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**Thermoresponsive phase behavior of poly(2-chloroethyl vinyl
ether-alt-maleic anhydride) solutions in propyl acetate/*n*-alkane
mixed solvents**

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Abstract

Thermoresponsive phase behavior of poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride) (P(CVE-MA)) in mixed solvent of propyl acetate (PrAc) and *n*-alkane has been investigated. At a proper solvent composition of PrAc/*n*-octane, the polymer solution was transparent at lower temperature, and became turbid with heating, which suggest that this polymer solution exhibits lower critical solution temperature (LCST) type phase behavior. Controllability of the cloud point of the polymer solution was studied by light scattering technique. At the fixed polymer concentration of 1 mass%, the cloud point value changed from 76 °C to 31 °C with increasing the *n*-octane content from 6 to 16 mass% in the mixed solvent, with excellent linear relationship. The cloud point curve plotted against polymer concentration shifted to higher temperature with decreasing molecular weight of P(CVE-MA). The cloud point curve also shifted to higher temperature when the chain length of the added *n*-alkane became longer, and this result was explained by *n*-alkane's polarity and molecular size.

Keywords: phase behavior; lower critical solution temperature (LCST); organic media; thermoresponsive polymer

Introduction

Lower critical solution temperature (LCST)-type thermoresponsive polymer solutions, which are transparent at low temperature and become turbid at high temperature, have been attracted significant attention due to its potential applications, including controlled drug delivery [1], two-phase separation technology [2], environmental sensing [3] and so on [4-6].

In past references, following approaches have been investigated in order for molecular design of LCST-type polymers in aqueous solution. One of them is to use a special monomer having hydrophobic-hydrophilic balance, for example, polyacrylamides [7], poly(N-isopropylacrylamide) (PNIPAM) [8,9] and poly(N-isopropylmethacrylamide) [10]. The other approach is a copolymerization of hydrophilic and hydrophobic monomers. For example, in aqueous solution of copolymer of vinyl acetate and N-vinylamide, phase separation into polymer-rich and polymer-poor phases occurred by dehydration of bounded water molecules upon heating, which induced its LCST-type phase behavior [11].

LCST-type thermoresponsive phase behavior has been also observed in a conventional polymer solution in organic media, however, its critical temperature is usually much higher than the boiling point of the solvent [12,13]. In this case, a large difference of free volume between polymer and solvent at high temperature is pointed out to cause the phase separation. This tough experimental condition restricted their research and application to a large extent [12,13]. Recently, a few novel solution systems revealing LCST-type phase separation at mild conditions in organic media

have been reported. Ueki et al. reported LCST behavior of polymers having solvophilic and solvophobic structures in an ionic liquid solution [14]. Seno et al. prepared vinyl ether polymers with imidazolium and pyridinium salt pendants, which revealed LCST-type phase separation in organic solvents at a relatively low temperature [15]. These systems obviously contain strongly polar groups and certain interactions between polymer and solvent, so the origin of the thermoresponsive phase behavior should be similar to the LCST-type aqueous polymer solutions with polymer-solvent hydrogen bonds. Sawada and co-workers reported LCST behavior of fluoroalkyl end-capped co-oligomeric nanoparticle in organic media, such as *tert*-butyl alcohol, due to its oleophilic–oleophobic balance [16-19].

In our previous report, thermoresponsive LCST-type phase behavior of poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride) (P(CVE-MA), see Scheme 1) in organic media, such as *n*-butyl acetate, has been reported [20-22]. P(CVE-MA) and solvent have no strongly polar functional group. Their solution was transparent at low temperature, but became turbid upon heating by phase separation, and the transition temperature was enough lower than the boiling point of the solvent. We pointed out that these solutions are novel LCST-type systems, because they were observed in conventional organic media and under mild conditions. [20-22].

In this study, LCST-type phase behavior of P(CVE-MA) in mixed solvents of propyl acetate (PrAc) and *n*-alkane have been investigated, with special focus on the influences of solvent composition, chain length of *n*-alkane, and molecular weight of the polymer. As well known, there are several methods for cloud point measurements,

such as visual observation [23], turbidity [24], light scattering [25], viscometry [26] and so on [27]. In this study, the light scattering technique was adopted in order to evaluate the cloud point of the solution more accurately. The effects of the above-mentioned parameters on LCST-type phase behavior will be presented by a form of phase diagram, which will provide some useful information for understanding this novel phase separation behavior and for controllability of the cloud point. It should be noted that P(CVE-MA) can be chemically-modified conveniently because it has functional alkyl chloride and carboxylic anhydride groups. Therefore, the obtained results in this paper are expected to discover applications of the tunable LCST behavior under mild condition as thermoresponsive smart materials, such as thermosensitive sensors, controlled release systems, dispersion stabilizers, and so on.

Experimental section

Materials

Materials used for polymer synthesis are as follows. Sodium hydroxide (NaOH; Nacalai tesque, [Kyoto, Japan](#); 97 %), anhydrous sodium sulfate (Na_2SO_4 ; Nacalai tesque; 97%), calcium hydride (CaH_2 ; Nacalai tesque; EP), and 2,2'-azobisisobutyronitrile (AIBN; Wako, [Osaka, Japan](#); >98%) were used as received. 2-Chloroethyl vinyl ether (CVE; TCI, [Tokyo, Japan](#); >97%) was washed three times with equal volume of NaOH aqueous solution, dried with Na_2SO_4 and refluxed in the presence of CaH_2 for 2h and distilled in reduced pressure. Maleic anhydride (MA; TCI; >99.0%) was recrystallized in benzene. 2-Butanone (MEK; TCI; >99.0%) and

tetrahydrofuran (THF; Wako; >99.5%) were refluxed in the presence of CaH₂ for 2h and distilled in normal pressure. Diethyl ether (Kishida Chemical, [Osaka, Japan](#); >99.0%) and methanol (Kanto Chemical, [Tokyo, Japan](#); >99.8%) were used without further purification.

For the cloud point measurements, propyl acetate (PrAc; TCI; manufacture purity >98.0% by GC), *n*-hexane (Kishida Chemical; manufacture purity 96% by GC), *n*-octane (TCI; manufacture purity >97.0% by GC), *n*-decane (TCI; manufacture purity >99.0% by GC) and *n*-dodecane (TCI; manufacture purity >99.0% by GC) were used without further purification.

Synthesis Procedure of P(CVE-MA)

Copolymerization of MA and CVE was carried out by typical free-radical solution polymerization. MA, CVE, solvent and AIBN were added into a three-necked flask equipped with a condenser and an inlet of nitrogen gas. The solution was stirred for 6~8 h at a certain fixed temperature. The used amounts of reagent are shown in Table 1. The resultant polymer was precipitated and stirred in diethyl ether for a day and dried in vacuum above 100 °C for 12 h. The polymer for measurements was used immediately after preparation and vacuum drying in order to avoid degradation, oxidation, or water absorption.

Characterization

Molecular Weight Measurement

Molecular weight of P(CVE-MA) was measured by gel permeation chromatography (GPC). The GPC apparatus (HLC-8020, Tosoh, [Tokyo, Japan](#)) was equipped 2 columns of TSKgel. Flow rate of *N,N*-dimethylformamide (DMF)/lithium bromide (LiBr) (the concentration of LiBr in DMF was 15 mg/L) was 1.0 mL/min. Refractive index detector and polystyrene standards were used for molecular weight calibration.

Preparation of Polymer Solution

Certain amount of polymer was added into PrAc and then the sample was kept in an oven at 60 °C for a moment in order to dissolve P(CVE-MA) quickly. After the polymer was dissolved absolutely, *n*-alkane was added as co-solvent into the solution. The prepared solution was sealed and stayed in a refrigerator at about 3 °C in order for preventing the solvent evaporation and dissolving the polymer completely below LCST.

LCST Measurements

Light scattering (LS) measurements were performed by a laboratory-made apparatus equipped with an ALV/SO-SIPD detector (ALV, [Langen, Germany](#)) using a He-Ne laser (the wavelength $\lambda_0 = 633$ nm) [28]. Sample solutions were optically purified by a Millipore filter (Millipore, [Billerica, MA, USA](#)) of nominal pore size of 1.0 μm and transferred into optical tube. The heating rate of system was about 0.2 °C/min. The thermoresponsive phase behavior was evaluated by scattered light intensity at different temperatures at a fixed scattering angle of 90°. The scattered light intensity was recorded immediately as the temperature of the system increased to

the desired value, and its uncertainty was $\pm 10\%$. The measured intensity was plotted against temperature, and the point at which the intensity increased sharply was defined as the cloud point of the polymer solution, as shown in [22]. From the repeated experimental measurements, the uncertainty of the measured cloud point was evaluated to be $\pm 0.5\text{ }^\circ\text{C}$.

Results and Discussion

Synthesis and Characterization of Copolymer

MA and CVE are reported to have no radical homopolymerizability [29,30], and an alternating structure of MA and CVE in the obtained copolymer had been confirmed by NMR spectrum [20]. The polymers with different molecular weights were synthesized by changing reaction conditions and amounts of reactant. In Table 1, values of weight- and number-averaged molecular weight (M_w and M_n , respectively) and molecular weight distribution index (M_w/M_n), evaluated from GPC measurement, are listed. M_w of P(CVE-MA) polymerized in THF was much lower than that in MEK, and similar result was also pointed out in [31]. Their mass fraction purities by ^1H NMR were at least 0.99.

===== Table 1 =====

Effects of *n*-Alkanes as Co-solvent

Effect of the added *n*-alkanes on the phase behavior of P(CVE-MA) solution in PrAc/*n*-alkane mixed solvent was investigated, by using P(CVE-MA) with $M_w = 9.03$

$\times 10^4$. Values of the scattered light intensity are plotted against the measured temperatures in Fig. 1. The intensity was weak at low temperature, and exhibited abrupt increase at a certain temperature in heating scan. That is to say, the polymer solution was clear at low temperature, and became cloudy as a result of phase separation above a critical temperature. In Figs. 1a – 1c, the effects of *n*-octane content as co-solvent on cloud point of P(CVE-MA)/PrAc solution are represented. The cloud point, defined as the temperature at which the scattered light intensity increased sharply, was higher than 100 °C when the mass percentage of *n*-octane in the mixed solvent was enough low. On the contrary, the solution was turbid even at room temperature when the *n*-octane content was enough high. This phenomenon suggests that the cloud point of polymer solution can be regulated in a wide range by changing the *n*-octane content. In this study, we used PrAc/*n*-alkane mixed solvents containing 6–16 mass% *n*-alkane, because of the temperature limitation of the LS apparatus.

===== Fig. 1 =====

The obtained cloud point values are listed in Table 2, and plotted against polymer concentration in Fig. 2 in order to obtain phase diagram for solutions with different *n*-alkane content. The higher the *n*-octane content in the solvent, the lower the cloud point of copolymer solution becomes. This result means that the one-phase transparent region becomes narrower with the increase of *n*-octane content, because PrAc is a good solvent and *n*-octane is a non-solvent for P(CVE-MA). Shapes of the phase diagrams with different *n*-octane contents are almost same, i.e., the cloud point

decreased with increasing of polymer concentration in dilute region, and then becomes almost constant at higher concentration region. Similar phase diagrams for LCST-type polymer solutions have been reported in other polymer systems, such as PNIPAM [32], poly(N-vinylacetamide-co-vinylacetate) [11] and so on [3,33].

===== Table 2, Fig. 2 =====

The effect of *n*-octane content on the cloud point was further investigated at a fixed polymer concentration of 1 mass%. As shown in Fig. 3a, the temperature at the abrupt increase in scattered light intensity shifted to lower temperature region with increase of *n*-octane content. The evaluated cloud points are listed in Table 3, and plotted against the *n*-octane content, which reveals excellent linear relationship as shown in Fig. 3b.

===== Table 3, Fig. 3 =====

Effect of the chain length of *n*-alkane was investigated by using *n*-hexane, *n*-decane, and *n*-dodecane with fixing the *n*-alkane content as 12 mass%. In these measurements, P(CVE-MA) with $M_w = 9.30 \times 10^4$ was used. The evaluated cloud points are listed in Table 4, and plotted against polymer concentration in Fig. 4. From this phase diagram, we can point out that *n*-hexane and *n*-octane decreased the cloud point most effectively, although the difference between *n*-decane or *n*-dodecane was small. The ability to decrease the cloud point was in the following order: *n*-dodecane < *n*-decane < *n*-octane \approx *n*-hexane.

===== Table 4, Fig. 4 =====

As pointed out in our previous report [21], dielectric constant (ϵ_r) or polarity term

in solubility parameter (δ_p) of the co-solvent added to *n*-butyl acetate influenced the cloud point value, for example, the co-solvent with higher ϵ_r increased the cloud point. The value of ϵ_r at 25 °C is reported to be 1.88 for *n*-hexane, slightly increases with the chain length, and $\epsilon_r = 2.01$ for *n*-dodecane [34]. The results in Fig. 4 can be explained by the same reason, i.e., the cloud point increased gradually with increasing of ϵ_r of *n*-alkane. As discussed in the previous report [21], possible reason for the LCST-type thermosensitive behavior of P(CVE-MA) solution should be owing to some specific polar interaction between P(CVE-MA) and PrAc, and the addition of *n*-alkanes weakens the interaction between PrAc and solvated polymer molecule. In addition, the shorter alkyl chain is possible to obstruct the interaction between P(CVE-MA) and PrAc, because the small-size co-solvent is easier to come close to the interacting site. Therefore, the influence of the addition of *n*-dodecane on the phase behavior was smaller than other shorter *n*-alkanes because of its higher polarity and larger molecular size. These effects should be similar in *n*-hexane and *n*-octane, as found by the almost overlapped phase diagrams for PrAc/*n*-hexane and PrAc/*n*-octane.

Effects of Molecular Weight

In this section, four P(CVE-MA) samples with different M_w were used to investigate the influence of M_w on the cloud point of P(CVE-MA)/PrAc/*n*-octane solution. The *n*-octane content of the mixed solvent was fixed at 12 mass%.

Results of the scattered light intensity measurements of P(CVE-MA) solutions

with $M_w = 15.3 \times 10^4$ and 1.79×10^4 are shown in Figs. 5a and 5b, respectively. With the decrease in M_w , the experimental temperature range was shifted to higher region, suggesting the increase of the cloud point. The intensity of the scattered light increased more drastically in Fig. 5a than in 5b, as found by the scale of the vertical axis. The same trend was also observed in visual observation by naked eye, i.e., the turbidity of solutions having same polymer concentration was more remarkable in higher-molecular-weight P(CVE-MA). In the lowest-molecular-weight P(CVE-MA), as shown in Fig. 5b, the increase of the scattered light intensity at the cloud point was not distinct, especially in dilute solution less than 0.1 mass%.

===== Fig. 5 =====

Fig. 6 shows the phase diagrams of P(CVE-MA) with different M_w , in PrAc/*n*-octane mixed solvent with 12 mass% *n*-octane content. Numerical data for Fig. 6 are listed in Tables 2 and 5. As pointed out above, the phase diagram shifted to lower temperature with the increase in M_w . The inverse M_w dependence of cloud point was also reported for P(CVE-MA) in other organic media [21,22] and LCST-type aqueous solution such as PNIPAM [35]. However, the M_w dependence for PNIPAM aqueous solution was reported to be very weak, because of the strong hydrogen bond between polymer and water molecule. On the other hand, the specific polar interaction between P(CVE-MA) and organic media, proposed in [21], should be weaker than the hydrogen bond, so their phase diagrams shifted sensitively with M_w . In other words, LCST-type cloud point of P(CVE-MA) solution can be changed largely with M_w .

===== Fig. 6, Table 5 =====

As shown in Fig. 6, the cloud point curve for the highest-molecular-weight sample ($M_w = 15.3 \times 10^4$) is almost parallel with the horizontal axis in the concentration range of 0.2–2.0 mass%. The cloud point for the lowest-molecular-weight sample ($M_w = 1.79 \times 10^4$) varied more sensitively with the concentration change. As the M_w becomes lower and lower, the position of the phase diagram shifted markedly to higher temperature region. Similar M_w dependences of the phase diagram were also observed in our previous reports [21,22].

Conclusion

LCST-type thermoresponsive phase behavior of P(CVE-MA) solution in PrAc/*n*-alkane mixed solvent was studied, and controllability of the cloud point temperature by changing the solvent composition, the chain length of *n*-alkane, and the M_w of P(CVE-MA) was investigated. P(CVE-MA)/PrAc was clear solution, and by adding *n*-octane within the range of 6–16 mass%, the solution became LCST-type thermoresponsive solution and its cloud point can be tuned from 76 °C to 31 °C with excellent linear relationship. The cloud point exhibited only small shift to higher temperature with the increase of the added *n*-alkane's chain length, and this result was explained by the polarity and molecular size of the *n*-alkane. M_w of P(CVE-MA) also exerted strong influence on the phase behavior, for example, the cloud point of 1 mass% solution increased from 45 °C to 72 °C with decreasing in M_w from 15.3×10^4 to 1.79×10^4 .

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Figure captions

Scheme 1. Chemical structure of poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride) (P(CVE-MA))

Fig. 1. Temperature dependence of scattered light intensity of polymer solution in PrAc/*n*-octane mixed solvent with different added amounts of *n*-octane: (a) 16 mass%, (b) 12 mass%, and (c) 8 mass%. Copolymer with $M_w = 9.03 \times 10^4$ was used. The polymer concentrations are 2 mass% (■), 1 mass% (●), 0.5 mass% (▲), 0.2 mass% (▼), 0.1 mass% (◆), and 0.05 mass% (▲).

Fig. 2. Plots of the cloud point for P(CVE-MA) solution in mixed PrAc/*n*-octane solvent against polymer concentration. The *n*-octane contents in the mixed solvents are 16 mass% (■), 12 mass% (●), and 8 mass% (▲). Copolymer with $M_w = 9.03 \times 10^4$ was used.

Fig. 3. (a) Temperature dependence of scattered light intensity of 1 mass% polymer solution ($M_w = 9.03 \times 10^4$) in PrAc/*n*-octane mixed solvent with *n*-octane content of 16 mass% (■), 14 mass% (●), 12 mass% (▲), 10 mass% (▼), 8 mass% (◆), and 6 mass% (▲). (b) Plots of the cloud point, derived from Fig. 3a, against *n*-octane content.

Fig. 4. Plots of the cloud point against polymer concentration for P(CVE-MA) solution ($M_w = 9.30 \times 10^4$) in PrAc/*n*-alkanes. The used *n*-alkanes are *n*-hexane (■), *n*-octane (●), *n*-decane (▲), and *n*-dodecane (▼).

Fig. 5. Temperature dependence of scattered light intensity of polymer solutions in PrAc/*n*-octane. *n*-Octane content is 12 mass%, and M_w of the used polymers are (a) 15.3×10^4 and (b) 1.79×10^4 . The polymer concentrations are 2 mass% (■), 1 mass% (●), 0.5 mass% (▲), 0.2 mass% (▼), 0.1 mass% (◆), and 0.05 mass% (▲).

Fig. 6. Plots of the cloud point against polymer concentration for P(CVE-MA) solution in PrAc/*n*-octane. The *n*-octane content is 12 mass%, and M_w of the used polymers are 15.3×10^4 (■), 9.03×10^4 (●), 4.01×10^4 (▲), and 1.79×10^4 (▼).

Table 1. Results of polymerization of 2-chloroethyl vinyl ether and maleic anhydride.

MA	CVE	AIBN	Solvent	Solvent	Temp. ^a	M_w^b	M_w/M_n
g	g	g		g	°C		
5.33	4.9	0.0512	THF	40	60	17,900	1.67
2.45	2.62	0.0402	MEK	55	70	40,100	1.58
5.33	4.90	0.0102	MEK	20	70	90,300	1.91
2.67	2.45	0.0102	MEK	10	70	93,100	1.98
2.67	2.45	0.0051	MEK	5	70	153,000	1.85

^aThe fixed reaction temperature.

^bDetermined by GPC using polystyrene standards and RI detector.

Table 2. Numerical results of the cloud point for P(CVE-MA) ($M_w = 9.03 \times 10^4$) solution in PrAc/*n*-octane.

<i>n</i> -octane content	polymer concentration	cloud point
mass%	mass%	°C
16	0.059	37.3
	0.103	35.5
	0.206	33.6
	0.520	31.2
	1.001	30.9
	1.997	29.8
12	0.054	54.7
	0.099	51.8
	0.201	50.6
	0.497	48.5
	0.998	48.0
	1.974	47.0
8	0.051	73.0
	0.101	70.6
	0.203	68.6
	0.524	66.7
	1.011	65.7
	1.968	64.7

Table 3. Numerical results of the cloud point for P(CVE-MA) ($M_w = 9.03 \times 10^4$) solution in PrAc/*n*-octane.

<i>n</i> -octane content	cloud point
mass%	°C
16.0	30.9
14.1	40.9
12.0	48.0
10.2	57.3
8.1	65.7
6.0	76.3

^aThe polymer concentration was fixed at 1 mass%.

Table 4. Numerical results of the cloud point for P(CVE-MA) ($M_w = 9.30 \times 10^4$) solution in PrAc/*n*-alkane.^a

<i>n</i> -alkane	polymer concentration	cloud point
	mass%	°C
<i>n</i> -hexane	0.048	52.5
	0.099	50.6
	0.200	48.1
	0.507	46.6
	0.988	45.2
	1.998	44.6
<i>n</i> -octane	0.051	50.2
	0.103	49.3
	0.202	47.3
	0.515	46.3
	1.005	45.2
	1.960	44.8
<i>n</i> -decane	0.048	54.2
	0.104	51.1
	0.198	50.3
	0.518	47.8
	0.996	46.2
	1.966	46.0
<i>n</i> -dodecane	0.050	55.1
	0.101	53.9
	0.203	50.6
	0.475	48.9
	1.006	49.2
	1.969	47.7

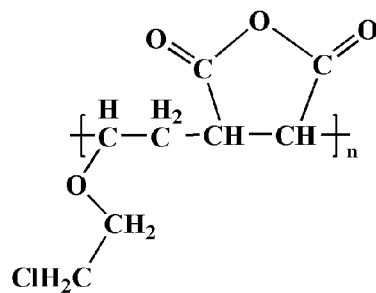
^aThe *n*-alkane content was fixed at 12 mass%.

Table 5. Numerical results of the cloud point for P(CVE-MA) solution in PrAc/*n*-octane.^{a,b}

M_w of P(CVE-MA)	polymer concentration	cloud point
	mass%	°C
15.3×10^4	0.049	51.3
	0.103	48.9
	0.206	47.1
	0.510	46.6
	1.009	45.4
	1.972	45.6
4.01×10^4	0.054	62.8
	0.119	61.5
	0.212	57.6
	0.517	54.0
	1.005	53.1
	1.976	51.9
1.79×10^4	0.111	84.3
	0.208	77.2
	0.510	73.5
	1.007	68.9
	1.967	66.0

^aThe *n*-octane content was fixed at 12 mass%.

^bThe data for $M_w = 9.03 \times 10^4$ are listed in Table 2.



Scheme 1. Chemical structure of poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride) (P(CVE-MA))

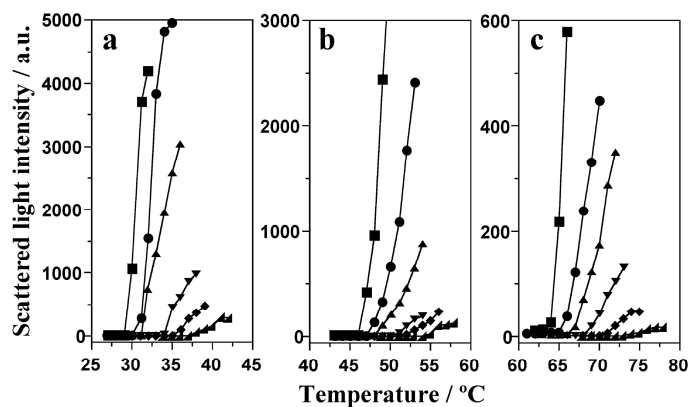


Fig. 1. Temperature dependence of scattered light intensity of polymer solution in PrAc/*n*-octane mixed solvent with different added amounts of *n*-octane: (a) 16 mass%, (b) 12 mass%, and (c) 8 mass%. Copolymer with $M_w = 9.03 \times 10^4$ was used. The polymer concentrations are 2 mass% (■), 1 mass% (●), 0.5 mass% (▲), 0.2 mass% (▼), 0.1 mass% (◆), and 0.05 mass% (▲).

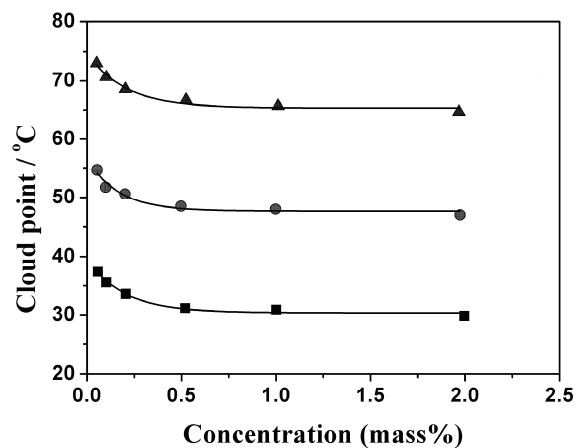


Fig. 2. Plots of the cloud point for P(CVE-MA) solution in mixed PrAc/*n*-octane solvent against temperature. The *n*-octane contents in the mixed solvents are 16 mass% (■), 12 mass% (●), and 8 mass% (▲). Copolymer with $M_w = 9.03 \times 10^4$ was used.

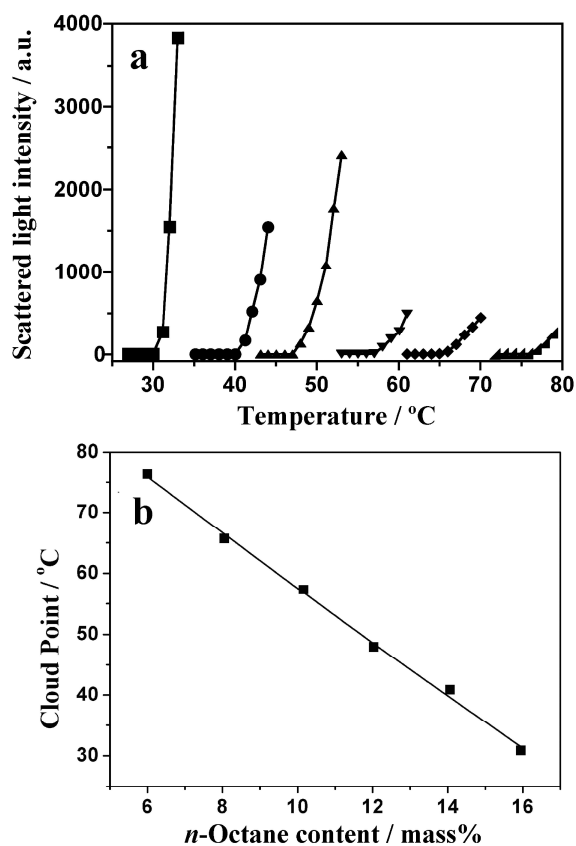


Fig. 3. (a) Temperature dependence of scattered light intensity of 1 mass% polymer solution ($M_w = 9.03 \times 10^4$) in PrAc/*n*-octane mixed solvent with *n*-octane content of

16 mass% (■), 14 mass% (●), 12 mass% (▲), 10 mass% (▼), 8 mass% (◆), and 6 mass% (▲). (b) Cloud point of polymer solution at different *n*-octane content, derived from (a).

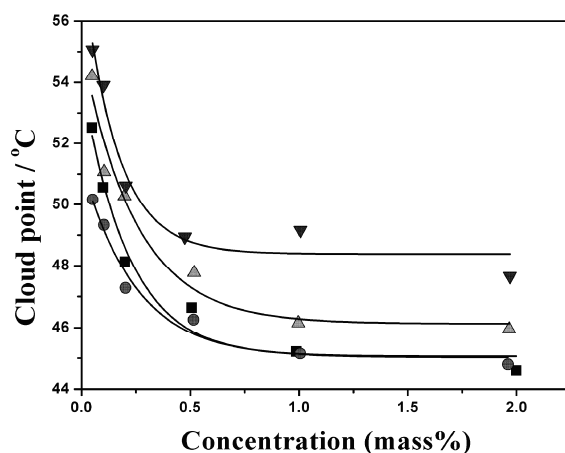


Fig. 4. Plots of the cloud point against temperature for P(CVE-MA) solution ($M_w = 9.30 \times 10^4$) in PrAc/*n*-alkanes. The used *n*-alkanes are *n*-hexane (■), *n*-octane (●), *n*-decane (▲), and *n*-dodecane (▼).

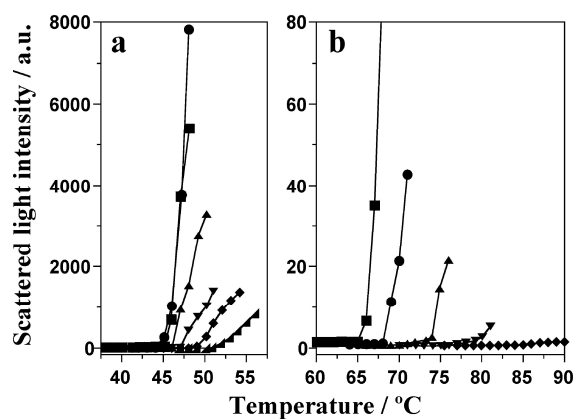


Fig. 5. Temperature dependence of scattered light intensity of polymer solutions in PrAc/*n*-octane. *n*-Octane content is 12 mass%, and M_w of the used polymers are (a) 15.3×10^4 and (b) 1.79×10^4 . The polymer concentrations are 2 mass% (■), 1 mass% (●), 0.5 mass% (▲), 0.2 mass% (▼), 0.1 mass% (◆), and 0.05 mass% (▲).

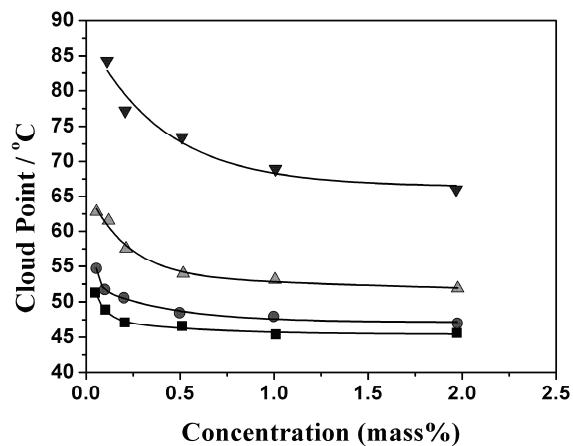


Fig. 6. Plots of the cloud point against temperature for P(CVE-MA) solution in PrAc/*n*-octane. The *n*-octane content is 12 mass%, and M_w of the used polymers are 15.3×10^4 (■), 9.03×10^4 (●), 4.01×10^4 (▲), and 1.79×10^4 (▼).