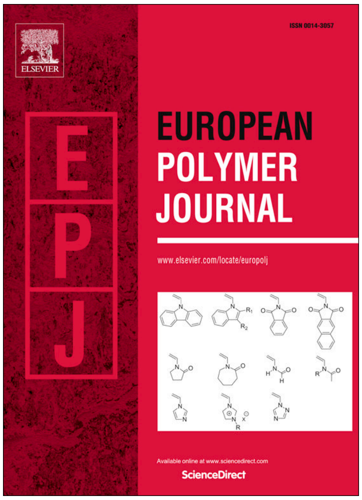

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PII: S0014-3057(17)32110-9
DOI: https://doi.org/10.1016/j.eurpolymj.2018.01.019
Reference: EPJ 8252

To appear in: *European Polymer Journal*

Received Date: 28 November 2017
Revised Date: 19 January 2018
Accepted Date: 21 January 2018

Please cite this article as: Konefał, R., Spěváček, J., Černoch, P., Thermoresponsive poly(2-oxazoline) homopolymers and copolymers in aqueous solutions studied by NMR spectroscopy and dynamic light scattering, *European Polymer Journal* (2018), doi: https://doi.org/10.1016/j.eurpolymj.2018.01.019

Thermoresponsive poly(2-oxazoline) homopolymers and copolymers in aqueous solutions studied by NMR spectroscopy and dynamic light scattering

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ABSTRACT

Structural changes during temperature-induced phase transition in D_2O solutions of poly(2-ethyl-2-oxazoline) (PEOx) and P(EOx-*grad*-2-methyl-2-oxazoline (MOx)) copolymers were investigated by ^1H NMR methods in combination with dynamic light scattering. NMR spectra showed that in PEOx solutions on molecular level structures formed during gradual heating are preserved during subsequent cooling. Phase transition in solutions of P(EOx-*grad*-MOx) copolymers as revealed by NMR exists irrespective the solution is turbid or nonturbid at higher temperatures. In contrast to PEOx homopolymers it is very broad, virtually independent of the copolymer composition and molecular weight, and reversible with some hysteresis. Reduced intensities of cross-peaks in NOESY spectra of copolymer solutions at elevated temperatures are mainly due to the changed mobility of copolymer segments. In all investigated solutions two types of water, „free“ and „bound“ with long and very short spin-spin relaxation times T_2, respectively, were detected in the transition region and above the transition. The existence of two T_2 components shows that exchange between „bound“ and „free“ water is slow regarding T_2 values.

Keywords:
Thermoresponsive polymer; poly(2-ethyl-2-oxazoline); poly(2-ethyl-oxazoline-*grad*-2-methyl-2-oxazoline) copolymer; aqueous solution; NMR; dynamic light scattering

1. Introduction

In recent years, smart polymers are one of the most exciting and intensively studied class of materials. They are able to change their properties by response to external stimuli such as changes in temperature, pH, ionic strength and light irradiation [1–4]. From this group, systems based on thermoresponsive polymers are widely investigated due to variety of prospective applications such as drug delivery, tissue engineering, bioseparation, thermoresponsive films, oil-gas industry and nanoreactors [5–11]. Most of the studies focus on polymers that show phase separation in water above the lower critical solution temperature (LCST). The best known and most widely studied polymer from this group is poly(*N*-isopropylacrylamide) (PNIPAm) with LCST around 305 K [12,13]. However, nowadays due to their biocompatibility and possible applications, poly(*2*-oxazoline)s (POx)s are receiving considerable attention [14,15]. Side chain of POx controls hydrophilicity of the polymer: poly(2-methyl-2-oxazoline) (PMOx) is hydrophilic and thus well soluble in water, poly(2-ethyl-2-oxazoline) (PEOx) and poly(2-propyl-2-oxazoline)s exhibit thermoresponsive LCST behavior in aqueous solutions where the respective LCST depends on molecular weight of polymer chains, while polymers with longer side chains are insoluble in water [16–23].