ARTICLE IN PRESS

European Polymer Journal xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

European Polymer Journal

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

Dual stimuli-responsive homopolymers: Thermo- and photo-responsive properties of coumarin-containing polymers in organic solvents

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ARTICLE INFO

Article history:
Received 30 November 2014
Received in revised form 11 May 2015
Accepted 11 May 2015
Available online xxxx

Keywords:
Dual stimuli-responsive polymer
Lower critical solution temperature
[2 + 2] cycloaddition
Coumarin derivatives

ABSTRACT

Thermoresponsive properties of poly(7-methacryloyloxycoumarin) (**P1a**) and its derivatives as homopolymers containing a photoreactive coumarin unit were systematically investigated. **P1a** showed a lower critical solution temperature (LCST)-type phase separation in dichloromethane, chloroform, and 1,1,2-trichloroethane. The temperature producing a 50% transmittance (T_c) of 0.1 wt% **P1a** in distilled chloroform was 26 °C, while the T_c value decreased to 21 °C in deuterated chloroform i.e., the deuterium isotope effect. The T_c values in chloroform were adjustable from 28 to 57 °C by the introduction of the ethyleneoxy spacer and the substitution of α-methyl group by hydrogen. While the polymers containing 4-substituted coumarins were soluble in chloroform and dichloromethane from 0 °C to their boiling points. In the distilled chloroform solution, the coumarin units in **P1a** underwent a [2 + 2] cycloaddition and the transmittance at 500 nm decreased from 98% to 29% at 25 °C by a 180-s photoirradiation (326 mJ/cm^2, emission band at 365 nm).

1. Introduction

Stimuli responsive polymers have gained fundamental and practical interests and various types of stimuli including temperature, light, pH, pressure, and magnetic and electric fields are available as external stimuli [1,2]. Multistimuli responsive polymers are recently attracting much attention because of the variation in property control [3–6]. As an example of the dual stimuli responsive polymers by temperature and light, the random copolymers of *N*-isopropylacrylamide and acrylamide derivatives containing the azobenzene unit were reported and the lower critical solution temperature (LCST) was controlled by the photoisomerization of the azobenzene units [7]. Théato et al. reported thermo- and light-responsive micellations using the block copolymers consisting of thermoresponsive and photoresponsive segments [8]. Multistimuli responsive polymers for the other combinations of stimuli were also reported, for instance, the temperature and salt responsive films [4], the selective radio-frequency actuations of composite films [5], and the triple stimuli, i.e., temperature, pH, and light, responsive polymers [6]. These multistimuli responsive polymers consist of more than two monomer units, each of which is responsive to different stimuli. There are some examples of the homopolymers response to multistimuli. The main-chain functional polymers consist of dibenzo-18-crown-6-ether units joined by azo-bridges and azocalix[4]arenes

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http://dx.doi.org/10.1016/j.eurpolymj.2015.05.010
0014-3057/

showed thermoresponsive properties tunable by *cis*-to-*trans* isomerization of the azobenzene moieties [9,10]. The UCST behavior of poly(*N*,*N*-dimethylaminoethyl methacrylate) was controlled by pH and light in the presence of photoreactive trivalent counterions [11]. Although these are the examples of multistimuli responsive homopolymers, the system consists of more than two functionalities each of which is responsive to individual stimuli. There are not a number of "absolute" multistimuli responsive homopolymers where the single functional group is responsive to more than two stimuli and such multistimuli responsive homopolymers are fascinating platforms as functional polymers because the multistimuli responsive units can be densely introduced without statistical distribution that will allow a sharp and sensitive response. The direct tuning of one stimuli responsive property by applying the other stimuli will also enable a highly sensitive stimuli response.

Coumarin derivatives undergo a [2 + 2] cycloaddition and the reverse reaction by irradiation of different wavelengths of light (Scheme 1). When the coumarin derivative units are introduced in the polymers, branching and cross-linking structures are formed by cycloaddition, and the cleavage of the branching and cross-linking points take place by the reverse reaction. Taking advantage of the reversible cross-linking, the polymers containing the coumarin derivative units have been applied to a variety of functional materials such as a reversible cluster formation [12], photoinduced bendable actuator [13], and two-photon optical memory [14]. We have recently reported that the film thickness of the coumarin-containing polymers in the side-chain can be reversibly controlled by photoinduced cross-linking and the reverse reaction [15]. During the course of our investigation, we discovered that poly(7-methacryloyloxycoumarin) (**P1a**) exhibited a thermoresponsive behavior in chloroform around room temperature.

The Gibbs energy change upon mixing (ΔG_{mix}) is determined by the enthalpy change (ΔH_{mix}) and entropy change (ΔS_{mix}) based on $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$, and the LCST-type phase separation occurs at a temperature where the ΔG_{mix} value changes from negative to positive. To produce a positive ΔG_{mix}, the contribution of $T\Delta S_{mix}$ on ΔG_{mix} is required to be greater than that of ΔH_{mix}, and such conditions are achieved in the presence of an ordered structure among the solvent and polymer molecules. Thermoresponsive polymers showing an LCST-type phase separation in water are well known and the polymers, such as poly(*N*-isopropylacrylamide) (PNIPAM) [16], polyethylene glycol, poly(2-oxazoline)s [17], poly(*N*-vinyl caprolactam) [18], and their derivatives including random and block copolymers, gels, and polymer brushes, have been theoretically and practically investigated [19,20]. As an example of polymers showing an LCST-type phase separation in solvents other than water, Watanabe et al. carried out comprehensive studies of thermoresponsive polymers in an ionic liquid [21]. On the other hand, there are only limited examples and unsystematic information of the polymers showing a LSCT in organic media under mild conditions, for example, the alternative copolymer of 2-chloroethyl vinyl ether and maleic anhydride [22], fluoroalkyl-end-capped 2-acrylamido-2-methylpropanesulfonic acid cooligomers containing adamantly segments [23], poly(vinyl ether)s with pendant salts [24], and urea-modified acrylate polymers with interactive low molecular weight compounds [25].

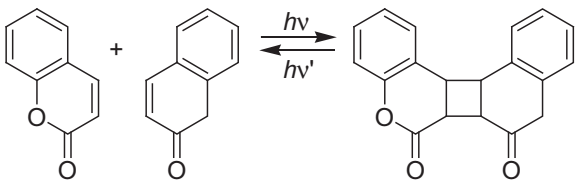
In this study, the thermoresponsive behavior of (meth)acrylic homopolymers containing the coumarin derivative units in organic solvents was systematically investigated to clarify the fundamental aspects. The effects of the polymer structure on the thermoresponsive behavior were explored by introducing the methyl, phenyl, and ethoxycarbonyl groups at the 4-position of the coumarin ring and the ethyleneoxy spacer in the side-chain. The controls of the thermoresponsive properties and the transmittance of the polymer solution by photoreaction were investigated in view of the application to the dual-stimuli responsive functional materials. To the best of our knowledge, this system is the first example of a thermoresponsive homopolymer displaying a photoreactivity.

2. Experimental

2.1. Materials

Coumarin-containing methacrylates and acrylates were synthesized according to a previous report [15]. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Chloroform (>99.7% (except for ethanol) containing 0.5–0.9% ethanol, Wako Pure Chemicals Co., Ltd.) and deuterated chloroform (99.8 atom% D, Across Organics) were used as received. The chloroform was distilled under atmospheric pressure. All other reagents and solvents were used without further purification or purified according to conventional methods.

A typical polymerization procedure was as follows. In a Pyrex glass tube, the mixture of 7-methacryloyloxycoumarin (**1a**, 0.60 g, 2.31×10^{-3} mol), AIBN (2.5 mg, 1.5×10^{-5} mol), and *N*,*N*-dimethylformamide (DMF) (5 mL) was placed and sealed



Scheme 1.

Please cite this article in press as: E. Sato et al., Dual stimuli-responsive homopolymers: Thermo- and photo-responsive properties of coumarin-containing polymers in organic solvents, Eur. Polym. J. (2015), http://dx.doi.org/10.1016/j.eurpolymj.2015.05.010