscometry measurements indicated no enhancement of molar mass, nor of intrinsic viscosity. Hence, the exclusion mechanism for SMA is interfered with by adsorption in the case of column set 3 and

Table 1 Characteristics of the s.e.c. columns used in this work

Set	Supplier	Number of columns	Pore size (Å)
1	Waters	5	$10^2, 10^3, 10^4, 10^5, 10^6$
2	Waters	5	$10^2, 10^3, 10^4, 10^5, 10^6$
3	Waters	5	$10^2, 10^3, 10^4, 10^5, 10^6$
4	Polymer Laboratories	4	$10^6, 10^5, 10^4, 10^3$

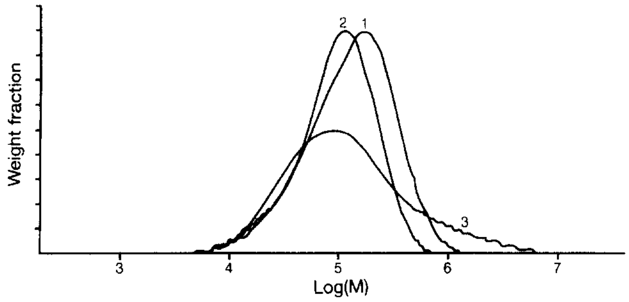

Figure 1 Molar mass distributions of one specific SMA copolymer ($M_w = 160$ kg mol^{-1}, 28 wt% MA) obtained using: (1) column set 1 (good result); (2) column set 3; (3) column set 1 (bad result)

Table 2 Data for various SMA copolymers obtained by light scattering measurements, viscometry, and s.e.c. using three different sets of columns

		Off-line measurements		Column set 1 (good result)		Column set 1 (bad result)		Column set 2		Column set 4	
No.	MA (wt%)	M_w (kg mol^{-1})	$[\eta]$ (dl g^{-1})	M_w (kg mol^{-1})	$[\eta]$ (dl g^{-1})	M_w (kg mol^{-1})	$[\eta]$ (dl g^{-1})	M_w (kg mol^{-1})	$[\eta]$ (dl g^{-1})	M_w (kg mol^{-1})	$[\eta]$ (dl g^{-1})
1	28	160	0.49	175	0.49	453	0.70	118	0.49	50	–
2	28	107	0.41	125	0.41	–	–	101	0.38	34	0.2
3	22	194	0.56	195	0.52	–	–	166	0.51	110	0.4
4	28	139	0.42	136	0.41	–	–	110	0.40	33	0.2
5	12	115	0.45	145	0.44	–	–	–	–	–	–
6	18	110	0.42	115	0.43	210	0.56	90	0.38	72	0.3

by repulsion in the case of column set 1 (bad result)[4]. The anomalous exclusion behaviour of SMA samples having low molar masses was also observed by Segudovic *et al.*[5].

Adsorption of the SMA copolymers on the non-polar packing material is not likely to occur unless the polymer contains dicarboxylic acid and the packing contains polar active sites. The dicarboxylic acid is formed by a ring-opening process. The anomalous exclusion of styrene–acrylic acid copolymers has also been observed[6]. The polar active sites might consist of the following:

(1) Oxidized packing material.
(2) Polar surfactant or initiator molecules used in the polymerization process to obtain the macroporous packing material. During polymerization, the surfactant could be incorporated into the copolymer[7].

Repulsion of copolymers is known to interfere very strongly with the exclusion mechanism. The anomalous exclusion behaviour of SMA must therefore be caused by electrical charges on the polymer and the packing material.

Deactivation of packing material

According to the reference manual[8] the column packing material can be reactivated with a solution of triphenylphosphine (TPP). Unfortunately, treatment of column set 1 did not result in the disappearance of the anomalies. This result was expected since TPP is a radical scavenger and will not react with existing stable polar groups formed by oxidation. Moreover, the oxidation of the packing material is not likely to occur at room temperature.

E.s.c.a. study of the packing material

In order to investigate the hypotheses concerning the existence of polar sites on the packing material and the adsorption of the polymer, we characterized various packing materials by using e.s.c.a., e.g. polystyrene, blank packing, and packing used for the analysis of SMA. The results (at% oxygen) are summarized in *Table 3*. From this table it appears that polystyrene contains no oxygen. Surprisingly, blank packing material contained 1.5 at% oxygen and minor quantities of aliphatic carbon atoms. Perhaps the polar polymer (e.g. poly(vinyl alcohol)) used in the synthesis of the macroporous packing remains chemically bound to the packing material. In accordance with our expectations, the packing used for various analyses of SMA contained 4 at% oxygen, thus indicating a strong adsorption of SMA to the surface.

Hydrolysis of SMA in THF

According to Heslinga and van der Willigen[9], SMA is sensitive to hydrolysis in blends with poly(vinyl acetate). The rate of hydrolysis is governed by the pH of the system. However, the rate of hydrolysis in THF containing minor quantities of water is unknown. Therefore, we prepared various solutions of copolymers having MA contents ranging from 0 to 28 wt%. The results are given in *Table 4*. It is clear that when the MA content exceeds a certain threshold value, the formation of maleic acid increases rapidly with increasing maleic anhydride content.

Table 3 Values obtained by e.s.c.a. for the oxygen content of polystyrene and the packing materials

Material	Oxygen (at%)
Polystyrene	0
Blank packing	1.5
Packing for SMA characterization	4

Table 4 Maleic acid content of various copolymers after dissolution for 2 h in THF

MA in SMA (wt%)	Acid (wt%)
0	0
12	0
18	2
27	7

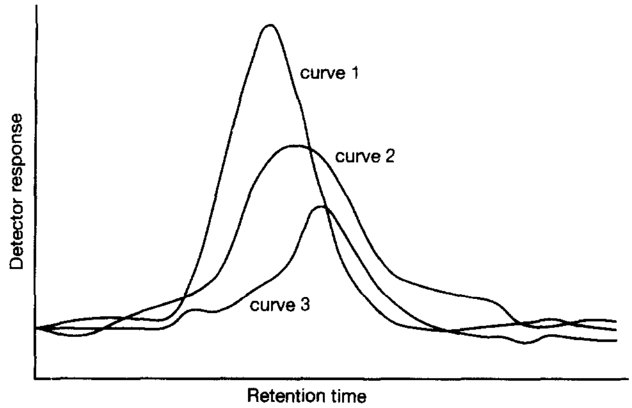

Figure 2 Three chromatograms of an SMA copolymer obtained at three different temperatures: (1) 30; (2) 45; (3) 57°C

Influence of temperature on the exclusion behaviour of SMA

The influence of adsorption is known to decrease with increasing temperature. *Figure 2* shows chromatograms of sample 1 run at various temperatures, i.e. 25, 45, and 57°C. Unfortunately, with increasing temperature the whole distribution shifts to higher retention times, thus indicating an increase in hydrolysis with increasing temperature. Moreover, the peak area decreases with increasing temperature, indicating that part of the injected copolymer remains on the packing material. The temperature of the detector remained constant. Therefore, any influence of the refractive index increment on the peak area can be eliminated.

Inhibition of the anomalies

SMA is capable of being hydrolysed in THF which contains minor quantities of water. The hydrolysed polymer might adsorb onto the active sites of the packing, resulting in too high retention times and hence too low molar masses, as was observed for column sets 2, 3 and 4. If SMA adsorbs onto the packing and also protolyses, then this results in electric charges on the surface, repulsion of eluted protolysed polymer, too low retention times, and hence too high molar masses, as observed for the column set 1 (bad result) case.

According to our assumption, the anomalous effects

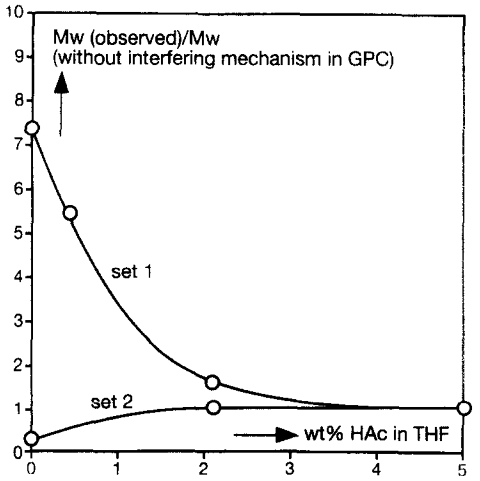

Figure 3 Ratio of M_w (observed)/M_w (without interfering mechanisms in s.e.c.) as a function of the amount of acetic acid added to THF; column sets 1 and 2 were used at 20°C

will disappear in the presence of an acid, which will have the following effects:

(1) stabilization of the anhydride ring;
(2) suppression of the charge on the polymer;
(3) competition with the copolymer for the active sites.

Reduction of the anomalous effects of carboxylic acid type materials in s.e.c. using polystyrene gel columns by the addition of acetic acid in THF was also observed by Ezrin and Brown[10]. In our investigations we also chose acetic acid. Addition of the acid to the THF eluent results in a slow decrease (over several days) of the anomalies. Results obtained at different levels of acetic acid content were obtained after reaching equilibrium. Some of the results obtained are presented in *Figure 3*. From these results it appears that the correct molar masses can be obtained, and that the results are not dependent on the type of styrene–divinylbenzene column being used. It is remarkable that characterization of SMA when using column set 1 resulted in reliable values during the time that other types of polymers were being measured (column set 1 (good result)). The other polymers are apparently coated on the active sites and cannot be reached by the SMA. During the time of measurement, the coated polymer is rinsed out, thus resulting in adsorption of the SMA at the active sites (column set 1 (bad result)).

An important result was that the presence of 5 wt% acetic acid in THF does not influence the intrinsic viscosity. Therefore the coil dimensions do not change and so the universal calibration remains valid.

CONCLUSIONS

From this present investigation it appears that other mechanisms (repulsion and adsorption) may be operative during the exclusion of SMA in s.e.c., while polystyrene reference materials showed no anomalies. This was attributed to the partial hydrolysis of the anhydride ring and to the presence of active polar sites on the packing material (styrene–divinylbenzene). At first, the polymer adsorbs to the surface, resulting in the calculated molar masses being too low. Subsequently, the adsorbed polymer might protolyse, resulting in too high values for the calculated molar masses. The interfering mechanisms could successfully be suppressed by the addition of 5 wt% acetic acid to both the solvent and the eluent.

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