Dual Stimuli-Responsive Homopolymers : Thermo-and Photo-responsive Properties of Coumarin-Containing Polymers in Organic Solvents

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Dual Stimuli-Responsive Homopolymers: Thermo- and Photo-responsive Properties of Coumarin-Containing Polymers in Organic Solvents

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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 α-methyl group to **P1a**. 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-sec photoirradiation (326 mJ/cm^2, emission band at 365 nm).

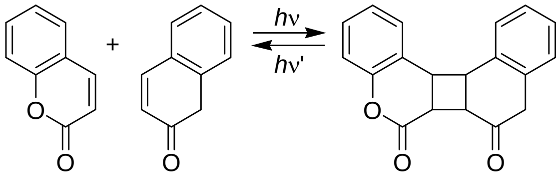
Key Words

dual stimuli-responsive polymer, lower critical solution temperature, [2+2] cycloaddition, coumarin derivatives

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 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 consist 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.



Scheme 1

The Gibbs energy change upon mixing (ΔG_{mix}) is determined by the enthalpy change (ΔH_{mix}) and entropy change (ΔS_{mix}) based on $\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$, 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 $T\Delta S_{\mathrm{mix}}$ 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.

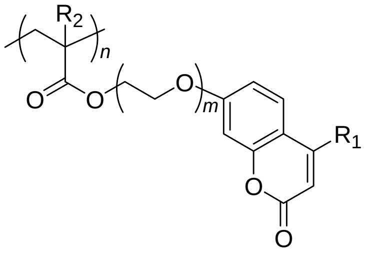
2. Experimental

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 under vacuum after three freeze-thaw cycles. The polymerization was carried out at 60 °C for 24 h, then quenched by cooling to -78 °C. The reaction mixture was poured into a 20-fold volume of methanol to isolate the polymer. The isolated polymer was purified by three times reprecipitation in methanol and was dried under vacuum for 24 h at room temperature.

The conversion of **1a** was 74 % and the M_n and M_w/M_n values were 1.4×10^4 and 1.16, respectively. The other coumarin-containing homopolymers were similarly synthesized and their structures and characteristics are shown in Scheme 2 and Table 5.



P1a R_1 = H, R_2 = Me, m = 0
P1b R_1 = H, R_2 = Me, m = 1
P1c R_1 = H, R_2 = H, m = 0
P1d R_1 = H, R_2 = H, m = 1
P2a R_1 = Me, R_2 = Me, m = 0
P2b R_1 = Me, R_2 = Me, m = 1
P2c R_1 = Me, R_2 = H, m = 0
P2d R_1 = Me, R_2 = H, m = 1
P3a R_1 = Ph, R_2 = H, m = 0
P4a R_1 = CO_2Et, R_2 = Me, m = 0

Scheme 2

2.2. Measurements

The NMR spectra were recorded by a Bruker AN300N spectrometer. The number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system at 40 °C or with chloroform as the eluent using a JAI GPC-908 at 19 °C, after calibration with standard polystyrenes. The thermogravimetric and differential thermal analyses (TG/DTA) were performed using a Seiko EXSTAR6000 at the heating rate of 10 °C/min in a nitrogen stream at the flow rate of 30 mL/min. The differential scanning calorimetric (DSC) analysis was performed using a Seiko EXSTAR6000 at the heating rate of 10 °C/min. Transmittance at 500 nm was recorded as a function of temperature using a Shimadzu UV-2400 UV/Vis spectrometer with an S-1700 temperature controller. The polymer solutions were held at a given temperature for 13 min before measurement except for Figure 8(b). In Figure 8(b), the polymer solutions were heated at 0.2 °C/min and the transmittance was measured immediately after reaching a given temperature. The temperature at 50% transmittance was defined as T_c.

Photoreaction was carried out under atmospheric conditions by light irradiation from an ultrahigh pressure mercury lamp (Moritex MSU-6, 250 W) with a strong emission at 365 nm passing through a Pyrex glass filter to cut $\lambda < 290$ nm. The polymer solution in a quartz cell was placed 20 cm from the light source. The light intensity of 1.81 mW/cm^2 was measured by a UV power meter (USHIO, UIT-101) equipped with a UVD-365PD optical receiver (330-390 nm). The progress of the [2+2] cycloaddition was monitored by a Shimadzu UV-2400 UV/Vis spectrometer and the degree of cycloaddition was evaluated by the relative absorbance at λ_{max} before and after the photoirradiation.

3. Results and discussion

3.1. Thermoresponsive Properties of **P1a** in Various Organic Solvents

The thermoresponsive properties of **P1a** in various organic solvents were investigated. Based on the fact that **P1a** showed an LCST-type phase separation in chloroform as mentioned in the Introduction, the series of chlorinated methanes and ethanes which are liquid at room temperature were first examined, and the

Table 1. Phase Separation and Solubility Characteristics of 0.3 wt% **P1a** in Chlorinated Methanes and Ethanes with Solvent Properties

Solvent	b.p. (°C)	δ[45]	Dielectric constant	Dipole moment (Debye)	AN	Characteristics[a]
dichloromethane	40	18.9	8.9[40]	1.5[40]	20.4[40]	LCST
chloroform	61	17.9	4.7[40]	1.1[40]	23.1[40]	LCST
tetrachloromethane	77	17.8	2.2[40]	0[40]	8.6[40]	insoluble
1,1-dichloroethane	57	18.0	9.90[41]	1.83[41]	-[b]	insoluble
1,2-dichloroethane	84	20.3	10.1[40]	1.75[40]	16.7[40]	insoluble
1,1,1-trichloroethane	74	17.3	7.33[36]	1.70[36]	-[b]	insoluble
1,1,2-trichloroethane	114	20.7	7.28[36]	1.55[36]	-[b]	LCST
1,1,1,2-tetrachloroethane	131	19.9	-[b]	-[b]	-[b]	insoluble
1,1,2,2-tetrachloroethane	146	21.1	8.42[36]	1.71[36]	-[b]	soluble
1,1,1,2,2-pentachloroethane	159	20.3	3.90[36]	0.94[36]	-[b]	insoluble
trichloroethylene	87	19.9	3.30[36]	0.80[36]	-[b]	insoluble

[a] Phase separation and solubility characteristics observed from 0 °C to the boiling point of the solvents.

[b] No data.

phase separation and solubility characteristics are summarized in Table 1 together with the solvent properties, i.e., Hansen solubility parameter (δ), dielectric constant, dipole moment, and acceptor number (AN). **P1a** was insoluble in most of the chlorinated methanes and ethanes including trichloroethylene and exhibited an LCST-type phase separation in dichloromethane and 1,1,2-trichloroethane in addition to chloroform. **P1a** was soluble only in 1,1,2,2-tetrachloroethane up to the boiling point. The δ values for the chlorinated methanes and ethanes were very similar and no specific relationship with the solubility characteristics was found. **P1a** seems to show an LCST-type phase separation in the chlorinated organic solvents having both moderate dielectric constant, i.e., 4.5 to 9.0, and dipole moment, i.e., 1.1 to 1.6 although determinate relationship between the solubility characteristics and these values was not found.

P1a was soluble in fluorinated alcohols, i.e., 2,2,2-trifluoroethanol, 2,2,2,2’,2’,2’-hexafluoroisopropanol, and 2,2,3,3-tetrafluoro-1-propanol (Table 2). **P1a** was insoluble in the aliphatic alcohols such as methanol and ethanol, and conventional good solvents such as acetone, toluene, and tetrahydrofuran.

Table 2. Phase Separation and Solubility Characteristics of 0.3 wt% **P1a** in Fluorinated Alcohols

Solvent	b.p. (°C)	δ[45]	Dielectric constant	AN	Characteristic[a]
2,2,2-trifluoroethanol	74	24.0	26.7[43]	53.3[42]	soluble
2,2,2,2',2',2'-hexafluoroisopropanol	58	23.1	16.6[43]	61.6[42]	soluble
2,2,3,3-tetrafluoro-1-propanol	109	-[b]	-[b]	-[b]	soluble

[a]Phase separation and solubility characteristics observed from 0 °C to the boiling point of the solvents. [b]No data.

Table 3. Phase Separation and Solubility Characteristics of 0.3 wt% **P1a** in Organic Solvents

Solvent	b.p. (°C)	δ[45]	Dielectric constant	Dipole moment (Debye)	AN	Characteristic[a]
ethylenediamine	117	25.4	12.9[44]	1.89[44]	20.9[44]	insoluble
acetonitrile	80	24.4	36.0[40]	3.44[40]	18.9[40]	insoluble
dimethyl sulfoxide	189	26.7	46.7[40]	3.90[40]	19.3[40]	soluble
DMF	153	24.9	36.7[40]	3.86[40]	16.0[40]	soluble
nitromethane	101	25.1	36.7[40]	3.57[40]	20.5[40]	insoluble

[a]Phase separation and solubility characteristics observed from 0 °C to the boiling point of the solvents.

The AN value is a criterion showing the Lewis acidity of a solvent. The AN values of dichloromethane (AN = 23.1) and chloroform (AN = 20.4) in which **P1a** exhibited an LCST-type phase separation were higher than those of the non-solvents, tetrachloromethane (AN = 8.2) and 1,2-dichloroethane (AN = 16.7), but lower than those of the good solvents, 2,2,2-trifluoroethanol (AN = 53.3) and 2,2,2,2',2',2'-hexafluoroisopropanol (AN = 61.6). With the expectation of finding other LCST solvents, the solvents having AN values ranging from 16 to 21 were examined (Table 3). However, **P1a** was soluble or insoluble in these solvents and no specific relationship between the solubility and the other solvent properties was found. An LCST-type phase separation of **P1a** is specifically observed in some chlorinated organic solvents.

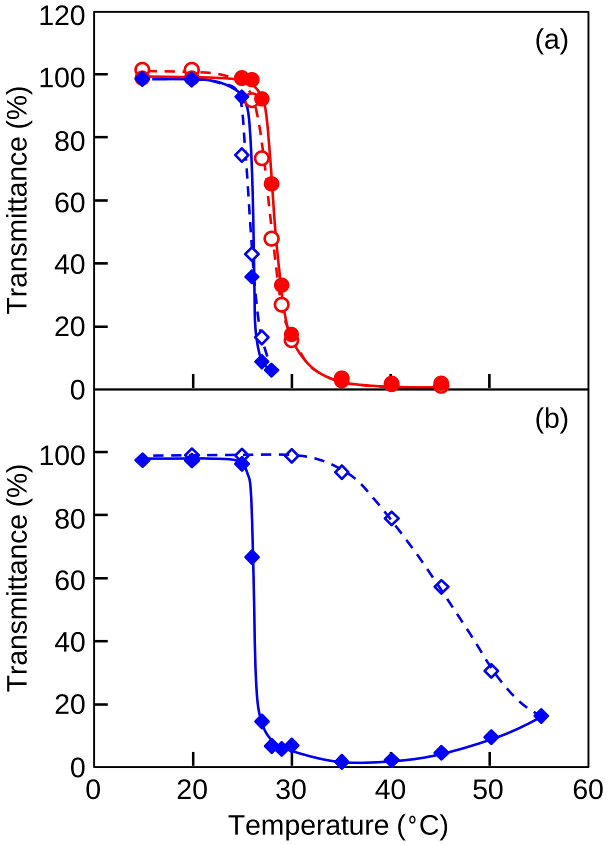


Figure 1. Temperature dependence of transmittance at 500 nm for the **P1a** solutions in chloroform during the heating (closed symbol) and cooling (open symbol) processes: (a) 0.1 wt% **P1a** between 20 to 45 °C (red circle) and 0.3 wt% **P1a** between 20 to 28 °C (blue diamond) and (b) 0.3 wt% **P1a** between 20 to 55 °C. Solid and dashed lines were drawn as visual guides for the heating and cooling process, respectively.

The thermoresponsive property of **P1a** in chloroform was investigated in detail by monitoring the transmittance at 500 nm during the heating and cooling process (Figure 1(a)). The chloroform solutions of **P1a** showed an LCST-type phase separation with a steep reduction in the transmittance, and the T_c values were 28 and 26 °C for the 0.1 and 0.3 wt% solutions, respectively (Table 4). The decreases in T_c with the increasing polymer concentration were reported for the other polymers in water, an ionic liquid, and organic solvents.[16, 24, 26, 27] The 0.3 wt% chloroform solution exhibited a different temperature-hysteresis of transmittance depending on the heating process. As shown in Figure 1(a), when the 0.3 wt% solution was cooled after heating to 28 °C, in which the transmittance sufficiently decreased, no temperature-hysteresis was observed. In contrast, when the 0.3 wt% solution was heated to 55 °C, the transmittance started to slightly increase above 35 °C and showed a significant temperature-hysteresis during the cooling process (Figure 1(b)). Cheng et al. reported that in the case of PNIPAM in water, the formation of additional hydrogen bonding between the C=O and H-N groups above the LCST resulted in a physical crosslinking which caused the further aggregation of PNIPAM into a globule state and the dissociation delay during the cooling processes, i.e., a temperature-hysteresis.[28] A similar aggregation due to the π-π and/or aromatic-CH/π interactions among the coumarin moieties can be expected for the 0.3 wt% **P1a** chloroform solution above the LCST. The apparent increase in the transmittance above 35 °C and the cooling process seems to be attributed to the sedimentation of the large aggregates and/or the dependence of the forward-scattered intensity on the aggregates size. Taking into account the fact that chloroform contains 0.5-0.9 % ethanol as a stabilizer, distilled chloroform was also examined. **P1a** exhibited the LCST-type phase separation in distilled chloroform and the T_c value of the 0.1 wt% **P1a** solution decreased to 26 °C with the temperature-hysteresis as observed in the 0.3 wt% **P1a** solution in chloroform containing ethanol (Figure 2, Table 4 and Supplementary Material). It seems that the existence of a small amount of ethanol somehow increased the interaction between **P1a** and the solvent, although **P1a** is insoluble in ethanol as already described. This observation may relate to the free volume theory[29] and the increased dielectric constant by the presence of a small amount of ethanol, although further details have not been investigated.

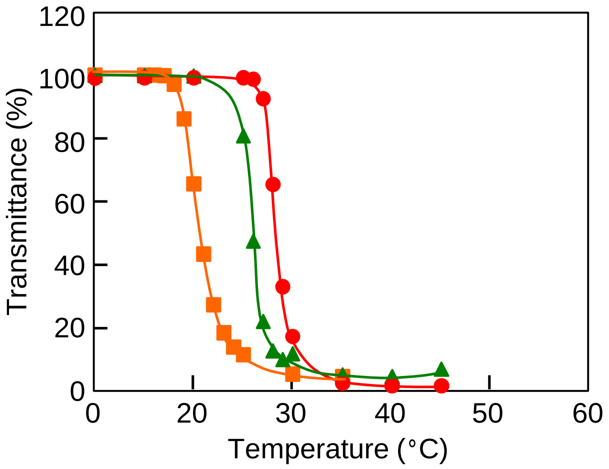


Figure 2. Temperature dependence of transmittance at 500 nm for the 0.1 wt% **P1a** in chloroform (●), distilled chloroform (▲), and deuterated chloroform (■) during the heating process. Solid lines were drawn as visual guides.

The deuterium isotope effect was investigated and the T_c value of the 0.1 wt% **P1a** solution in deuterated chloroform was 21 °C which was 5 °C lower than that in the distilled chloroform (Figure 2 and Table 4). As described later, **P1b** also showed an LCST-type phase separation and the T_c value in deuterated chloroform was 12 °C lower than that in chloroform containing ethanol (Supplementary Material). In the case of PNIPAM and PNIPAM gels, the phase transition in heavy water was reported to be 1-2 °C higher than that in water.[30-32] The deuterium isotope effect for PNIPAM was attributed to the difference in the chain dimension[32] and enthalpy of the polymer-solvent interaction.[31] Previously, it was reported that poly[*N*-(4-vinylbenzyl)-*N*,*N*-diethylamine] resulted in a lower T_c value in deuterated methanol than that in methanol by more than 16 °C, although the reason was not clear.[33] The deuterium isotope effect was also reported for the UCST-type phase separation of polystyrene in cyclohexane and the critical temperature was 3-5 °C higher in deuterated cyclohexane.[34] Considering the reported deuterium isotope effects, the changes in T_c observed for **P1a** and **P1b** are high, although the origin is not clear.

Table 4. Characteristics of **P1a** Solutions

Solvent	concentration (wt%)	temperature range (°C)	T_c (°C)	reversibility of transmittance
chloroform	0.1	20-45	28	reversible[a]
	0.3	20-28	26	reversible[a]
	0.3	20-55	26	temperature-hysteresis[b]
distilled chloroform	0.1	20-45	26	temperature-hysteresis[b]
deuterated chloroform	0.1	10-35	21	temperature-hysteresis[b]

[a] Transmittance was reversibly changed during the heating and cooling process. [b] Transmittance showed a temperature-hysteresis during the heating and cooling process.

3.2. Structural Effects of Coumarin-Containing Homopolymers on Thermoresponsive Properties

The effects of the structural variation of the coumarin-containing homopolymers on the thermoresponsive properties were investigated by introducing an ethyleneoxy spacer (n = 1) and changing the substituents R_1 and R_2 (Scheme 2 and Table 5). When R_1 = H, i.e., **P1b**, **P1c**, and **P1d**, an LCST-type phase separation was observed in chloroform (Table 5 and Figure 3). In the case of **P1c**, the polymer was partly insoluble in chloroform, thus the soluble part was isolated, then subjected to the transmittance measurement. Although the M_n values ranged from 8,900 to 20,200 and a precise comparison cannot be made, the introduction of the ethyleneoxy spacer obviously increased the T_c values, that is, the T_c values for **P1b** and **P1d** were higher than those for **P1a** and **P1c**. The apparent inverse trend was reported for the poly(phenylalkyl methacrylate)s in the ionic liquids that the T_c values decreased with the increasing chain length of the alkyl spacer.[35] The result was rationalized by the fact that the hydrophobic alkyl groups were solvophobic groups in the ionic liquids and decreased the compatibility of the polymers in the ionic liquids, i.e., resulting in decreased T_c. In our case, the flexible ethyleneoxy spacer was expected to be a solvophilic group and increased the T_c values. No difference was observed in the T_c values for **P1a** and **P1c**. However, they showed a much different temperature-hysteresis, and the large temperature-hysteresis of **P1c** is probably due to the formation of aggregates (Figure 3). In dichloromethane, only the 0.3 wt% **P1a** showed an LCST-type phase separation near the boiling point. **P1b** and **P1d** were soluble, while **P1c** was insoluble up to the boiling point of dichloromethane. Considering the characteristics of the **P1**s in chloroform, i.e., the lowest T_c for **P1a** and partial insoluble nature of **P1c**, the results in dichloromethane are understandable.

Table 5. Phase Separation and Solubility Characteristics of 0.3 wt% Coumarin-Containing Homopolymers in Chloroform and Dichloromethane

Polymer	R_1	R_2	m	M_n (M_w/M_n)	T_g (°C)	Characteristics[a]	
						chloroform	dichloromethane
P1a	H	Me	0	14,400 (1.16)[b]	171	LCST, 26 (LCST, 28)	LCST (soluble)
P1b	H	Me	1	20,200 (1.67)[b]	103	LCST (LCST, 37)	soluble
P1c	H	H	0	-[c]	142	LCST (LCST, 28)[d]	insoluble
P1d	H	H	1	8,900 (1.29)[b]	88	LCST (LCST, 57)	soluble
P2a	Me	Me	0	38,900 (2.12)[b]	191	soluble	soluble
P2b	Me	Me	1	-[c]	119	soluble	soluble
P2c	Me	H	0	11,000 (1.50)[b]	131	soluble	soluble
P2d	Me	H	1	7,400 (1.70)[b]	89	soluble	soluble
P3a	Ph	H	0	10,500 (1.83)[e]	128	soluble	soluble
P4a	CO_2Et	Me	0	64,900 (2.10)[e]	81	soluble	soluble

[a] Phase separation and solubility characteristics observed from 0 °C to the boiling point of the solvents and the numerical values indicate the T_c. Characteristics in parenthesss were observed for the 0.1 wt%

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solution. [b]Determined by GPC using chloroform as the eluent. [c]Not determined. [d]The soluble part of **P1c** in chloroform was separated and subjected to a transmittance measurement. [e]Determined by GPC using tetrahydrofuran as the eluent.

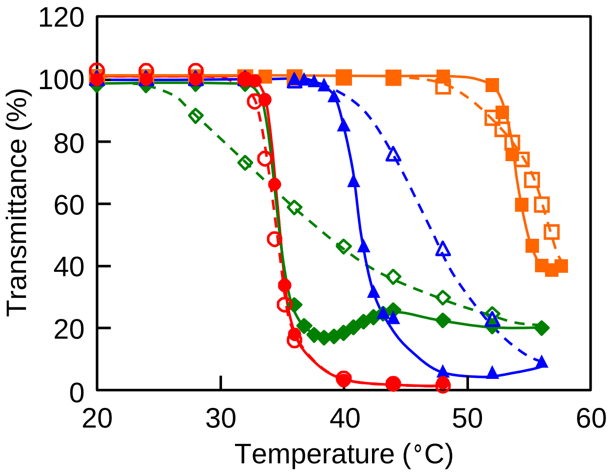

Figure 3. Temperature dependence of transmittance at 500 nm for 0.1 wt% of **P1a** (circle), **P1b** (triangle), **P1c** (diamond), and **P1d** (square) solutions of chloroform containing ethanol as a stabilizer during the heating (closed symbol) and cooling (open symbol) processes. The solid and dashed lines were drawn as visual guides for the heating and cooling process, respectively.

With the expectation that the introduction of electron-donating and electron-withdrawing substituents to the coumarin ring changes the π-electron density and then the extent of the interaction with the solvent molecules, methyl, phenyl, and ethoxycarbonyl groups were introduced into the 4-position of the coumarin ring, i.e., the substituent R_1, and the thermoresponsive properties were investigated (Table 5). However, regardless of the electron-donating and electron-withdrawing properties of R_1, all the polymers, **P2**s, **P3a**, and **P4a**, were soluble in chloroform and dichloromethane from 0 °C to the boiling point of the solvents. This suggested that the introduction of substituents at the 4-position prevents the solvophobic interactions of the polymers, such as the aromatic-CH/π and π/π interactions between the coumarin moieties, and increases the compatibility of the polymers with the solvents.

3.3. ^{1}H NMR Analysis of **P1b** in Deuterated Chloroform

The ^{1}H NMR spectra of the 1.0 wt% **P1b** in deuterated chloroform were recorded at -30 to 55 °C and the representative two spectra obtained at 0 and 45 °C are shown in Figure 4 together with the peak assignments. The solution was transparent at 0 °C, i.e., below the LCST, and the relative peak intensities were in good agreement with the theoretical values based on the number of protons of **P1b**. At 45 °C, the solution became turbid and the peak intensities relative to that of DMF at around 8 ppm as the internal standard become lower than those at 0 °C. The relative peak intensities to DMF at the respective temperatures were normalized by the relative intensity of peak *a* at 0 °C and are shown in Figure 5. Each peak intensity was almost constant and in agreement with the theoretical number of protons up to 20 °C, but started to decrease above 20 °C showing that the insolubilization of **P1b** occurred above 20 °C. The relative peak intensities above 20 °C did not drop to zero indicating that **P1b** is partly soluble even above the LCST.

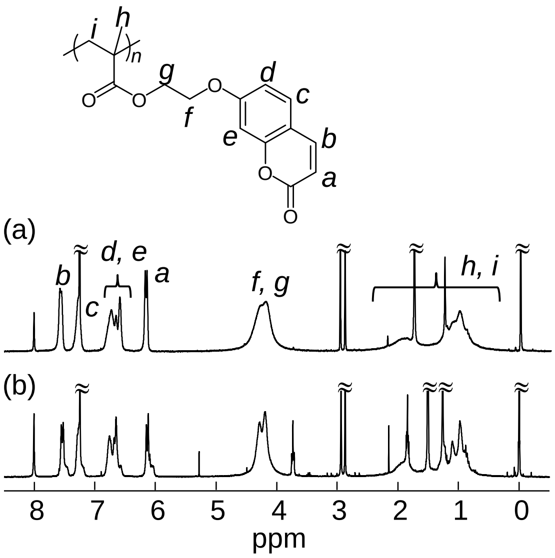

Figure 4. ^{1}H NMR spectra of the 1.0 wt% solution of **P1b** in $CDCl_3$ with DMF as the internal standard recorded at (a) 0 and (b) 45 °C.

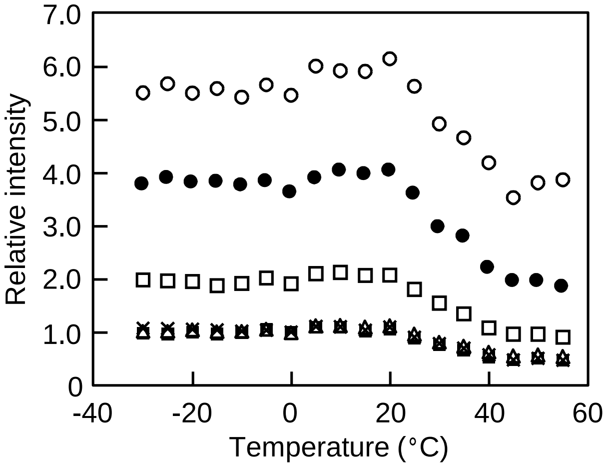

Figure 5. ^{1}H NMR peak intensities of **P1b** relative to that of the H-C=O group in DMF normalized by the relative intensity of peak *a* at 0 °C: *a* (×), *b* (■), *c* (△), *d* and *e* (□), *f* and *g* (●), and *h* and *i* (○) in Figure 4.

In the ^{1}H NMR spectrum observed at 45 °C, new peaks appeared at a slightly higher magnetic field for the aromatic protons, i.e., peaks *a*, *b*, *c*, *d*, and *e* (Figure 4(b)). The new peaks were observed above 35 °C and the extent of the peak shift to the higher magnetic field increased with the increasing temperature (Figure 6). The relative peak intensities of the aromatic protons with and without the new peaks at a higher magnetic field are plotted in Figure 7. It is obvious that the contribution of the peaks at the higher magnetic field increased with the increasing temperature. The high-field shift of the aromatic protons is attributed to an increase in the electron density of the coumarin ring and two phenomena are expected. One is the collapse of the electron-donating interaction of the coumarin ring and the other is the formation of the electron-accepting interaction of the coumarin ring. Tsuzuki et al. reported that the C-H bond in the chlorinated methanes such as chloroform and dichloromethane, was activated compared to that in methane due to the significant contribution of the dispersion energy and thus benzene and the chlorinated methanes result in the high attraction, i.e., strong CH/π interaction.[36] Based on the ^{1}H NMR observation, it is suggested that the CH/π interaction between chloroform and the coumarin ring is formed below 35 °C and starts to be collapsed together with the formation of the π/π interaction of the coumarin ring with increasing temperature. In the other words, the intermolecular interaction between the solvent and polymer changes to the intramolecular interaction between polymers with increasing temperature. When the concentration of free coumarin in deuterated chloroform increased from 1 to 40 wt%, such marked high-field shift as seen in Figure 6 was not observed, and therefore it is indicated that the π/π interaction of the coumarin units has a minor contribution to the high-field sift observed for **P1b** and/or the significant π/π interaction is specific for the coumarin unit in polymers.

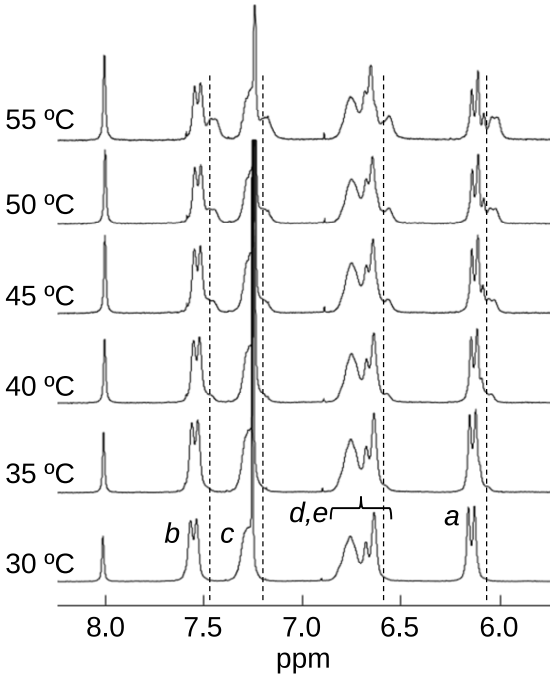

Figure 6. The magnified ^{1}H NMR spectra of the 1wt% **P1b** in $CDCl_3$ with DMF as the internal standard recorded every 5 °C from 30 to 55 °C. The dashed lines were drawn as visual guides to identify the peak shift of the newly appeared peaks.

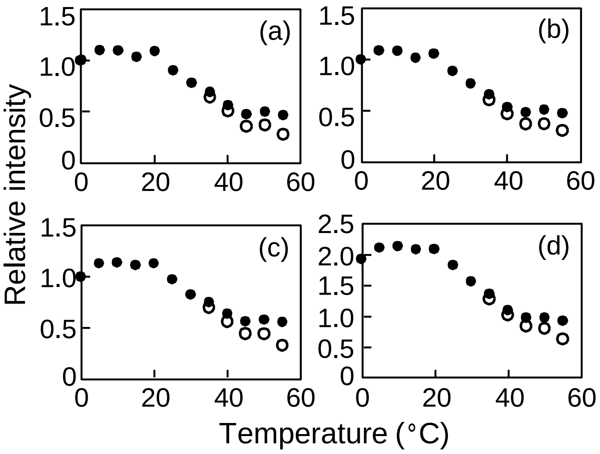

Figure 7. ^{1}H NMR peak intensities of **P1b** relative to that of the H-C=O group in DMF normalized by the relative intensity of peak a at 0 °C: peak *a* (a), *b* (b), *c* (c), and *d* and *e* (d) in Figure 4 with (●) and without (○) the new peaks at the higher magnetic field.

3.4. Photoresponsive Properties of **P1a**

The thermoresponsive polymers, **P1**s, contain the photoreactive coumarin unit as the side-chain of each monomer unit and undergo [2+2] cycloaddition by photoirradiation (Scheme 1). The effects of the photoreaction on the thermoresponsive properties were investigated. A 0.1 wt % distilled chloroform solution of **P1a** in a quartz cell underwent irradiation by an ultrahigh pressure mercury lamp and the subsequent measurements of the UV-vis spectra at room temperature and the transmittance at elevated temperature. The intensity of the UV-vis spectrum decreased with the increasing irradiation, and after a 180-sec irradiation (326 mJ/cm^2), the UV-vis spectrum became broad and the solution turned slightly turbid (Figure 8(a)). It was reported that in the case of water soluble copolymers containing 8 mol% of the coumarin derivative unit in the side-chain, an intermolecular cycloaddition took place in a concentrated solution such as 10 wt%, whereas the intramolecular cycloaddition was the major reaction in a diluted solution such as 0.1 and 1 wt%.[37] Although the concentration of **P1a** (0.1 wt%) seems to be sufficiently low to avoid any intermolecular cycloaddition, the dense coumarin unit in **P1a**, i.e. the homopolymer, is expected to increase the frequency of the intermolecular cycloaddition. The degree of the cycloaddition was estimated from the absorbance at λ_{max} = 313 nm before and after the photoirradiation. Under the experimental conditions, the degree of cycloaddition almost linearly increased with the increasing irradiation time and reached 16 % after a 180-sec irradiation (326 mJ/cm^2). The temperature dependence of the transmittance after each irradiation time is shown in Figure 8(b). The transmittance of the distilled chloroform solution started to decrease at a lower temperature with the increasing irradiation time, i.e., the degree of cycloaddition, and the T_c values gradually decreased from 27 to 24 °C (Figure 8(c)). It has been reported that the thermoresponsive properties were affected by the molecular weight of the polymers,[24] topological effect of the polymer chains,[37, 38] and changes in the solvophobicity due to isomerization of the photoreactive unit.[7, 39] Figure 8(d) shows the transmittance change at 25 °C by photoirradiation and it was revealed that the transmittance at 500 nm significantly decreased from 98 to 29% by the short photoirradiation of 180 sec (326 mJ/cm^2).

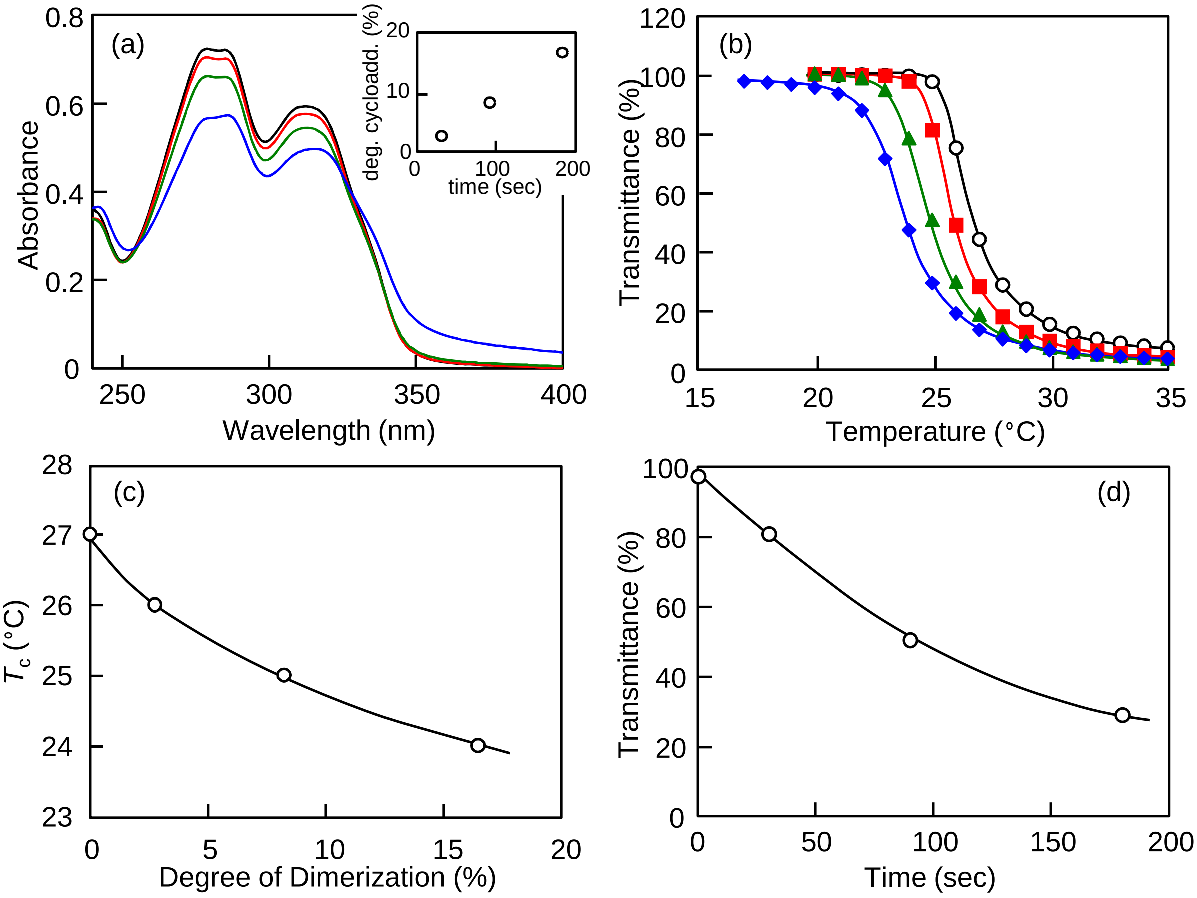

Figure 8. (a) UV-Vis absorption spectra of 0.001 wt% **P1a** solution in distilled chloroform before (—) and after photoirradiation for 30 (—), 90 (—), and 180 sec (—). The inset is a plot of the degree of dimerization vs. irradiation time. (b) Temperature dependence of transmittance at 500 nm for 0.1 wt% **P1a** in distilled chloroform during the heating processes before (○) and after photoirradiation for 30 (■), 90 (▲), and 180 sec (◆). (c) The plot of T_c vs. the degree of dimerization. (d) The plot of transmittance at 25 °C vs. UV irradiation time. Solid lines were drawn as visual guides.

4. Conclusions

The thermoresponsive properties of photoreactive coumarin-containing acrylic and methacrylic homopolymers in various organic solvents were systematically investigated. **P1a** exhibited an LCST-type phase separation in chlorinated methanes and ethane, such as dichloromethane, chloroform, and 1,1,2-trichloroethane, which have the moderate dielectric constant and dipole moment. The collapse of the CH/π interaction of the solvents and the coumarin ring and the formation of the π/π interaction between the coumarin units with increasing temperature were suggested by the high-field shift of the aromatic protons in **P1b** by variable temperature ^{1}H NMR analysis. The deuterium isotope effect was observed and the T_c value of 0.1 wt% **P1a** decreased from 26 °C in chloroform to 21 °C in deuterated chloroform. The T_c values were varied from 26 to 57 °C by changing the polymer structure, i.e., an ethyleneoxy spacer in the side-chain and the α-methyl group in the main-chain. The polymers having the methyl and phenyl groups as electron-donating groups and the ethoxycarbonyl group as an electron-withdrawing group at the 4-position of the coumarin unit were soluble in chloroform. The introduction of the substituents to the coumarin units suppresses the solvophobic polymer and polymer interaction such as aromatic-CH/π and π-π interactions. The T_c values of **P1a** were controlled by the photoirradiation due to the occurrence of the [2+2] cycloaddition of the coumarin units and the transmittance at 500 nm was controlled from 98% to 29% at 25 °C by the 180-sec photoirradiation (326 mJ/cm^{2}). It was revealed that homopolymers containing the coumarin unit not having the substituent at the 4-position, **P1**s, are thermos- and photo-responsive polymers where a single unit is responsive to dual-stimuli.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.eurpolymj.2015.05.010.

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