Progress in Polymer Science 48 (2015) 122–142

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Polymers with upper critical solution temperature behavior in alcohol/water solvent mixtures

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ARTICLE INFO

Article history:
Available online 12 March 2015

Keywords:
Thermoresponsive polymer
UCST
Ethanol/water solvent mixture
Co-solvent
Co-nonsolvent
Self-assembly

ABSTRACT

Thermoresponsive polymers are of great importance in numerous nanotechnological and biomedical applications. Compared to polymers that undergo a lower critical solution temperature (LCST) phase transition in aqueous solution, i.e., demixing occurs upon heating, polymers exhibiting the reversed upper critical solution temperature (UCST) behavior in aqueous solution have been much less documented as it is more challenging to achieve this behavior in aqueous solutions. Furthermore, the high sensitivity of UCST behavior to minor variation in polymer structure and solution composition hampered the development of applications based on these polymers [18]. However, polymers with UCST transition in alcohol/water solvent mixtures are more commonly reported and exhibit promising properties for the preparation of 'smart' materials. This review will focus on the theory and development of such polymers with UCST behavior in alcohol/water solvent mixtures. By highlighting reported examples of UCST polymers in alcohol/water solvent mixtures, we aim to demonstrate the versatility and potential that such UCST polymers possess as biomedical and 'smart' materials.

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Abbreviations: CROP, cationic ring-opening polymerization; HEMA, hydroxyethyl methacrylate; IBVE-*r*-13FVE, poly((isobutyl vinyl ether)-*r*-(2-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyloxy)ethyl vinyl ether)); LCST, lower critical solution temperature; ODVE, octadecyl vinyl ether; PAAEM, poly(acetoacetoxyethyl methacrylate); PACHE, poly(*N*-alkyl-2-cyanohex-4-enamide); PAOx, poly(2-alkyl-2-oxazoline); PBenzOx, poly(2-benzyl-2-oxazoline); PDEGMA, poly[di(ethylene glycol) methyl ether methacrylate]; PEG, poly(ethylene glycol); PEtOx, poly(2-ethyl-2-oxazoline); PFPMA, poly(pentafluorophenyl methacrylate); PiBuOx, poly(2-isobutyl-2-oxazoline); PMA, poly(methyl acrylate); PMEMA, poly(2-methoxyethyl methacrylate); PMeOx, poly(2-methyl-2-oxazoline); PMMA, poly(methyl methacrylate); PMPC, poly(2-methacryloyloxyethyl phosphorylcholine); PNIPAM, poly(*N*-isopropylacrylamide); PNonOx, poly(2-nonyl-2-oxazoline); PO3G, poly(trimethylene ether) glycol; POEGA, poly[oligo(ethylene glycol) methyl ether acrylate]; POEGAM, poly[oligo(ethylene glycol) methyl ether acrylamide]; POEGMA, poly[oligo(ethylene glycol) methyl ether methacrylate]; POEGMAM, poly[oligo(ethylene glycol) methyl ether methacrylamide]; PPhOEGA, poly(oligo(ethylene glycol) phenyl ether acrylate); PPhOx, poly(2-phenyl-2-oxazoline); PS, polystyrene; PVBA, poly[*N*-(4-vinylbenzyl)-*N*,*N*-dibutylamine]; PVE, poly(vinyl ether); PVEA, poly[*N*-(4-vinylbenzyl)-N,N-diethylamine]; SANS, small angle neutron scattering; T_{CP}, cloud point temperature; UCST, upper critical solution temperature.

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http://dx.doi.org/10.1016/j.progpolymsci.2015.02.003
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1. Introduction

Stimuli-responsive or "*smart*" polymers undergo dramatic property changes in response to small changes in the environment, such as temperature, pH, light or small molecules [1–17]. Proteins can be also regarded as smart polymers from natural systems. The primary structure of the poly(amino acid)s controls folding into 3D protein structures that have a wide range of adaptive functions ranging from, e.g., catalysis (enzymes) to switching of permeation (ion channels). Inspired by nature, polymer scientists have developed artificial stimuli-responsive polymers to mimic this behavior and, although far less sophisticated than proteins, have made exciting progress in the last decades.

Amongst the various applicable stimuli, temperature is most extensively exploited in the field of 'smart' polymers. Temperature responsive polymers, also called thermoresponsive polymers, are polymers that respond with a solution phase transition to a change in the environmental temperature [1,9,18]. Because of the sophisticated and highly reversible responsive behavior, thermoresponsive polymers have a variety of applications in, e.g., drug delivery system, smart surface modification, nanotechnology and catalysis [1–3,9,19–23]. The first reported and most studied thermoresponsive polymer is poly(*N*-isopropylacrylamide) (PNIPAM), which exhibits phase transition from a soluble state to an aggregated state at its lower critical solution temperature (LCST) [24–26]. Apart from PNIPAM, other LCST polymers like poly(oligo(ethylene glycol) (meth)acrylate)s [21,27–30], poly(2-oxazoline)s [3,31], poly(vinyl ether)s [32] or polypeptides [33,34] have also been widely studied and have various applications as smart materials. In comparison to the widely reported LCST polymers, polymers with the reverse behavior, i.e., polymers that are solubilized above the upper critical solution temperature (UCST) in aqueous solution, have been much less documented since on the one hand it is more challenging to achieve this behavior in aqueous solutions and on the other hand the UCST transition temperature is very sensitive to the environment [18]. In contrast to the commonly observed LCST behavior of polymers in water based on entropy driven dehydration, UCST behavior in water requires strong supramolecular attraction of the polymer chains. Upon heating the supramolecular interactions are weakened leading to an enthalpy driven solubility phase transition, i.e., solubilization of the polymer chains. The main types of reported polymers with UCST behavior in water are zwitterionic polymers [35,36], polymers with strong intermolecular hydrogen bonding [37] and polymer solutions with supramolecular crosslinking additives [38–41]. For most of these systems, the UCST behavior is very sensitive to, e.g., (co)polymer composition, electrolytes or concentration, which greatly limits broad application of these polymers [18]. As an alternative, UCST polymers in organic solvents or in water-organic binary solvent mixtures have shown attractive properties [42–47].

Ethanol/water solvent mixtures are environmentally friendly solvents that exhibit interesting abnormal properties due to the presence of hydration shells around the ethanol molecules [48–50]. For example, the presence of such hydration shells has been reported to result in solubility maxima for drug molecules in ethanol/water mixtures with certain ratios [51,52]. Benefiting from the non-ideal solvent mixture and its large change in polarity with varying temperatures, thermoresponsive polymers with UCST behavior have been developed for which the transition temperature depends on the structure of the alcohol and the composition of the alcohol/water binary solvent. Such UCST systems with low toxicity solvents have promising potential for, *e.g.*, personal care, medical or pharmaceutical applications. In addition, the responsive behavior of such polymers could be well controlled by solvent composition, which allows tuning of the self-assembly of copolymers bearing such UCST polymer block(s) [53,54]. Nonetheless, surprisingly few publications have appeared in recent years concerning UCST behavior of polymers in alcohol/water solvent mixtures, especially compared to the large amount of publications regarding LCST polymers. Two reasons may be ascribed to the low activity of this field: (i) the importance of such ternary systems has been underestimated and overlooked; and (ii) the alcohol–water–polymer ternary systems are very complicated and not well understood. Hence, this review aims at highlighting the recent progress in this area and to discuss the fundamentals of such UCST

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