



Editorial/Preface

Thermo-responsive block copolymers with multiple phase transition temperatures in aqueous solutions



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ABSTRACT

Stimuli-responsive block copolymers that exhibit multiple thermal transitions are an emerging topic, important for understanding thermo-sensitive self-assembling processes and furthermore, for developing interesting molecular devices. This review describes synthetic strategies for building di- and multiblock copolymers composed of several thermo-responsive segments that provide multiple transitions. The structural and compositional factors that affect the transition temperatures (upper or lower critical solution temperatures, UCST and LCST) are discussed. The aggregation behavior is highlighted through several examples of diblock and multiblock copolymers showing sequential thermal transitions.

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Abbreviations: AA, acrylamide; AAC, acrylic acid; ATRP, atom transfer radical polymerization; CA, cholic acid; CP, cloud point; CTA, chain transfer agent; dNbpy, 4,4'-dinonyl-2,2'-dipyridyl; DEA, N,N-diethylacrylamide; DEAEMA, 2-(diethylamino)ethyl methacrylate; DEGEA, ethoxydi(ethylene glycol) acrylate; DEGMA, di(ethyleneglycol) methyl ether methacrylate; DLS, dynamic light scattering; DMA, N,N-dimethylacrylamide; DMP, 2-dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid; DMSO, dimethyl sulfoxide; DP, degree of polymerization; DSC, differential scanning calorimetry; EA, N-ethylacrylamide; EEGE, ethoxyethyl glycidyl ether; EMA, N,N-ethylmethacrylamide; HEA, N-hydroxyethyl acrylamide; HMTETA, 1,1,4,7,10,10-hexamethyltriethylene-tetramine; HS-DSC, high-sensitivity differential scanning calorimetry; iBA, N-isobutylacrylamide; iBMA, N-(isobutoxymethyl)acrylamide; iPA, N-isopropylacrylamide (also known as NIPA or NIPAm); iPMA, N-isopropylmethacrylamide; I-S, insolubility-solubility transition; LCST, lower critical solution temperature; MAPTAC, 3-(methacryloylamino)propyl-trimethylammonium chloride; MDEGA, methoxydiethyleneglycol acrylate; MEO₂MA, 2-(2-methoxyethoxy)ethyl methacrylate; Me₆TREN, tris [2-(dimethylamino)ethyl]amine; M_n^{theor} , theoretical number-average molar mass; MOTAC, [2-(methacryloyloxy)ethyl]trimethyl-ammonium chloride; mPEG, methoxypoly(ethylene glycol); MVA, N-methylvinylacetamide; nBA, N-n-butylacrylamide; NMP, nitroxide-mediated polymerization; NMR, nuclear magnetic resonance spectroscopy; nPA, N-n-propylacrylamide; OEGMA, oligo(ethylene glycol) methacrylate; P4VP, poly(4-vinylpyridine); PAGE, poly(allyl glycidyl ether); P(A-Hyp-OH), poly(N-acryloyl-4-trans-hydroxy-L-proline); P(A-Pro-OMe), poly(N-acryloyl-L-proline methyl ester); PDI, polydispersity index; PDMAEMA, poly(dimethylamino)ethyl methacrylate; PEG, poly(ethylene glycol); PEOVE, poly(2-ethoxyethyl vinyl ether); PEOEOVE, poly(2-(2-ethoxy)ethoxyethyl vinyl ether); PEtOx, poly(2-ethyl-2-oxazoline); PHEMA, poly(2-hydroxyethyl methacrylate); PiPrOx, poly(2-isopropyl-2-oxazoline); PMDETA, N,N,N',N',N'-pentamethyldiethylenetriamine; PMEMA, poly(2-(N-morpholino)ethyl methacrylate); PMPC, poly(2-methacroyloxyethyl phosphoryl choline); PVCL, poly(N-vinylcaprolactam); POG(M)A, poly(oligo ethylene glycol) (meth)acrylate; PPO, poly(propylene oxide); PPropOx, poly(2-n-propyl-2-oxazoline); PTEGSt, poly(4-vinylbenzyl methoxytris-(oxyethylene) ether); RAFT, reversible addition-fragmentation chain transfer (polymerization); sBA, N-sec-butylacrylamide; S-I, solubility-insolubility transition; SLS, static light scattering; SS, styrene sulfonic acid; tBA, N-tert-butylacrylamide; T_{dem} , demixing temperature; TEGMA, methoxytri(ethylene glycol) methacrylate; T_{mix} , mixing temperature; TMS, trimethylsilyl; UCST, upper critical solution temperature; UV-vis, ultraviolet-visible light spectroscopy; VA, N-vinylacetamide; VAc, vinyl acetate; VBA, vinylbenzoic acid; VPI, vinyl pivalate.

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1. Introduction

Stimuli-sensitive or so-called “smart” polymers that are capable of undergoing a transition from hydrophilic to hydrophobic in response to an external stimulus have been investigated and reviewed extensively [1–6]. While most of the fundamental studies have focused on thermo-responsive systems with a single phase transition temperature, more complex tailored polymers with multiple transitions between soluble and insoluble states have recently been designed and studied for better understanding of the structural effects on phase transitions, necessary for developing interesting molecular devices [7,8]. Recent reviews have highlighted the advances in multi-stimuli responsive systems capable of multiple phase transitions in response to other types of stimuli, such as pH, ionic strength, light, magnetic fields, enzymatic action or redox agent [9–14], but less emphasis has been put on the emerging systems that can exhibit stepwise temperature-sensitive phase transitions. Therefore, these systems will be the focus of this review. Some of the suggested applications of stimuli-responsive materials lie in biomedical and pharmaceutical fields, such as gene or drug delivery, cell carrier systems and imaging [15–21], analytical field, such as chromatography and biosensing [22], and membrane and separation technology [23–25]. Many of these applications require controlled interactions with (bio)molecules and a precise non-linear response to the stimuli. Advanced synthetic techniques have given researchers a toolkit to design copolymers with pre-defined distributions of responsive and functional segments that could eventually fulfill such requirements.

The thermo-responsiveness of polymers may be generally described by two threshold temperatures. The polymers are soluble at all compositions above the upper

critical solution temperature (UCST) and below the lower critical solution temperature (LCST). There are considerably fewer reports on the UCST-type systems in aqueous solutions [26] than on polymers exhibiting the LCST transition. The latter type of behavior is attributed to a local structural transition involving water molecules that surround specific segments of the polymer, which depends on the delicate balance between polymer-solvent hydrogen bonding and hydrophobic and hydrophilic polymer-polymer interactions [1]. However, simply analyzing the balance of hydrophobic and hydrophilic molecular fragments does not always predict the exact LCST [27], as it is affected also by other factors, such as molar mass, polymer architecture, end groups, neighboring blocks and possible linkers in the case of block copolymers, concentration, spatial separation between the comonomers, and the presence of salts or additives [1,28,29]. The order of hydrophilic and hydrophobic segments in multiblock systems can be controlled by block copolymerization, and amphiphilic or double-hydrophilic thermo-responsive diblock copolymers exhibiting a single thermal transition have been widely studied, particularly for their self-assembling characteristics [30–34]. Di- or multiblock copolymers with at least two blocks that show well distinguishable LCSTs enable sequential changes in amphiphilicity and thus, graded temperature-controlled self-assembling behavior in aqueous solutions.

In this review, we will first present the synthetic strategies for building thermo-responsive di- and multiblock copolymers, focusing especially on the controlled syntheses of systems that consist of several thermo-responsive segments in the same polymer. We will then review the factors that influence the phase transition temperatures and how these can be used in tailoring the thermo-responsive self-assembling behavior. Finally, the

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