



Novel developments in the multidimensional characterization of segmented copolymers



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This article is dedicated to Prof. Dr. Bernd Trathnigg, Karl-Franzens University Graz, Austria, on the occasion of his retirement for his outstanding contributions to analytical polymer science over the last few decades.

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ABSTRACT

Controlled radical polymerization (CRP) provides the polymer chemist with the ability to produce tailor-made polymers with controlled molar masses, molar mass distributions, chemical compositions and macromolecular architectures. Segmented copolymers can be synthesized having polymer segments arranged in a linear fashion (linear block copolymers), however, polymer segments can also be attached to pre-synthesized macromolecules or to multifunctional core molecules to produce branched (graft) copolymers, polymer stars or dendrimers. Although there are many ways to control the chain growth and the architecture of the target macromolecules, side reactions cannot be completely avoided. Accordingly, even with CRP, obtained products exhibit chemical composition and topology distributions along with the molar mass distribution.

In this review article, recent developments in multidimensional characterization of segmented copolymers are presented. Liquid chromatography (LC) is the most widely used and versatile polymer fractionation technique to address different aspects of copolymer heterogeneity. The potential and limitations of different modes of liquid chromatography of polymers (size exclusion chromatography, different modes of interaction chromatography) and spectroscopic techniques (FTIR, NMR, and MALDI-TOF-MS) are elaborated. Possible method combinations including comprehensive two-dimensional LC and the hyphenation of various modes of LC with spectroscopic techniques are discussed. Advantages and limitations of various off-line and on-line approaches to method hyphenation are highlighted. Examples from recent literature with special focus on segmented copolymers (e.g. block, graft, miktoarm, multibranch or star copolymers) will be reviewed.

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Abbreviations: ATRP, atom transfer radical polymerization; CAP, critical adsorption point; CRP, controlled radical polymerization; DLS, dynamic light scattering; 2D-LC, two-dimensional liquid chromatography; ELSD, evaporative light scattering detector; EO-PO, ethylene oxide-propylene oxide; ESI, electrospray ionization; FTIR, Fourier transform infrared; GC, gas chromatography; GPEC, gradient polymer elution chromatography; HILIC, hydrophilic interaction liquid chromatography; HPLC, high performance liquid chromatography; IC, interaction chromatography; LAC, liquid adsorption chromatography; LALLS, low angle laser light scattering; LC, liquid chromatography; LCCC, liquid chromatography at critical conditions; LC-LC, liquid chromatography under limiting conditions; LEAC, liquid exclusion-adsorption chromatography; MALDI-TOF-MS, matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy; MALLS, multiangle laser light scattering; MMD, molar mass distribution; NMR, nuclear magnetic resonance; NP, normal phase; PBO, polybutene oxide; PCL, polycaprolactone; PDMS, polydimethylsiloxane; PEG, polyethylene glycol; P2EHA, poly(2-ethylhexyl acrylate); PEO, polyethylene oxide; PHBV, poly(3-hydroxy butyrate-co-3-hydroxy valerate); PHO, polyhexene oxide; PI, polyisoprene; PnBMA, poly(*n*-butyl methacrylate); PMA, polymethyl acrylate; PMMA, polymethyl methacrylate; PPO, polypropylene oxide; PS, polystyrene; P2VP, poly(2-vinylpyridine); QELS, quasi elastic light scattering; RI, refractive index; RP, reversed phase; SBS, styrene-butadiene star; SEC, size exclusion chromatography; TGIC, temperature gradient interaction chromatography; THF, tetrahydrofuran; UV, ultraviolet; VISC, viscometry.

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1. Introduction

Segmented copolymers are a very important group of materials in advanced polymer science. This fascinating class of polymers found applications in every aspect of human life due to their versatility and ability to provide unique properties that result from the properties of their building blocks being combined in a single product [1–4]. In some cases, these copolymers can be used for specific properties and applications that intrinsically cannot be achieved by pure homopolymers. These include, e.g., amphiphilic copolymers that are composed of covalently bonded polymer segments that are not compatible with each other and with good solvents of the other segment [1,5]. Amphiphilic copolymers form micelles in a variety of solvents depending upon the polarity and solubility of different segments and are used for many fascinating applications such as drug delivery systems, surfactants, elastomers, compatibilizers, etc. [1–9].

There are several synthetic routes for the synthesis of segmented copolymers [2]. The development of living anionic polymerization or methods of controlled radical polymerization (CRP) has given a new vigor to both academic and industrial research of segmented copolymers. Anionic polymerization, for example, allows the sequential addition of monomers to a copolymerization system leading to controlled architectures, microstructures and narrow molar mass distributions [10,11]. The coupling of pre-synthesized functional homopolymers is another method used for segmented copolymer synthesis [2,8]. A large variety of different macromolecular architectures can also be prepared by atom transfer radical polymerization (ATRP) as has been shown by the group of Matyjaszewski [12–15].

In either case, side reactions leading to non-targeted species are inevitable. Particularly, the formation of some amounts of homopolymers of all monomers involved is very difficult to avoid if not impossible. These side products may have enormous effects on the final properties and

performance of the materials [5]. With regard to molecular topology, linear macromolecules can be formed along with branched macromolecules and, thus, the product exhibits a topology type distribution.

The varieties of polymers that can be synthesized via CRP are summarized in Fig. 1.

Segmented copolymers can be classified into linear block copolymers like diblock, triblock or linear multi-block copolymers and nonlinear block copolymers such as graft copolymers, star block copolymers or miktoarm star copolymers, etc. [12–20]. Typically, these copolymers are complex mixtures of several species namely homopolymers of almost all types of monomers involved with different functionalities and molar mass distributions along with the targeted products. The targeted products have several distributions within themselves such as total molar mass distribution, molar mass distributions of individual blocks, chemical composition distributions, tacticity type distributions, topology distributions, etc. These distributions are usually superimposed over each other. Obviously, the comprehensive analysis of all distributions is not possible by simple techniques and multidimensional characterization techniques are necessary to address the molecular heterogeneity of complex segmented copolymers.

It is pertinent to mention at this point that spectroscopic techniques like NMR, FTIR, etc., can only reveal average values of molecular properties and not the different distributions of molecular heterogeneity if applied to bulk materials. Furthermore, these techniques are often misleading and generally cannot differentiate between copolymers and mixtures of their respective homopolymers. However, these are very effective, when coupled to chromatographic separations. Liquid chromatographic techniques are the most effective and versatile choice as a first dimension in a multidimensional setup, and fractions from the first dimension can be collected and subjected to spectroscopic analyses. There are several reviews and monographs about the liquid chromatographic

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