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LCST-type Phase Behavior of Poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride) in *n*-Butyl Acetate

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Running head: LCST behavior of alternating copolymer in *n*-butyl acetate

ABSTRACT:

Novel polymer solution systems exhibiting lower critical solution temperature (LCST) has been studied. Alternating copolymer of 2-chloroethyl vinyl ether and maleic anhydride was synthesized by free-radical solution polymerization. This copolymer can exhibit LCST-type phase behavior in *n*-butyl acetate at relatively mild condition enough below its boiling point. Effects of molecular weight, polymer concentration, and addition of co-solvent on temperature of cloud point (T_{cp}) of polymer solution were investigated. The T_{cp} value was higher at lower polymer concentration, and then became almost constant at a wide range of concentration above a certain concentration value. Experimental LCST-type phase diagram can be reasonably described by Flory-Huggins theory. Addition of non-solvents could make the T_{cp} of polymer solution in *n*-butyl acetate decrease, while good solvents could make the T_{cp} increase. These LCST-type phase behaviors may be attributed to some specific polar interaction between polymer and solvent.

Keywords:

thermoresponive polymers / cloud point / lower critical solution temperature (LCST) / mild conditions / polymer solution / organic media

INTRODUCTION

Much attention to lower critical solution temperature (LCST)-type phase behavior of polymer solution has been attracted. Polymers with LCST are kind of stimuli-sensitive polymers which are soluble at the temperature below LCST and become insoluble above LCST. A lot of LCST-type phase behaviors of aqueous polymer solution have been studied, and many theories and applications have been developed in the past.[1-3] Nowadays LCST-type phase behavior of polymer in some other nonaqueous media is also coming into study in order to research and develop some smart materials. For example, LCST polymer solutions of thermoresponsive polymer/ionic liquid systems have been reported.[4-7]

In conventional LCST polymer solutions in organic media, the critical temperature is usually higher than the boiling point (BP) of solvent.[8-14] These reported systems can exhibit LCST-type phase behavior at some tough conditions such as in sealed high-pressure cells above the BP of solvent or with considerably high molecular weight polymers. Some theories have been tried to explain or predict this kind of LCST-type phase behavior.[15-17] In free-volume theories, the difference of density or expansion coefficient between polymer and solvent above BP is proposed to lead to phase separation at elevated temperatures.[17] Because these conditions is not convenient to research, a novel solution system of polymer/organic media which can present LCST at some mild conditions is expected to be discovered. Recently, very a few these novel polymer solution systems in organic media have been reported,[18-20] for example, polymers with some unique structure or chemical composition can exhibit LCST-type phase behavior. Fluoroalkyl-end-capped polymer presented LCST behavior which may be mainly related to the oleophilic-oleophobic balance corresponding to the oleophilic character from adamantyl segments and the oleophobic character from fluoroalkyl groups.[18] Thermally reversible, heat-set gel-like networks with LCST characteristic in organic media were developed by combining the elements of the 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 system in common organic media which can present LCST behavior at mild conditions. As it has been reported in our recent communication,[21] alternating copolymer of 2-chloroethyl vinyl ether (CVE) and maleic anhydride (MA), poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride), P(CVE-MA), can occur LCST-type phase separation in *n*-butyl acetate (BuAc), while the critical temperature was enough lower than BP of BuAc. In this paper, detailed phase behavior of BuAc solutions of P(CVE-MA) with various molecular weight will be described, and effect of addition of various co-solvents on LCST behavior will also presented.

EXPERIMENTAL

Materials

Benzene (Nacalai tesque; 99.5%), toluene (Nacalai tesque; 99.5%), cyclohexane (Nacalai tesque; 99.5%), dimethylsulfoxide (DMSO; Kishida Chemical Co. LTD; 99%), 2-hexanone (TCI; > 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 (AIBN; Wako; > 98%) were used as received. 2-Chloroethyl vinyl ether (CVE; TCI; > 97.0%) was washed three times with equal volume of water made slight alkaline with NaOH, dried with Na_2SO_4 and refluxed in the presence of CaH_2 for 2 hours and distilled under reduced pressure. Maleic anhydride (MA; TCI; > 99.0%) was recrystallized in benzene. Methyl ethyl ketone (MEK; TCI; > 99.0%) was refluxed in the presence of CaH_2 for 2 hours, distilled under reduced pressure and kept in the presence of molecular sieve. Propyl acetate (TCI; > 98.0%), *n*-butyl acetate (BuAc; Aldrich; ACS reagent; ≥ 99.5%), 1,2-dichloroethane (Wako; > 99.5%), and tetrahydrofuran (THF; Wako; > 99.5%) were distilled before using.

Synthesis of Copolymer

Copolymerization of MA and CVE was carried out by free-radical solution polymerization. Typically, certain amounts of MA, CVE, AIBN, and solvent were added into a 50 mL three-neck flask equipped with a condenser and an inlet of nitrogen gas. The reaction solution was stirred for certain hours at a certain temperature. The resultant polymer was precipitated in diethyl ether and dried in vacuum at 100 °C for at least 8 hours.

Gel Permeation Chromatograph (GPC)

Molecular weight of the prepared copolymer was determined by GPC using 2 columns of TSKgel α-3000 and α-5000 connected to SD-8022 system (Tosoh) at a 1.0 mL/min flow rate of *N*,*N*-dimethylformamide/lithium bromide (the concentration of lithium bromide was 15 mg/L). Polystyrene standards were used for molecular weight calibration.

Preparation of Polymer Solutions

Polymer solutions in BuAc were prepared by direct dissolution of certain amounts of polymer in BuAc. The bottle containing polymer and BuAc was placed in an oven at 60 °C for about 8 hours in order to dissolve the polymer. Then the bottle containing the polymer solution was kept in a refrigerator at about 3 °C before measurements.

Polymer solutions in BuAc/co-solvent were prepared as follows: firstly, certain amount of polymer was added into BuAc and then the bottle was kept in an oven at 60 °C for about 8 hours, and secondly certain amount of co-solvent was added into the prepared polymer solution. The bottle containing polymer solution in BuAc/co-solvent was kept in a refrigerator at about 3 °C before measurements.

Polymers for measurements were used immediately after polymerization in order to avoid degradation, oxidation, or water absorption.

Light Scattering

The thermoresponsive phase behavior of the polymer solution was characterized by using light scattering technique. The scattered light intensity (I_s) at different temperatures at a fixed angle of 90° was measured by a laboratory-made apparatus equipped with an ALV/SO-SIPD detector using He-Ne laser (the wavelength λ_o = 633 nm).[22] Sample solutions were optically purified by a Millipore filter of nominal pore size of 1.0 μm and transferred into optical tube. The heating and cooling rate of the system were about 0.2 °C/min. I_s of the polymer solution was measured immediately as the temperature of the system reached the desired temperature.

RESULTS AND DISCUSSION

Synthesis of Copolymers

CVE has electron-releasing alkoxyl group and is usually used in the cationic polymerization,[23-27] while MA contains electron-withdrawing group of carboxylic anhydride. They can form charge transfer complexes of donor-acceptor monomer systems, in which MA and CVE act as accepter monomer and donor monomer, respectively.[28] It is well known that an alternating copolymers of vinyl ether and MA can be formed in free-radical polymerization.[29-32] As pointed out in our previous report,[21] the molar composition of MA and CVE in the formed copolymer evaluated from ^{1}H NMR was 1:1, and these monomers were alternately polymerized as suggested by ^{13}C NMR spectrum.

Copolymers with different weight-averaged molecular weight (M_w) were synthesized. Their reaction conditions and M_w evaluated from the GPC are listed in Table 1, and they are designated as P(CVE-MA)-1, -2, -3, -4 and -5. Higher molecular weight polymers (M_w = 36,400, 77,200 and 92,200 g/mol) were synthesized in MEK, and polymer with lower M_w (7,700 and 17,500 g/mol) was synthesized in THF with much more added amounts of initiator.

LCST-type Phase Behavior of Polymer Solution

Temperature-sensitive behavior of polymer solution can be studied by various methods such as turbidity, differential scanning calorimetry, light scattering measurement, viscometry, fluorescence and so on.[3] In our research, the temperature-sensitive behavior was characterized by scattered light intensity I_s at a fixed 90° angle. It can be seen in Figure 1 that I_s of polymer solution increased abruptly at a certain temperature in heating process. Above a certain polymer concentration (> 0.1 wt%), the polymer solution became turbid visually, means the phase separation occurred above a certain temperature, and this is called cloud point temperature (T_{cp}). In other words, polymer is soluble below T_{cp} and insoluble above T_{cp}, which is the character of LCST-type phase behavior of polymer solution. In our experiment, the T_{cp} is defined from the temperature dependence of I_s in Figure 1, i.e., the temperature at the intersection point of the tangent derived from the plots for upper and lower temperature region around T_{cp} (the points A, B, C and D for different polymer solutions in Figure 1).

T_{cp} of polymer solution decreased with the increase of M_w of polymer. Higher molecular weight polymer (P(CVE-MA)-1, 2 and 3) can exhibit LCST-type phase behavior at a relative lower T_{cp} (< 90 °C) at lower polymer concentration range, and T_{cp} of lower molecular weight polymer P(CVE-MA)-4 was about 97 °C even at relative higher polymer concentration of 1wt%. The lowest molecular weight polymer P(CVE-MA)-5 could not exhibit thermoresponsive phase behavior until 99 °C (the upper limit of the apparatus) even at concentration of 10 wt%. In order to evaluate T_{cp} for P(CVE-MA)-5 in pure BuAc, *n*-octane as a nonslovent was added into the polymer solution of BuAc. As shown in the latter part of this report, the addition of co-solvent can influence T_{cp} with depending on solvent quality of the co-solvent. Figure 2 indicates that a small amount of *n*-octane (5 wt%) added into the polymer solution in BuAc could not induce the thermoresponsive behavior below 100 °C. As the weight percentage of *n*-octane in mixed solvent was over 10wt%, the LCST-type phase behavior can be recognized, and by further increase in *n*-octane content in mixed solvent, the increasing ratio of I_s became distinct and T_{cp} became small. In Figure 3, T_{cp} values for 1 wt% polymer solutions in BuAc/*n*-octane are plotted against *n*-octane content in the mixed solution. T_{cp}

decreased linearly with increase in *n*-octane content, and the intercept on the vertical axis by the extrapolated line was about 132 ºC, which is higher than BP of BuAc. This value could be a clue about the T_{cp} of P(CVE-MA)-5 in pure BuAc with polymer concentration of 1 wt%.

The plots of T_{cp} of polymer solution versus polymer concentration in BuAc are shown in Figure 4. T_{cp} values increased with the decrease of M_w of P(CVE-MA), and this kind of molecular weight dependence of T_{cp} or LCST behavior has been often observed in aqueous polymer solutions.[33-35] As mentioned above, the lowest molecular weight P(CVE-MA)-5 could not exhibit thermoresponsive phase behavior even in 10 wt% solution, and evaluated T_{cp} from the extrapolation method in Figure 3 is indicated in Figure 4. The T_{cp} of P(CVE-MA)-4/BuAc was much higher than that of other higher molecular weight polymers such as P(CVE-MA)-1, -2, and -3, and can be changed in a wide polymer concentration range from 1 w% to 10 wt%. Molecular weight dependence on T_{cp} became small as the M_w of polymer approached higher values. For these polymers, T_{cp} initially decreased significantly with increase of polymer concentration and then converged to an almost constant value above a certain polymer concentration (> 1 wt%). Similar polymer concentration dependences of T_{cp} have been reported in other water soluble polymers.[36-39]

It should be noted that the T_{cp} for P(CVE-MA)/BuAc with higher M_w is enough below the BP of BuAc (126 °C), so this LCST phase behavior is not caused by the free-volume difference between the polymer and solvent, but probably originated from some specific interaction between polymer and solvent. This kind of phase behavior of polymer solution can be conventionally described by Flory-Huggins (F-H) lattice model based on mean-field theory, in which the chemical potential of the solvent (1) and polymer (2) is expressed by Equations (1) and (2), respectively, considering that used polymers are monodisperse in molecular weight.

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

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

Here, 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 polymer in solution. χ is the thermodynamic segmental interaction parameter between polymer and solvent, and its temperature dependence is conventionally assumed by Shultz-Flory equation[40] defined by Equation (3).

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

In Equation (3), Θ is the theta temperature and ψ is the entropy parameter. The lower molecular weight polymer revealed the higher critical temperature, which means that the apparent χ value becomes larger with the increase of temperature, so the sign of parameter ψ must be negative. According to Equation (3), T_{cp} at the critical point, T_c, can be represented by Equation (4).[40]

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

Because the minimum value of T_{cp} for each polymer in Figure 4 can be regarded as the critical point, inverse of the minimum T_{cp} was plotted against $1/\sqrt{P} + 1/2P$ as shown in Figure 5. Here, P was evaluated by M_w/M_0, where M_0 = 204.6 is the molecular weight for repeating unit of P(CVE-MA). Derived values of intercept and slop for the straight line in Figure 5 give the parameters in Equations (3) and (4), and evaluated as $\Theta = 333$ K and $\psi = -1.62$. The value of $\Theta = 333$ K = 60 ºC means that BuAc is a good solvent for P(CVE-MA) below 60 ºC ($\chi < 1/2$), and above 60 °C ($\chi > 1/2$), BuAc becomes a poor solvent and the quality of solvent for polymer becomes poorer and poorer with increase in temperature, resulting in the phase separation at a certain temperature.

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

$$\Delta\mu_1(\phi',T,P)=\Delta\mu_1(\phi'',T,P) \tag{5}$$

$$\Delta\mu_2(\phi',T,P)=\Delta\mu_2(\phi'',T,P) \tag{6}$$

Here, ϕ' and ϕ'' are the volume fractions of polymer in the phase-separated dilute and concentrated solutions, respectively. For solution of polymer with its degree of polymerization is P, χ can be calculated at a given temperature T from Equation (3), and by solving Equations (5) and (6), values of ϕ' and ϕ'' for each separated phase can be obtained at the given temperature. By this procedure, binodal curves for P(CVE-MA)/BuAc with different molecular weight can be calculated, and are shown by lines in Figure 4. In these calculations, P values for P(CVE-MA)-1 (M_w = 77,200), -2 (92,200), -3 (36,400), -4 (17,500), and -5 (7,700) was assumed to be 378, 451, 178, 86, and 38, respectively. The calculated curves almost reproduced the experimental phase diagram reasonably, i.e., (i) the binodal lines exhibit lower-critical-type curve, (ii) the lines shift to lower temperature with increase in molecular weight of polymer, and (iii) when M_w is high, the lines shows sudden decrease in lower concentration region and level off in higher concentration region. The deduced value of T_{cp} = 132 °C for P(CVE-MA)-5 from BuAc/octane mixed 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 used polymers in experiments own a certain molecular weight distribution. This may be a reason why some quantitative discrepancies between the experimental and calculated T_{cp} was observed, for example, the concentration dependence of T_{cp} for P(CVE-MA)-3 was broader than the calculated binodal line, and in P(CVE-MA)-1, the calculated line locates at lower temperature region than the experimental results. In spite of these discrepancies, the trend of T_{cp} variation with polymer concentration and molecular weight can be reproduced by F-H calculation, which suggests that the LCST-type phase diagram of P(CVE-MA)/BuAc can be described within the framework of the basic F-H theory. However, the negative temperature dependence of χ parameter cannot be explained by the original concept for χ based on van Laar type segmental interaction between polymer and solvent, so some other specific interactions should exist.

Effect of Addition of Co-solvent on the T_{cp} of P(CVE-MA)/BuAc

The effect of the addition of various co-solvents on T_{cp} of P(CVE-MA)/BuAc solution was investigated by using P(CVE-MA)-2. In these experiments, the polymer concentration was fixed at 0.1 wt%. The temperature dependences of I_s in different mixed solvents are shown in Figure 6. Similarly with the behavior in pure BuAc, I_s of polymer solution increased sharply at a certain T_{cp}. When the co-solvents were benzene, toluene, cyclohexane, and 1,2-dichloroethane, T_{cp} decreased with the increase of added amounts of co-solvent in BuAc as shown in Figure 6a, 6b, 6c, and 6d, respectively, as observed in P(CVE-MA)-5/BuAc/*n*-octane solutions in Figure 2. This phenomenon can be ascribed to that these solvents make the mixed solvent more poor than BuAc, in other words, these used solvents as well as *n*-octane should be non-solvent for P(CVE-MA).

Relationship between T_{cp} and added amounts of these solvents is shown in Figure 7. There exists an overall tendency that T_{cp} of polymer solution decreased with increasing added amounts of co-solvents. In case of addition of benzene, toluene and 1,2-dichloroethane, there was a little difference among the slope of lines although the effectiveness for lowering the T_{cp} was in the following order: 1,2-dichloroethane > benzene > toluene. As for cyclohexane, it owns a highest effectiveness for lowering the T_{cp}. This means that the aliphatic cyclohexane is the most non-solvent for P(CVE-MA) among the solvents in Figure 7.

On the other hand, in Figure 6e – 6g, 2-hexanone, propyl acetate, and DMSO were used as co-solvents added to P(CVE-MA)/BuAc solutions. As 2-hexanone was added into the polymer solution in BuAc, T_{cp} shifted to higher temperature until the added weight percentage of 2-hexanone was up to 15 wt%, at which no thermoresponsive behavior was observed below 100 °C (Figure 6e). T_{cp} shifted to higher temperature slowly with increasing added amount of propyl acetate into BuAc (Figure 6f). In the experiments of addition of DMSO in Figure 6g, the solution maintained in transparent until 100 °C without any thermoresponsive behavior even when the added DMSO amounts was 2 wt%.

Figure 8 shows T_{cp} of polymer solution as a function of added amounts of solvents such as 2-hexanone and propyl acetate. It is obvious that 2-hexanone was more effective for increasing the T_{cp} of polymer solution in BuAc than propyl acetate. The behavior that T_{cp} increases with increasing addition of good solvent was also observed in aqueous poly(vinyl methyl ether) solutions, and these phenomena may be attributed to that interaction between added good solvent and polymers are much more favored than the interaction between polymer and original solvent.[41] The increase of T_{cp} in Figure 8 may be attributed to that these co-solvents interact with polymer more strongly than with BuAc. These phenomena in Figure 7 and 8 present a clue about the quality of solvent for polymer. In our experiments, P(CVE-MA) can be dissolved in 2-hexanone and propyl acetate, but can not be dissolved in solvents in Figure 7. Figure 6g shows that DMSO should be the most good solvent used in this work, and gave a pink solution by dissolution of polymer.

The slope of the curve in Figures 7 and 8 should represent the quality of solvent for P(CVE-MA). Evaluated values of the slope for the used co-solvents are listed in Table 2. For these solvents, dielectric constant (ε) and solubility parameter (δ) are also indicated; the former value relates to polarity of solvent, and the latter value is conventionally used to consider the solubility of polymer solution.[42] These lists indicate that δ values do not have linear relationship with the solubility of P(CVE-MA), on the other hand, the value of slope seems to increase with ε except for 1,2-dichloroethane. In Table 2, polar term in solubility parameter proposed by Hansene, δ_p, is also listed.[42] Values of δ_p and the slope have similar relationship with the case of ε. In Figure 9, values of slope are plotted against δ_p, which shows good linear relationship except for 1,2-dichloroethane. Therefore, except for the results of 1,2-dichloroethane, we can point out that the solvent quality of P(CVE-MA) is determined by the polarity of the solvent. As reported in our recent studies,[21,43] THF is good solvent for P(CVE-MA), and *n*-hexane is non-solvent. Probably, some polar interactions between P(CVE-MA) and solvent might be an important factor for solubilization, and which seems reasonable that P(CVE-MA) contains polar ether and carboxylic anhydride groups and the good solvents also contain oxygen atoms in its chemical structure, but the non-solvents are oxygen-free non-polar solvents. The LCST behavior of P(CVE-MA)/BuAc suggest that the polar interaction between polymer and solvent become weak with increase of temperature, which results in the segregation and precipitation of P(CVE-MA). Because of the similar chemical structure, 1,2-dichloroethane would prefer to make interaction between the 2-chloroethyl group in P(CVE-MA) and prevent the interaction between the polymer and BuAc, which might be the reason why 1,2-dichloroethane did not follow the linear relatioship in Figure 9.

CONCLUSION

Novel LCST-type phase behavior for polymer solutions in common organic media at mild conditions has been investigated. Alternating copolymers of 2-chloroethyl vinyl ether and maleic anhydride gave LCST-type solution when dissolved in BuAc, and T_{cp} values for higher molecular weight polymers were much lower than the boiling temperature of the solvent. With the increase of M_w of polymers, the T_{cp} of polymer solution decreased. Experimental LCST-type phase diagram of polymer solution can be reasonably described by Flory-Huggins theory. The T_{cp} of polymer solution in BuAc can be tuned by addition of co-solvent. Addition of non-solvent can decrease the T_{cp}, and addition of proper good solvent can increase the T_{cp} of polymer solution in BuAc, which can be ascribed into the polar interaction between P(CVE-MA) and solvent. Effects that can strengthen the polar interaction between polymers and solvents are inclined to increase T_{cp} of polymer solution.

In order to understand these LCST behavior of P(MA-CVE)/BuAc systems, dilute polymer solution properties such as second virial coefficient A_2 and its temperature dependency from precise light scattering or viscosity measurements around the evaluated Θ temperature (= 60 ºC) will offer useful information. Further investigations for these novel polymer solution systems with LCST-type phase behavior will be reported in our future study.

Finally, we should point out that this copolymer can be chemically modified conveniently because it has functional alkyl chloride and carboxilic anhydride groups, so developments of some research and application are expected based on this novel polymer solution in organic solvent exhibiting the tunable LCST thermoresponsive behavior at mild condition.

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Figure captions

Figure 1 Temperature dependence of scattered light intensity (I_s) of polymer solutions in BuAc with different weight-averaged molecular weight. (◇) 0.05wt% 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 =7,700). The points A, B, C and D indicate T_{cp} for each solution, and the broken lines are tangent lines in order to evaluate T_{cp}.

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

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

Figure 4 T_{cp} of polymer solutions at different polymer concentrations in BuAc. M_w is (○) 7,700, (□) 17,500, (△) 36,400, (▽) 77,200 (◇) 92,200 g/mol. For these molecular weight polymers, binodal curves were calculated by using

Equations (5) and (6), and presented by solid ($P = 38$), broken ($P = 86$), dashed ($P = 178$), thin solid ($P = 378$) and thin broken ($P = 451$) lines, respectively.

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

Figure 6 Temperature dependence of I_s of polymer solution with different added amounts of various co-solvents. (a) benzene, (b) toluene, (c) 1,2-dichloroethane, (d) cyclohexane, (e) 2-hexanone, (f) propyl acetate, (g) DMSO.

Figure 7 T_{cp} of polymer solutions in BuAc with different added amounts of co-solvents as indicated.

Figure 8 T_{cp} of polymer solutions in BuAc with different added amounts of co-solvents as indicated.

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

Table 1 Polymerization condition of P(CVE-MA) with different molecular weight.

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	2.165	5.3	2.615
AIBN / g	0.0200	0.0248	0.04	0.04	0.4
solvent / g	40	20	55	40	100
reaction temp. / °C	60	70	70	60	60
reaction time / hour	6	2	2	6	6
M_w / g/mol	77,200	92,200	36,400	17,500	7,700
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

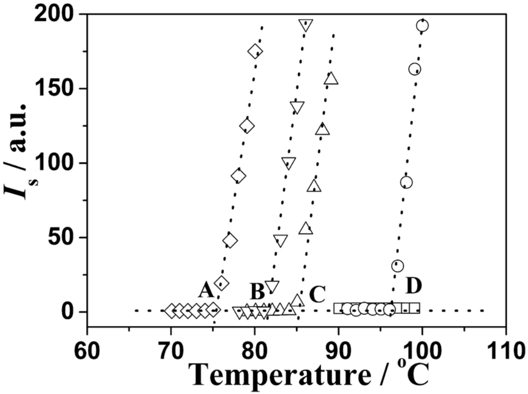
Table 2 Various physical properties of used co-solvents

co-solvent	slope[a] (ºC/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

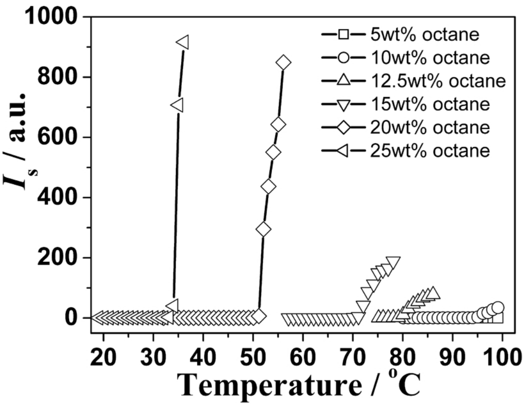
[a] Slope of the plot for T_{cp} against co-solvent's weight fraction in Figures 7 and 8.

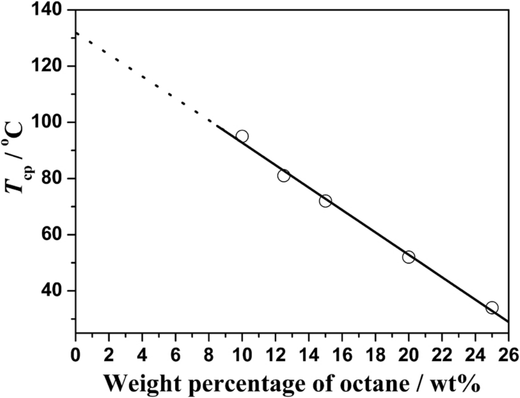
[b] Approximated value from ethyl acetate and *n*-butyl acetate.

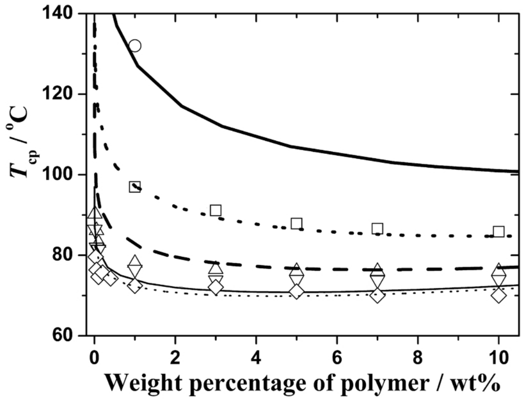
[c] Approximated value from 2-butanone and cyclohexanone.

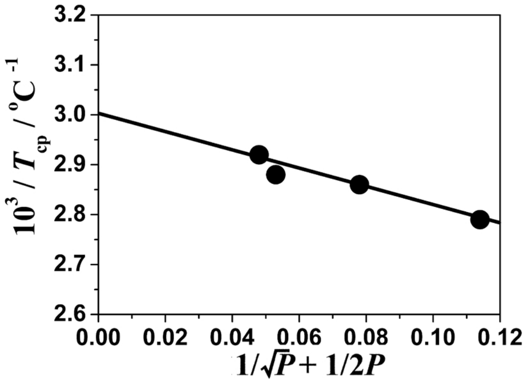


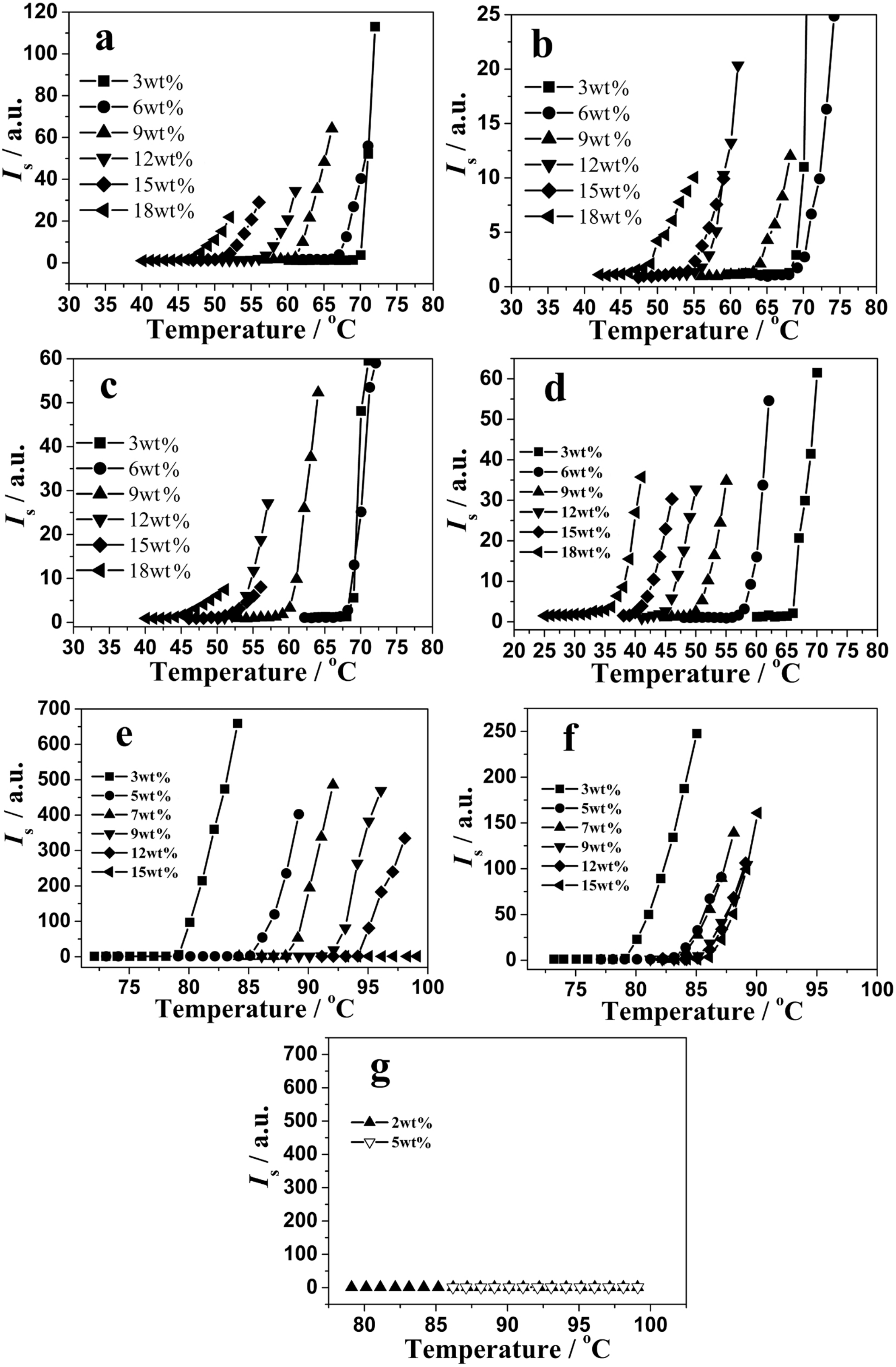
I_s / a.u.
200
150
100
50
0
60
70
80
90
100
110
Temperature / °C
A
B
C
D

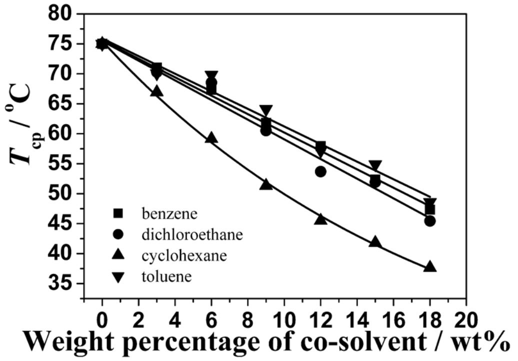

1000
800
600
400
200
0
I_s / a.u.
20
30
40
50
60
70
80
90
100
Temperature / °C
5wt% octane
10wt% octane
12.5wt% octane
15wt% octane
20wt% octane
25wt% octane


T_{cp} / °C
140
120
100
80
60
40
0
2
4
6
8
10
12
14
16
18
20
22
24
26
Weight percentage of octane / wt%

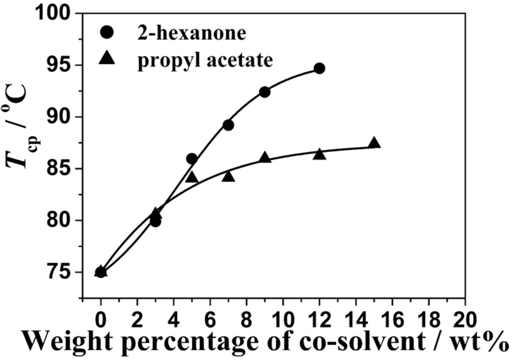

T_{cp} / ^{0}C
140
120
100
80
60
0
2
4
6
8
10
Weight percentage of polymer / wt%

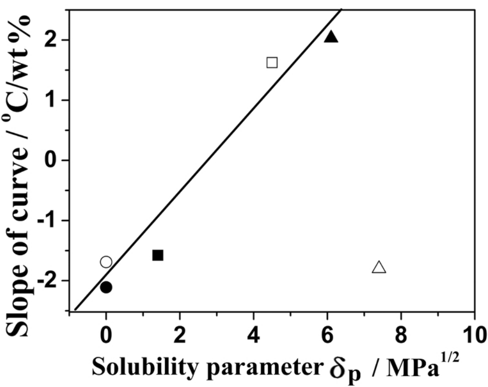

3.2
3.1
3.0
2.9
2.8
2.7
2.6
$10^3 / T_{cp} / {}^oC^{-1}$
0.00
0.02
0.04
0.06
0.08
0.10
0.12
$1/\sqrt{P} + 1/2P$


a
3wt%
6wt%
9wt%
12wt%
15wt%
18wt%
I_s / a.u.
0 20 40 60 80 100 120
30 35 40 45 50 55 60 65 70 75 80
Temperature / ^{o}C
b
3wt%
6wt%
9wt%
12wt%
15wt%
18wt%
I_s / a.u.
0 5 10 15 20 25
30 35 40 45 50 55 60 65 70 75 80
Temperature / ^{o}C
c
3wt%
6wt%
9wt%
12wt%
15wt%
18wt%
I_s / a.u.
0 10 20 30 40 50 60
30 35 40 45 50 55 60 65 70 75 80
Temperature / ^{o}C
d
3wt%
6wt%
9wt%
12wt%
15wt%
18wt%
I_s / a.u.
0 10 20 30 40 50 60
20 25 30 35 40 45 50 55 60 65 70 75 80
Temperature / ^{o}C
e
3wt%
5wt%
7wt%
9wt%
12wt%
15wt%
I_s / a.u.
0 100 200 300 400 500 600 700
75 80 85 90 95 100
Temperature / ^{o}C
f
3wt%
5wt%
7wt%
9wt%
12wt%
15wt%
I_s / a.u.
0 50 100 150 200 250
75 80 85 90 95 100
Temperature / ^{o}C
g
2wt%
5wt%
I_s / a.u.
0 100 200 300 400 500 600 700
80 85 90 95 100
Temperature / ^{o}C



80
75
70
65
60
55
50
45
40
35
T_{cp} / ^{o}C
0
2
4
6
8
10
12
14
16
18
20
Weight percentage of co-solvent / wt%
■ benzene
● dichloroethane
▲ cyclohexane
▼ toluene


● 2-hexanone
▲ propyl acetate
T_{cp} / ^{0}C
100
95
90
85
80
75
0
2
4
6
8
10
12
14
16
18
20
Weight percentage of co-solvent / wt%


Slope of curve / °C/wt %
2
1
0
-1
-2
0
2
4
6
8
10
Solubility parameter δp / MPa1/2