

ORIGINAL ARTICLE

LCST-type phase behavior of poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride) in *n*-butyl acetateZhenjie Liu¹, Yongliang Guo^{1,2} and Katsuhiko Inomata¹

Novel polymer solutions exhibiting lower critical solution temperatures (LCSTs) have been studied. An alternating copolymer of 2-chloroethyl vinyl ether and maleic anhydride was synthesized through free-radical solution polymerization. This copolymer can exhibit LCST-type phase behavior in *n*-butyl acetate (BuAc) under relatively mild conditions at temperatures sufficiently below its boiling point. The effects of molecular weight, polymer concentration and addition of cosolvent on the polymer solution's cloud point temperature (T_{cp}) were investigated. The T_{cp} value was nearly constant over a wide range of concentrations and increased when the polymer concentration was reduced below a certain value. The experimental LCST-type phase diagram can be reasonably described by Flory–Huggins theory. The addition of non-solvents could reduce the T_{cp} of the polymer solution in BuAc, whereas the addition of good solvents could increase the T_{cp} . These LCST-type phase behaviors may be attributed to specific polar interactions between the polymer and the solvent.

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INTRODUCTION

Lower critical solution temperature (LCST)-type phase behavior in polymer solutions has been attracting a great deal of attention over the past decade. Polymers that exhibit LCST are a class of stimuli-sensitive polymers that are soluble at temperatures below the LCST and become insoluble above the LCST. Many studies have focused on LCST-type phase behavior in aqueous polymer solutions, and many theories and applications have been developed.^{1–3} Today, LCST-type phase behavior of polymers in nonaqueous media is also attracting interest as an opportunity for research and development of smart materials. For example, LCST polymer solutions of thermoresponsive polymer/ionic liquid systems have been reported.^{4–7}

Conventional LCST polymer solutions in organic media have critical temperatures that are higher than the boiling points (BPs) of the solvents.^{8–14} These reported systems can exhibit LCST-type phase behavior under some extreme conditions, for example, in sealed high-pressure cells above the BP of the solvent or using considerably high-molecular-weight polymers. Some theories have been proposed to explain or predict this type of LCST-type phase behavior.^{15–17} In free-volume theories, the difference between the densities or the expansion coefficients of the polymer and the solvent above the solvent's BP is proposed to cause phase separation at elevated temperatures.¹⁷ Because these conditions are inconvenient to study, a novel polymer/organic media solution that can present LCST under mild

conditions is expected to be discovered. Recently, a few of these novel polymer solution systems in organic media have been reported.^{18–20} For example, polymers with certain unique structures or chemical compositions can exhibit LCST-type phase behavior. Fluoroalkyl-end-capped polymers present LCST behavior that may be primarily related to the balance between the oleophilic character of the adamantyl segments and the oleophobic character of the fluoroalkyl groups.¹⁸ Thermally reversible, heat-set gel-like networks in organic media with LCST characteristics were developed by combining elements of one-dimensional metal complexes and mesoscopic supramolecular assemblies.¹⁹ Poly(vinyl ether) with ionic liquid pendants of imidazolium or pyridinium salt can also undergo sensitive LCST-type phase separation in organic media.²⁰

Herein, we report a novel polymer solution in common organic media that can present LCST behavior under mild conditions. As has been reported in our recent communication,²¹ the alternating copolymer of 2-chloroethyl vinyl ether (CVE) and maleic anhydride (MA) known as poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride), henceforth P(CVE-MA), can exhibit LCST-type phase separation in *n*-butyl acetate (BuAc) with a critical temperature sufficiently lower than the BP of BuAc. In this paper, the detailed phase behavior of BuAc solutions of P(CVE-MA) with various molecular weights will be described, and the effects of various cosolvents on LCST behavior will also be presented.

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EXPERIMENTAL PROCEDURE

Materials

Benzene (Nacalai tesque, Kyoto, Japan; 99.5%), toluene (Nacalai tesque; 99.5%), cyclohexane (Nacalai tesque; 99.5%), dimethylsulfoxide (DMSO; Kishida Chemical; 99%), 2-hexanone (TCI, Tokyo, Japan; >98.0%), sodium hydroxide (NaOH; Nacalai tesque; 97%), anhydrous sodium sulfate (Na_2SO_4 ; Nacalai tesque; 97%), calcium hydride (CaH_2 ; Nacalai tesque; EP) and 2,2'-azobisisobutyronitrile (Wako, Osaka, Japan; >98%) were used as received. CVE (TCI; >97.0%) was washed three times with an equal volume of water made slightly alkaline with NaOH, dried with Na_2SO_4 , refluxed in the presence of CaH_2 for 2 h and distilled under reduced pressure. MA (TCI; >99.0%) was recrystallized in benzene. Methyl ethyl ketone (TCI; >99.0%) was refluxed in the presence of CaH_2 for 2 h, distilled under reduced pressure and kept in the presence of a molecular sieve. Propyl acetate (TCI; >98.0%), BuAc (Aldrich, St Louis, MO, USA; ACS reagent; $\geq 99.5\%$), 1,2-dichloroethane (Wako; >99.5%) and tetrahydrofuran (Wako; >99.5%) were distilled before use.

Synthesis of copolymer

MA and CVE were copolymerized by free-radical solution polymerization. Typically, specific amounts of MA, CVE, 2,2'-azobisisobutyronitrile and solvent were added to a 50 ml three-neck flask equipped with a condenser and a nitrogen gas inlet. The reaction solution was stirred for a specified time at a given temperature. The resultant polymer was precipitated in diethyl ether and dried in vacuum at 100 °C for at least 8 h.

Gel permeation chromatograph

The molecular weight of the prepared copolymer was determined by gel permeation chromatograph using two columns of TSKgel, α -3000 and α -5000, connected to an SD-8022 system (Tosoh, Tokyo, Japan) with a 1.0 ml min^{-1} *N,N*-dimethylformamide/lithium bromide flow rate (the concentration of lithium bromide was 15 mg l^{-1}). Polystyrene standards were used to calibrate the molecular weight during measurement.

Preparation of polymer solutions

Polymer solutions in BuAc were prepared by direct dissolution of specified amounts of polymer in BuAc. The bottle containing the polymer and BuAc was placed in an oven at 60 °C for about 8 h to dissolve the polymer. The bottle containing the polymer solution was then kept in a refrigerator at about 3 °C until measurements were made.

Polymer solutions in BuAc/cosolvent were prepared as follows: a certain amount of the polymer was added to BuAc, the bottle was kept in an oven at 60 °C for about 8 h, and then a specified amount of the cosolvent was added to the prepared polymer solution. The bottle containing the polymer solution in BuAc/cosolvent was kept in a refrigerator at about 3 °C until measurements were performed.

The polymers were measured immediately after polymerization to prevent degradation, oxidation or water absorption.

Light scattering

The thermoresponsive phase behavior of the polymer solution was characterized using a light scattering technique. The scattered light intensity (I_s) at a

fixed angle of 90° and at various temperatures was measured using a laboratory-made apparatus equipped with an ALV/SO-SIPD detector (ALV, Langen, Germany) and a He-Ne laser (wavelength $\lambda_0=633$ nm).²² The sample solutions were optically purified by a Millipore filter (Millipore, Billerica, MA, USA) with a nominal pore size of 1.0 μm and then transferred into the optical tube. The heating and cooling rates of the system were both about 0.2 °C min^{-1} . The I_s of the polymer solution was measured immediately when the temperature of the system reached the desired temperature.

RESULTS AND DISCUSSION

Synthesis of copolymers

CVE has an electron-releasing alkoxy group and is usually used in cationic polymerization,^{23–27} whereas MA contains an electron-accepting carboxylic anhydride group. These two groups can form charge transfer complexes of donor–acceptor monomer systems in which MA and CVE act as the acceptor monomer and the donor monomer, respectively.²⁸ It is well known that alternating copolymers of vinyl ether and MA can be formed in free-radical polymerization.^{29–32} Our previous report²¹ used ^1H nuclear magnetic resonance to show that the molar composition of MA and CVE of the formed copolymer was 1:1, and the ^{13}C nuclear magnetic resonance spectrum suggested that these monomers were alternately polymerized.

Copolymers with different weight-averaged molecular weights (M_w) were synthesized. The reaction conditions and the M_w values measured through gel permeation chromatograph are listed in Table 1. The various copolymers are designated P(CVE-MA)-1, -2, -3, -4 and -5. Higher molecular weight polymers ($M_w=36\,400$, 77 200 and 92 200 g mol^{-1}) were synthesized in methyl ethyl ketone, and polymers with lower M_w (7700 and 17 500 g mol^{-1}) were synthesized in tetrahydrofuran with much more initiator added.

LCST-type phase behavior of polymer solution

The temperature-sensitive behavior of the polymer solution can be studied through various methods, such as turbidity, differential scanning calorimetry, light scattering measurements, viscometry and fluorescence.³ In our research, the temperature-sensitive behavior was characterized using the scattered light intensity I_s at a fixed 90° angle. Figure 1 shows that the I_s of the polymer solution increased abruptly as the temperature increased above a certain temperature. Above a certain polymer concentration (>0.1 wt%), the polymer solution became visually turbid, meaning that phase separation occurred above a certain temperature. This point is called the cloud point temperature (T_{cp}). In other words, the polymer is soluble below T_{cp} and insoluble above T_{cp} , which is characteristic of LCST-type phase behavior in a polymer solution. In our experiment, T_{cp} is defined from

Table 1 Polymerization conditions of P(CVE-MA) with different molecular weights

Condition	P(CVE-MA)-1	P(CVE-MA)-2	P(CVE-MA)-3	P(CVE-MA)-4	P(CVE-MA)-5
Solvent	MEK	MEK	MEK	THF	THF
MA (g)	4.9	4.9	2.452	4.9	2.452
CVE (g)	5.3	5.3	2.615	5.3	2.615
AIBN (g)	0.0200	0.0248	0.04	0.04	0.4
Solvent (g)	40	20	55	40	100
Reaction temperature (°C)	60	70	70	60	60
Reaction time (h)	6	2	2	6	6
M_w (g mol^{-1})	77 200	92 200	36 400	17 500	7700
M_w/M_n	1.87	1.90	1.42	2.77	1.48
Conversion (%)	57.8	58.8	52.5	90.7	40.5

Abbreviations: AIBN, 2,2'-azobisisobutyronitrile; CVE, 2-chloroethyl vinyl ether; MA, maleic anhydride; MEK, methyl ethyl ketone; THF, tetrahydrofuran.

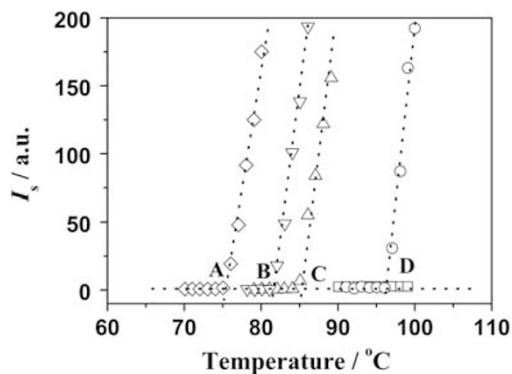


Figure 1 Temperature dependence of the scattered light intensity (I_s) of polymer/*n*-butyl acetate solutions with different weight-averaged molecular weights. (◇) 0.05 wt% solution of P(CVE-MA)-2 ($M_w=92\,200$), (▽) 0.05 wt% solution of P(CVE-MA)-1 ($M_w=77\,200$), (△) 0.05 wt% solution of P(CVE-MA)-3 ($M_w=36\,400$), (○) 1 wt% solution of P(CVE-MA)-4 ($M_w=17\,500$) and (□) 10 wt% solution of P(CVE-MA)-5 ($M_w=7700$). The points A, B, C and D indicate the T_{cp} of each solution, and the broken lines are tangent lines for evaluating T_{cp} .

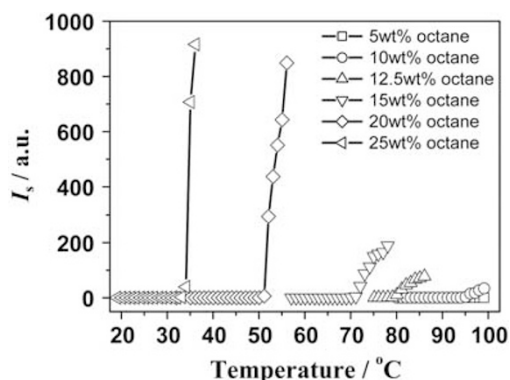


Figure 2 Temperature dependence of scattered light intensity (I_s) of P(CVE-MA)-5 solutions with 1 wt% polymer concentration in a solvent mixture of *n*-butyl acetate and *n*-octane. The weight percentage of *n*-octane is indicated in the graph.

the temperature dependence of I_s in Figure 1, that is, T_{cp} is the temperature at which the tangents to the lines in the higher and lower temperature regimes intersect (the points A, B, C and D for different polymer solutions in Figure 1).

The value of T_{cp} decreased as the M_w of the polymer increased. The higher molecular weight polymers (P(CVE-MA)-1, 2 and 3) exhibited LCST-type phase behavior at a relative low T_{cp} ($<90^\circ\text{C}$) and low polymer concentrations. In contrast, the T_{cp} of the polymer P(CVE-MA)-4, with a lower molecular weight, was about 97°C even at a relatively high polymer concentration of 1 wt%. The lowest molecular weight polymer, P(CVE-MA)-5, did not exhibit thermoresponsive phase behavior until 99°C (the upper limit of the apparatus) even at a concentration of 10 wt%. To evaluate the T_{cp} of P(CVE-MA)-5 in pure BuAc, the non-solvent *n*-octane was added to the BuAc-polymer solution. As shown in the latter part of this report, the addition of a cosolvent can influence T_{cp} in a manner dependent on the solvent quality of the cosolvent. Figure 2 indicates that a small amount of *n*-octane (5 wt%) added to the BuAc-polymer solution did not induce thermoresponsive behavior below 100°C . As the amount of *n*-octane in the mixed solvent increased over 10 wt%, LCST-type phase behavior was recognized, and further increasing the *n*-octane content of the

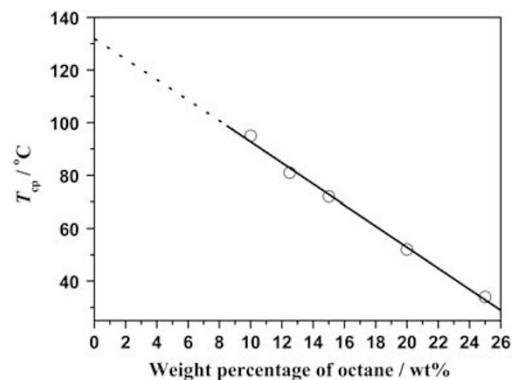


Figure 3 Octane weight percentage dependence of the T_{cp} of the P(CVE-MA)-5 solution.

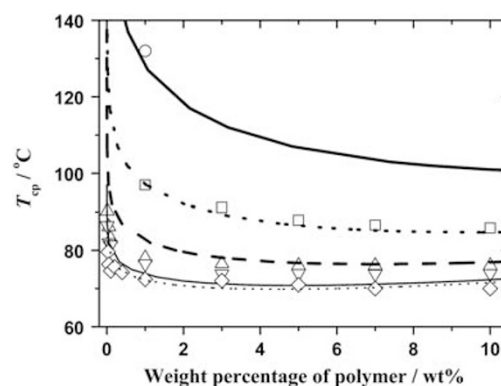


Figure 4 T_{cp} of polymer/*n*-butyl acetate solutions at different polymer concentrations. M_w is (○) 7700, (□) 17 500, (△) 36 400, (▽) 77 200 and (◇) 92 200 g mol^{-1} . Binodal curves for these polymers were calculated by using Equations (5) and (6) and are presented as solid ($P=38$), broken ($P=86$), dashed ($P=178$), thin solid ($P=378$) and thin broken ($P=451$) lines, respectively.

mixed solvent caused the I_s ratio to increase and T_{cp} to be reduced. In Figure 3, the T_{cp} values of 1 wt% polymer solutions in BuAc/*n*-octane are plotted against the *n*-octane content in the mixed solution. T_{cp} decreased linearly with increasing *n*-octane content, and the extrapolated line intersects the vertical axis at about 132°C , which is higher than the BP of BuAc. This value could provide information about the T_{cp} of P(CVE-MA)-5 in pure BuAc with a polymer concentration of 1 wt%.

Plots of T_{cp} versus polymer concentration of the BuAc-polymer solutions are shown in Figure 4. The value of T_{cp} increased as the M_w of P(CVE-MA) decreased. Similar molecular weight dependence of T_{cp} or LCST behavior has frequently been observed in aqueous polymer solutions.^{33–35} As mentioned above, the lowest molecular weight P(CVE-MA)-5 did not exhibit thermoresponsive phase behavior even in a 10 wt% solution, and the value of evaluated T_{cp} indicated in Figure 4 was derived from extrapolating the measurements shown in Figure 3. The T_{cp} of P(CVE-MA)-4/BuAc was much higher than that of the higher molecular weight polymers P(CVE-MA)-1, -2, and -3 and varies over a wide range of polymer concentrations from 1 to 10 wt%. The molecular weight dependence of T_{cp} became weaker as the M_w of the polymer increased to higher values. For the higher molecular weight polymers, T_{cp} initially decreased significantly as the polymer concentration increased and then converged to an almost constant value above a certain polymer concentration

(>1 wt%). Similar dependences of T_{cp} on polymer concentration have been reported in other water-soluble polymers.^{36–39}

It should be noted that the T_{cp} of P(CVE-MA)/BuAc at higher M_w is sufficiently below the BP of BuAc (126 °C) such that this LCST phase behavior is not caused by the free-volume difference between the polymer and solvent but instead probably originates from some specific interaction between the polymer and the solvent. This kind of phase behavior in polymer solutions can be conventionally described by the Flory–Huggins (F–H) lattice model based on mean-field theory in which the chemical potential of the solvent (1) and the polymer (2) are expressed by Equations (1) and (2), respectively. The molecular weights of the polymers are considered to be monodisperse.

$$\mu_1 - \mu_1^0 = \Delta\mu_1 = RT \left\{ \ln(1 - \phi) + \left(1 - \frac{1}{P}\right) \phi + \chi \phi^2 \right\} \quad (1)$$

$$\mu_2 - \mu_2^0 = \Delta\mu_2 = RT \{ \ln \phi - (P - 1)(1 - \phi) + \chi P(1 - \phi)^2 \} \quad (2)$$

In these equations, R is the gas constant, T is the absolute temperature, P is the number of segments per polymer chain and ϕ is the volume fraction of the polymer in solution. χ is the thermodynamic segmental interaction parameter between the polymer and the solvent, and its temperature dependence is conventionally assumed to follow the Shultz–Flory equation⁴⁰ shown in Equation (3).

$$\chi(T) = \frac{1}{2} - \psi \left(1 - \frac{\Theta}{T}\right) \quad (3)$$

In Equation (3), Θ is the theta temperature and ψ is the entropy parameter. The lower molecular weight polymers revealed higher critical temperatures; this finding means that the apparent χ value becomes larger as the temperature increases, so the sign of the parameter ψ must be negative. According to Equation (3), T_{cp} at the critical point T_c can be calculated from Equation (4).⁴⁰

$$\frac{1}{T_c} = \frac{1}{\Theta} + \frac{1}{\Theta\psi} \left(\frac{1}{\sqrt{P}} + \frac{1}{2P} \right) \quad (4)$$

Because the minimum value of T_{cp} for each polymer in Figure 4 can be regarded as its critical point, the inverse of the minimum T_{cp} was plotted against $1/\sqrt{P} + 1/2P$ and displayed in Figure 5. P was evaluated as M_w/M_0 , where $M_0=204.6$ is the molecular weight of the repeating unit of P(CVE-MA). The derived values of the intercept and slope of the straight line in Figure 5 can be related to the parameters in Equations (3) and (4) and give $\Theta=333$ K and $\psi=-1.62$. The value of $\Theta=333$ K means that BuAc is a good solvent for P(CVE-MA) below

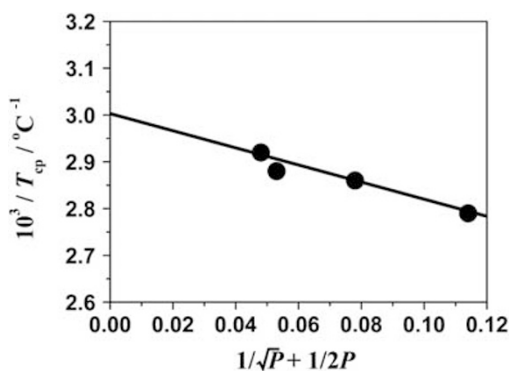


Figure 5 Plot of $1/T_{cp}$ versus $(1/\sqrt{P} + 1/2P)$.

60 °C ($\chi < 1/2$). Above 60 °C ($\chi > 1/2$), BuAc becomes a poor solvent, and its solvent quality for this polymer becomes poorer and poorer as the temperature increases, resulting in phase separation at a certain temperature.

Because the χ parameter varies with temperature, the chemical potentials in Equations (1) and (2) can be represented as functions of P , T and ϕ , that is, $\Delta\mu_i(\phi, T, P)$. In the liquid–liquid phase-separated state, the chemical potentials of the solvent ($i=1$) and the polymer ($i=2$) should satisfy Equations (5) and (6), respectively.

$$\Delta\mu_1(\phi', T, P) = \Delta\mu_1(\phi'', T, P) \quad (5)$$

$$\Delta\mu_2(\phi', T, P) = \Delta\mu_2(\phi'', T, P) \quad (6)$$

Here, ϕ' and ϕ'' are the volume fractions of the polymer in the phase-separated dilute and concentrated solutions, respectively. For a solution of polymer with a degree of polymerization of P , χ can be calculated at a given temperature T from Equation (3), and by solving Equations (5) and (6), the values of ϕ' and ϕ'' for the separated phases can be obtained at that temperature. Through this procedure, binodal curves for P(CVE-MA)/BuAc of different molecular weights can be computed and are shown as lines in Figure 4. In these calculations, the P values for P(CVE-MA)-1 ($M_w=77\,200$), -2 (92 200), -3 (36 400), -4 (17 500) and -5 (7700) were assumed to be 378, 451, 178, 86 and 38, respectively. The calculated curves reasonably reproduced the experimental phase diagram, that is, (i) the binodal lines exhibit LCST-type behavior, (ii) the lines shift to lower temperatures as the molecular weight of the polymer increases, and (iii) when M_w is high, the lines exhibit sudden decreases in the lower concentration region and level off in the higher concentration region. The value of T_{cp} (=132 °C) for P(CVE-MA)-5 deduced from the mixed BuAc/octane solvent at 1 wt% is also located near the calculated line. Of course, the present calculation is based on the condition that the polymer is monodisperse, although the polymers used in the experiments have a certain molecular weight distribution. The M_w distribution may be the reason for some observed quantitative discrepancies between the experimental and calculated T_{cp} . For example, the concentration dependence of T_{cp} for P(CVE-MA)-3 was broader than the calculated binodal line, and the calculated line for P(CVE-MA)-1 is located in a lower temperature regime than the experimental results. Despite these discrepancies, the overall trend of T_{cp} variation with polymer concentration and molecular weight can be reproduced with the F–H calculation, which suggests that the LCST-type phase diagram of P(CVE-MA)/BuAc can be described within the framework of basic F–H theory. However, the negative temperature dependence of the χ parameter cannot be explained by the original concept for χ , which was based on a van Laar-type segmental interaction between the polymer and the solvent, suggesting that some other specific interactions may exist.

Effect of addition of cosolvent on the T_{cp} of P(CVE-MA)/BuAc

The effect of adding various cosolvents on the T_{cp} of the P(CVE-MA)/BuAc solution was investigated using P(CVE-MA)-2 at a fixed polymer concentration of 0.1 wt%. The temperature dependences of I_s in different solvent mixtures are shown in Figure 6. As observed in pure BuAc, the I_s of the polymer solution increased sharply at a certain T_{cp} . The cosolvents benzene, toluene, cyclohexane and 1,2-dichloroethane all caused T_{cp} to decrease as the amount of cosolvent added to BuAc increased, as shown in Figures 6a–d, respectively. This phenomenon was also observed in the P(CVE-MA)-5/BuAc/*n*-octane solutions of Figure 2 and arises because these solvents make the solvent mixture

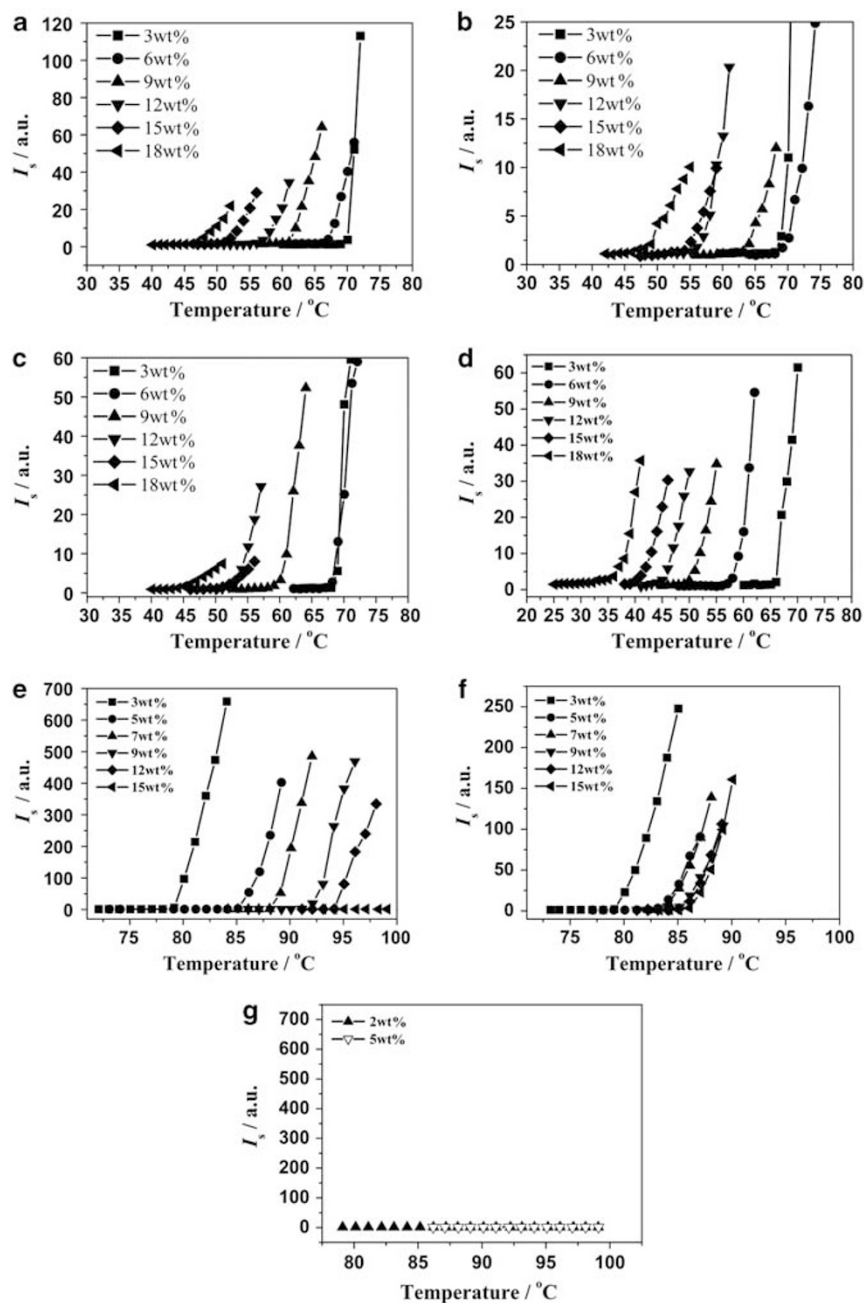


Figure 6 Temperature dependence of I_s of polymer solutions with different amounts of various cosolvents added. (a) Benzene, (b) toluene, (c) 1,2-dichloroethane, (d) cyclohexane, (e) 2-hexanone, (f) propyl acetate and (g) dimethylsulfoxide.

more poor than pure BuAc. In other words, these solvents as well as *n*-octane should be non-solvent for P(CVE-MA).

The relationship between T_{cp} and the added amounts of these solvents is shown in Figure 7. There exists an overall tendency that the T_{cp} of the polymer solution decreased as the amount of cosolvent increased. In the cases of benzene, toluene and 1,2-dichloroethane, the slopes of the T_{cp} versus added solvent lines were similar, and the effectiveness of these solvents at reducing T_{cp} is ranked as follows: 1,2-dichloroethane > benzene > toluene. Cyclohexane exhibits the highest effectiveness at reducing T_{cp} , meaning that aliphatic cyclohexane is the least powerful solvent of P(CVE-MA) among the solvents in Figure 7.

By contrast, in Figures 6e–g, 2-hexanone, propyl acetate and DMSO were the cosolvents added to the P(CVE-MA)/BuAc solutions. As

2-hexanone was added to the polymer/BuAc solution, T_{cp} shifted to higher temperatures until the amount of added 2-hexanone reached 15 wt%, at which no thermoresponsive behavior was observed below 100 °C (Figure 6e). T_{cp} shifted to higher temperature slowly as the amount of added propyl acetate to BuAc increased (Figure 6f). When DMSO was added, shown in Figure 6g, the solution remained transparent until 100 °C without any thermoresponsive behavior, even when the amount of added DMSO reached 2 wt%.

Figure 8 shows the T_{cp} of the polymer solution as a function of the amount of other added solvents including 2-hexanone and propyl acetate. It is clear that 2-hexanone increased the T_{cp} of the polymer/BuAc solution more effectively than propyl acetate. The phenomenon of T_{cp} increasing as larger amounts of good solvents are added has also

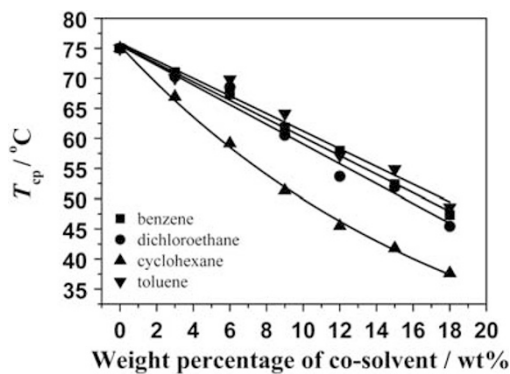


Figure 7 T_{cp} of polymer solutions in *n*-butyl acetate with different amounts of the indicated cosolvents added.

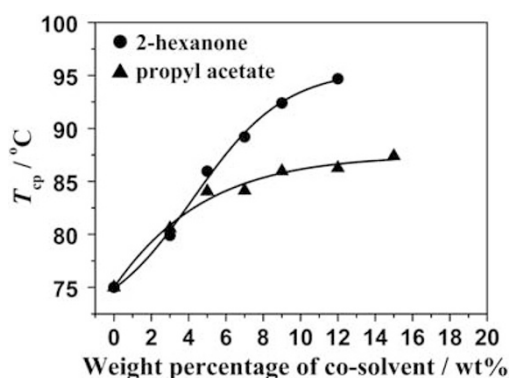


Figure 8 T_{cp} of polymer solutions in *n*-butyl acetate with different amounts of the indicated cosolvents added.

been observed in aqueous poly(vinyl methyl ether) solutions and may arise because the interactions between the good solvents and the polymers are heavily favored over the interaction between the polymer and the original solvent.⁴¹ The T_{cp} in Figure 8 may increase because these cosolvents interact with the polymer more strongly than BuAc, and the phenomena in Figures 7 and 8 present clues about the ability of each solvent to dissolve this polymer. Our experiments showed that P(CVE-MA) can be dissolved in 2-hexanone and propyl acetate but cannot be dissolved in the solvents shown in Figure 7. Figure 6g shows that DMSO, which produced a pink solution after dissolving the polymer, should be the best solvent of P(CVE-MA) used in this work.

The slope of the curves in Figures 7 and 8 should represent the ability of each solvent to dissolve P(CVE-MA). The values of this slope for each of the tested cosolvents are listed in Table 2. The dielectric constants (ϵ) and solubility parameters (δ) of these solvents are also indicated; the former value relates to the polarity of the solvent, and the latter value is conventionally used to indicate the solubility of the polymer solution.⁴² These lists indicate that the δ values do not exhibit a linear relationship with the solubility of P(CVE-MA). In contrast, the value of the slope seems to increase with ϵ , with the exception of 1,2-dichloroethane. In Table 2, the polar contribution to the solubility parameter proposed by Hansen,⁴³ δ_p , is also listed. δ_p and ϵ exhibit similar relationships with the slope of the curve. In Figure 9, the values of the slope are plotted against δ_p , and a good linear relationship can be seen, with the exception of 1,2-dichloroethane. Therefore, except for 1,2-dichloroethane, we can mention that a solvent's ability to dissolve P(CVE-MA) is determined by the polarity of the solvent.

Table 2 Various physical properties of the tested cosolvents

Cosolvent	Slope ^a (°C/wt%)	Dielectric constant ϵ	Solubility parameter δ	Polar term in solubility parameter δ_p
Cyclohexane	-2.1	2.02	16.8	0
1,2-Dichloroethane	-1.8	10.4	20.9	7.4
Benzene	-1.7	2.27	18.6	0
Toluene	-1.6	2.38	18.2	1.4
Propyl acetate	1.6	~5.5 ^b	17.8 ^b	4.5 ^b
2-Hexanone	2.0	~17 ^c	17	6.1
DMSO	Very large	46.5	26.6	16.4

Abbreviation: DMSO, dimethyl sulfoxide.

^aSlope of the plot of T_{cp} versus cosolvent's weight fraction in Figures 7 and 8.

^bApproximate value from ethyl acetate and *n*-butyl acetate.

^cApproximate value from 2-butanone and cyclohexanone.

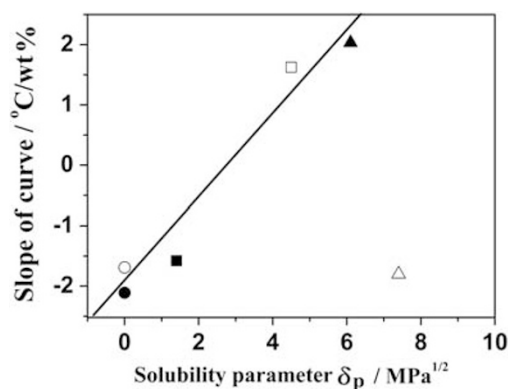


Figure 9 Relationship between the slope of the curve of T_{cp} versus the added cosolvent amounts evaluated from Figures 7 and 8 and the polar contribution to the solubility parameter (δ_p) of the cosolvent. (●) Cyclohexane, (○) benzene, (■) toluene, (□) propyl acetate, (▲) 2-hexanone and (Δ) 1,2-dichloroethane. The straight line is a guide for the eye.

As reported in our recent studies,^{21,44} tetrahydrofuran is a good solvent of P(CVE-MA), whereas *n*-hexane is a non-solvent. Some polar interaction between P(CVE-MA) and the solvent is likely to be an important factor for solubilization. This hypothesis seems reasonable because P(CVE-MA) contains polar ether and carboxylic anhydride groups and the good solvents also contain oxygen atoms in their chemical structures, whereas the non-solvents are oxygen-free non-polar solvents. The LCST behavior of P(CVE-MA)/BuAc suggests that the polar interaction between the polymer and the solvent becomes weak as the temperature increases, which results in the segregation and precipitation of P(CVE-MA). Because of chemical structure similarities, 1,2-dichloroethane would prefer to interact with the 2-chloroethyl group in P(CVE-MA) and prevent the interaction between the polymer and BuAc, which might be the reason that 1,2-dichloroethane did not follow the linear relationship in Figure 9.

CONCLUSION

Novel LCST-type phase behavior of polymer solutions in common organic media under mild conditions has been investigated. Alternating copolymers of CVE and MA produced an LCST-type solution when dissolved in BuAc, and the T_{cp} values of the higher molecular weight polymers were much lower than the boiling temperature of the solvent. As the M_w of the polymers increased, the T_{cp} of the polymer solution decreased. The experimental LCST-type phase diagram of this polymer solution can be reasonably described by F-H theory. The T_{cp}

of the polymer solution in BuAc can also be tuned by adding cosolvents. Adding non-solvent decreases the T_{cp} , whereas adding proper good solvents increases the T_{cp} of the polymer/BuAc solution. This increase can be ascribed to the polar interaction between P(CVE-MA) and the solvent. Effects that strengthen the polar interaction between the polymer and the solvents are inclined to increase the T_{cp} of the polymer solution.

To understand the LCST behavior of P(MA-CVE)/BuAc systems, dilute polymer solution properties such as the second virial coefficient A_2 and its temperature dependence measured through precise light scattering or viscosity measurements around the evaluated Θ temperature ($=60^\circ\text{C}$) will offer useful information. Further investigations of these novel polymer solutions with LCST-type phase behavior will be reported in future studies.

Finally, we should mention that this copolymer can be conveniently chemically modified because it has functional alkyl chloride and carboxylic anhydride groups. Thus, research and development can be expected to discover applications of the tunable LCST thermo-responsive behavior under mild conditions of this novel polymer solution in organic solvent.

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