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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.

1. 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 solvatophilic and solvatophobic 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

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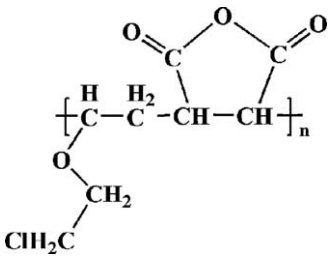

Scheme 1. Chemical structure of poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride) (P(CVE-MA)).

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.

2. Experimental

2.1. 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 2 h 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 CaH_2 for 2 h 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.

2.2. 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.

2.3. Characterization

2.3.1. 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.

2.4. 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.

2.5. 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 ±10%. The measured intensity was plotted against temperature, and the point at which

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

MA (g)	CVE (g)	AIBN (g)	Solvent	Solvent (g)	Temp.[a] (°C)	M_w [b]	M_w/M_n
5.33	4.90	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

[a] The fixed reaction temperature.
[b] Determined by GPC using polystyrene standards and RI detector.