

# Molecular Characterization of Amphiphilic Copolymers by Size Exclusion Chromatography Equipped with On-Line Triple Detectors.

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## Introduction

Simultaneous measurement of intrinsic viscosity  $[\eta]$ , refractive index (RI) and light scattering (LS) properties of a macromolecule is a powerful method to characterize polymeric materials in solution. This can be possibly achieved by on-line installation of the above detectors (TAD) to a size exclusion chromatography (SEC) system (SEC-TAD). With a single experiment, the  $[\eta]$ , weight average molecular weight ( $\bar{M}_w$ ), number average molecular weight ( $\bar{M}_n$ ), hydrodynamic radius ( $R_H$ ), radius of gyration ( $R_G$ ), and  $dn/dc$  of macromolecules can be obtained.<sup>[1]</sup> However, ionic “smart” macromolecules<sup>[2]</sup>, which have sensitive and reversible responses to small triggers in environmental conditions (temperature, pH, light, ionic strength, electric and magnetic fields, etc.), do not respond to SEC easily, unless the ionic strength of a mobile phase can be modified by certain salts.<sup>[3]</sup> In this work, we present characterization of two ionic copolymers that are classified as amphiphilic smart materials, a cobaltocenium statistical copolymer<sup>[4]</sup> and a statistical copolymer of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and butyl methacrylate (BMA) (poly(DMAEMA-stat-BMA)).<sup>[5]</sup>

## Methodology

Herein we characterized a cobaltocenium statistical copolymer using a 10 mmol/L solution of  $KPF_6$  in *N,N*-dimethylformamide (DMF) as a mobile phase at 50 °C. Also, both samples of cobaltocenium copolymer and poly(DMAEMA-stat-BMA) showed peaks when they were dissolved in a mixture of 10 mmol/L of  $KPF_6$  in tetrahydrofuran (THF):acetone; triethyl amine (46:46:8 by volume) or THF:methyl ethyl ketone (MEK):triethyl amine (46:46:8 by volume) when the same solvent was used as a mobile phase.

## Results

Poly(DMAEMA-stat-BMA) did not show any peaks by SEC-TDA when the mobile phase was THF as shown in **Fig 1a**. However, it showed signals when triethyl amine (8%) was added to the mobile phase (**Fig 1b**).

The resulted number average molecular weight ( $\bar{M}_n = 9.6$  kDa) was in agreement with the values of  $\bar{M}_n$  obtained via nuclear magnetic resonance end group analysis.<sup>[2]</sup> The weight average molecular weight ( $\bar{M}_w = 10.0$  kDa), intrinsic viscosity ( $[\eta] = 13.6$  mL/g), and the hydrodynamic radius ( $R_H = 2.76$  nm) were obtained from corresponding traces of the chromatograms. Also, the chromatogram data were used to construct double logarithmic plots of  $\bar{M}_w$  versus  $[\eta]$ , known as Mark-Houwink-Kuhn-Sakurada (MH) relationship,  $[\eta] = kM^a$ <sup>[6,7]</sup>. The MH parameters for this copolymer are  $a = 0.655$ , and  $\ln k = -3.482$ . The Stockmayer-Fixman (S-F)<sup>[8,9]</sup> parameters are  $K_\Theta = 0.107$  (cgs) and slope 3.95 (mcgs).

**The cobaltocenium statistical copolymer** in DMF at 50 °C and in the mixture of THF: acetone (50:50 by volume) did not show visible SEC-TAD peaks. However, when the mobile phase contained 10 mmol/L solution of  $KPF_6$ , the SEC-TAD signals became visible. **Table 1** shows the characteristic parameters of this copolymer in both solvents.

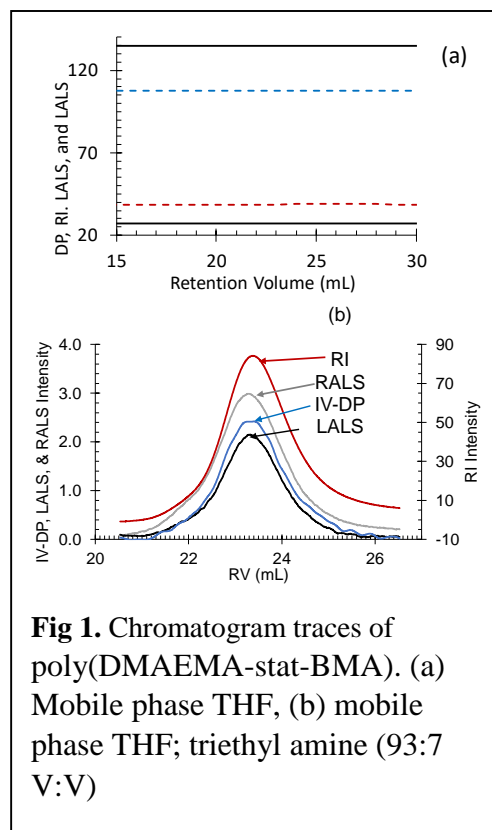
**Table 1** Characteristic parameters of cobaltocenium statistical copolymer in DMF at 50 °C and in the mixture of THF:acetone (50:50, v:v) at 30°C.

Solvent	t (°C)	$\bar{M}_n$	$\bar{M}_w$	$[\eta]$	a	k
DMF	50	61,800	307,000	1.1661	0.594	-3.138
THF-Acetone	30	62,100	94,600	0.4066	0.601	-3.808

While attempts with pure solvents did not succeed, it was found that addition of 10 mM  $KPF_6$  into the DMF or mixture of THF:Actone eluent resulted in “normal” SEC peaks of cobaltocenium copolymer. In a figurative manner, the general chemical principle that like dissolves like explains this behavior. In this case, the  $PF_6^-$  anions in the SEC eluent appear to act as screening electrolyte that diminishes the polyelectrolyte effect (polymer chain expansion). This effect decreases the association of ionic groups and reduces the polymer-column interactions, which are characteristic phenomena associated with polyelectrolytes.<sup>[10]</sup> In the case of poly(DMAEMA-stat-BMA), triethyl amine was added into THF eluent to obtain SEC peaks. Since the presence of triethyl amine could diminish the adsorption of the amino-containing copolymer on the columns.<sup>11</sup>

## Conclusions

When the mobile phase was a pure solvent or a mixture of liquids, the SEC-TAD peaks was not visible. Adding small amount of triethyl amine to the mobile phase made the SEC-TAD traces of Poly(DMAEMA-stat-BMA) visible, resulting in a fast method to characterize this copolymer. Adding small amount of  $KPF_6$ , (10 mM) to the mobile phase resulted in visibility of SEC-TAD



**Fig 1.** Chromatogram traces of poly(DMAEMA-stat-BMA). (a) Mobile phase THF, (b) mobile phase THF; triethyl amine (93:7 V:V)

peaks of cobaltocenium statistical copolymer in DMF and in the mixture of THF:acetone (50:50, v:v). This made the SEC-TAD technique be a useful method to characterize ionic macromolecules. Over all it seems that the presence of the same type of anions and organic counterions in the SEC mobile phase could create a similar environment for the polyelectrolytes, counterbalancing the effect of the ionic groups in the macromolecules on their flow behavior in the columns.

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