

Thermoreversible UCST-type Phase Behavior of Comb-like Poly(*N*-phenyl maleimide-*co*-*n*-octadecyl vinyl ether) in Organic Media

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Abstract

Comb-like copolymer of *N*-phenyl maleimide and *n*-octadecyl vinyl ether was synthesized by conventional free radical solution polymerization. The molecular weight and molecular weight distribution were measured by GPC. The chemical composition of copolymer was characterized by FT-IR, ¹H NMR and ¹³C NMR, and the results indicated that the obtained copolymer contained much more content of *N*-phenyl maleimide rather than equal molar ratio of monomer unit. The comb-like copolymer can exhibit upper critical solution temperature thermoresponsive phase behavior reversibly in *N,N*-dimethylformamide and some proper alcohols such as 1-butanol, 1-hexanol, etc. The effect of polymer concentration and co-solvent on thermoresponsive behavior of polymer solution was investigated, and the cloud point of polymer solution can be tuned conveniently. The high resolution ¹H NMR method was used to comprehend the reversible thermoresponsive behavior in molecular level and the results revealed that as temperature decreased the pendent long alkyl side chain aggregated and phase separation occurred at cloud point temperature, however, the mobility of main polymer chain decreased at lower temperature.

Keywords: stimuli-sensitive polymer · thermoresponsive polymer · upper critical solution temperature · phase behavior · solution properties

Introduction

Thermoresponsive polymers can respond to change of temperature in the environment, and as one class of stimuli responsive polymers many important applications such as sensors [1], controlled release [2,3], intelligent gels [4,5] and smart materials [6] have been developed. Usually, there exist two kinds of solution phase behavior according to the phase diagram. One is that polymer solution is homogeneous at lower temperature and becomes heterogeneous at higher temperature. In this case, the polymer solution owns lower critical solution temperature (LCST) and this thermoresponsive behavior can be called LCST-type phase behavior. In contrast, the other behavior is that polymer solution is homogeneous at higher temperature and phase separation will occur at lower temperature. This kind of polymer solution presents upper critical solution temperature (UCST) in the phase diagram and this phase behavior is called UCST-type. UCST-type as well as LCST-type polymer solution has been studied a lot in the past [7-9] and the enthusiasm for research on thermoresponsive polymers is still full nowadays [10-13].

LCST-type thermoresponsive water soluble polymer systems have been paid much attention and many theories and applications have been developed [8,9,12,14], and UCST-type thermoresponsive polymer systems also attract much research interest in the past and nowadays [15-17], for example, aqueous solution systems for some applications such as drug delivery [18,19]. It is also necessary and important to investigate the UCST-type phase behavior of polymer in organic media [16,17], which can help to understand the properties of polymer solution and can present some useful clues for some industrial applications [16,20-25].

Recently, besides those studies on the conventional UCST-type polymer solutions [16,17], some new UCST-type thermoresponsive polymer systems, in which the phase separation and the cloud point (CP) of polymer solutions in organic media can be well tuned, have been attracting much attention [26-31]. Stereocontrolled poly(*N*-isopropylacrylamide) can exhibit UCST-type thermoresponsive behavior and study on the UCST-type behavior of stereocontrolled poly(*N*-isopropylacrylamide) in organic media can help to understand the rule of tacticity of polymer chain on thermoresponsive behavior [26]. Poly(vinyl ethers) with proper pendants can exhibit UCST-type phase behavior in some certain organic media, and phase separation can be controlled by solvent species, polymer concentration and so on [28,29]. Recently well-tunable UCST-type phase behavior of poly[oligo(ethylene glycol) methyl ether methacrylate] in organic media was also studied, and the CP of polymer solution in organic media depended on the solvent species, addition of co-solvent, molecular weight and chemical structure of polymer chain [30]. As polymer chains were grafted onto the surface of some colloid particles, based on the UCST-type thermoresponsive behavior in organic media, the aggregation of related colloidal particles can be controlled by temperature, e.g., temperature-induced aggregation of magnetic nanoparticles grafted by poly(2-methoxyethyl methacrylate) in methanol [27] or polystyrene in cyclohexane [31]. Based on UCST-type behavior in organic media some potential applications may be developed, for instance smart materials or self assembly of related macromolecules.

Herein a novel reversible thermoresponsive UCST-type behavior in organic media is reported. The copolymer of *N*-phenyl maleimide and *n*-octadecyl vinyl ether can exhibit UCST-type behavior in some proper organic media and the CP of polymer solution can be tuned by some aspects such as solvent and addition of co-solvent conveniently.

Experimental

Materials

Toluene (Nacalai tesque; 99.5%), dimethylsulfoxide (DMSO; Kishida Chemical Co. LTD; 99%), azobisisobutyronitrile (AIBN; Wako; > 98%), ethylene glycol (Nacalai tesque; 99%), 1-butanol (Nacalai tesque; 99%), 1-octanol (TCI; >98.0%), 1-hexanol (TCI; >98.0%), *n*-octadecyl vinyl ether (ODVE; TCI; >85.0%), *N*-phenylmaleimide (PMI; TCI; >97%), ethanol (Nacalai tesque; 99.5%), ethylene glycol (EG; Nacalai tesque; 99%), diethyl ether (Kishida Chemical Co. LTD; >99.0%), chloroform (Wako; >99.0%), 1,2-dichloroethane (Nacalai tesque; 99.5%), dichloromethane (Nacalai tesque; 99.5%), 1,4-dioxane (Kishida Chemical Co. LTD;>99.0%), methanol (Kanto Chemical Co. LTD; >99.8%), isopropanol (Nacalai tesque; 99.7%) acetone

(Kishida Chemical Co. LTD;>99.0%), cyclohexane (Nacalai tesque; 99.5%), benzene (Nacalai tesque; 99.5%), *N,N*-dimethylformamide (DMF; Nacalai tesque; 99.5%), *N,N*-dimethylacetamide (DMAc; Kishida Chemical Co. LTD; 99.0%), chloroform- d_1 ($CDCl_3$; SCETI Co. LTD; 99.9%), *N,N*-dimethylformamide- d_7 (DMF- d_7 ; Aldrich; 99.5 atom% D) were used as received.

Synthesis of polymers

N-Phenyl maleimide (2.165 g), *n*-octadecyl vinyl ether (3.707 g), AIBN (0.01 g), toluene (15 g) were added into a 50 mL three-neck flask. The reaction was carried out at an atmosphere of nitrogen at 70 °C for 4 hours. Resultant copolymer solution was poured into ethanol and precipitated polymers were filtered and dried in vacuum drying oven at 80 °C for 12 hours.

Gel Permeation Chromatograph (GPC)

Molecular weight of the prepared copolymer was determined by GPC using 2 columns of TSKgel -3000 and -5000 connected to SD-8022 system (Tosoh) at a 1.0 mL/min flow rate of THF. Polystyrene standards were used for molecular weight calibration.

FT-IR measurement

Infrared spectrum of copolymer was recorded in a Nicolet AVATAR 320S FT-IR spectrophotometer in KBr pellet.

1H NMR measurement

1H NMR in $CDCl_3$: Polymer solution with 1wt.% polymer concentration was added into a NMR tube with an outer diameter of 5 mm, and 1H NMR spectrum in $CDCl_3$ at 40 °C was measured using BRUKER AVANCE 600 (600 MHz) spectrometer.

1H NMR in DMF- d_7 : Polymer solution with 1wt.% polymer concentration was added into a NMR tube with an outer diameter of 5 mm, and 1H NMR spectra in DMF- d_7 at different temperature were measured using BRUKER AVANCE 600 (600 MHz) spectrometer. The temperature was heated to the desired value and kept constant at least in 10 minutes, and then the 1H NMR spectrum was measured at the desired temperature. Scanning times was 128, [the resolution of the spectrum was \$2.1 \times 10^{-4}\$ ppm](#), and receiver gain was kept constant in all NMR measuring experiments.

^{13}C NMR measurement

Polymer solution with 10wt.% polymer concentration was added into a NMR tube with an outer diameter of 5 mm, and ^{13}C NMR spectrum in $CDCl_3$ at room temperature was measured using BRUKER AVANCE 200 (50 MHz) spectrometer.

Preparation of polymer solution

Polymer solutions were prepared by dissolving certain amount of polymer in various organic solvents above temperature of cloud point (T_{cp}), above which polymer can dissolve in solvent resulting in a homogeneous transparent solution.

5-2-8 Static Light Scattering (SLS) Measurement

Thermoresponsive phase behavior of the polymer solution was characterized by the scattered light intensity (I_s) at different temperatures at a fixed angle of 90° [32-34]. I_s was measured by a laboratory-made apparatus equipped with an ALV/SO-SIPD detector using He-Ne laser (the wavelength $\lambda_0 = 633$ nm) [35]. The transparent polymer solution above T_{cp} was transferred into optical tube immediately and then the static light scattering (SLS) measurement was carried out

directly. The heating and cooling rate of the system was about 0.2 °C/min. I_s of the polymer solution was measured immediately as the temperature of the system reached the desired temperature. Unless pointing out, the I_s was measured during cooling process.

Results and discussion

Synthesis of copolymer

It is well known that the copolymer of maleimide owned some useful applications such as thermo stable materials, Langmuir-Blodgett (LB) films and functional surface [36-39]. Herein, copolymer of *N*-phenyl maleimide (PMI) and *n*-octadecyl vinyl ether (ODVE) was synthesized by conventional free radical polymerization in the solution of toluene with AIBN as initiator and 1:1 molar mixture of PMI and ODVE. After copolymerization, copolymer of PMI and ODVE was obtained with a conversion of 60% (conversion is defined as W_p/W_m , where W_p is quantity of obtained polymer, and W_m is the total quantity of added monomer of PMI and ODVE). Due to long *n*-alkyl (*n*-octadecyl) group of ODVE, a copolymer with comb-like side chains would be obtained after copolymerization as shown in Fig. 1a. The GPC graph of synthesized copolymer is shown in Fig. 1b, and the weight-averaged molecular weight (M_w) of copolymer was 79,600 and the value of molecular weight distribution index (M_w/M_n , where M_n is the number-averaged molecular weight) was 3.06.

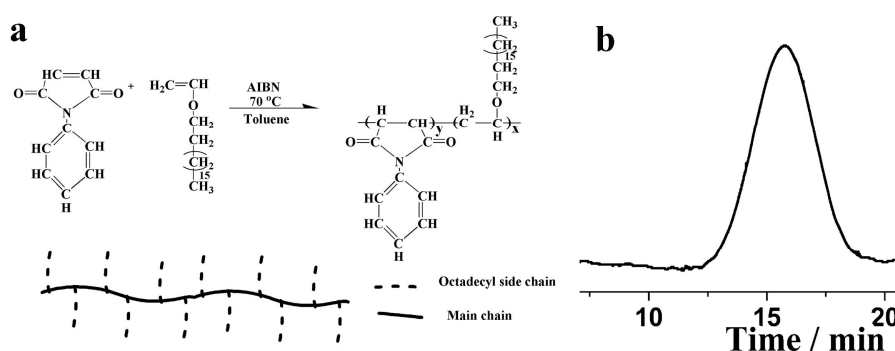


Fig. 1 (a) Scheme for synthesis and chemical architecture of copolymer. (b) GPC graph of synthesized copolymer.

In order to determine the chemical composition of copolymer, spectroscopy of FT-IR, ^1H and ^{13}C NMR was used and related spectra were shown in Fig. 2. In FT-IR spectrum, the peaks between 2932 and 2830 cm^{-1} associated with the C-H stretching vibrations. Peaks at 1467 and 1389 cm^{-1} associated with the $-\text{CH}_3$ asymmetric and symmetric vibrations. Peaks at 3070, 1193, 1082 and 750 cm^{-1} are characteristic adsorption of CH vibration of phenyl group. Peaks between 1600 and 1450 cm^{-1} associated with the C-C vibration of phenyl group. The peak around 1785 cm^{-1} should correspond to imide ring and strong peaks at 1722 cm^{-1} associated the C=O vibrations. It can be deduced from the FT-IR spectra shown in Fig. 2a that the synthesized copolymer was a copolymer of PMI and ODVE. The ^1H NMR spectrum and the assignments of proton resonances of copolymer was shown in Fig. 2b. The molar ratio of PMI to ODVE (y/x) in copolymer was calculated by the following formula,

$$\frac{y}{x} = (A_{\text{phenyl}} / 5) / (A_{\text{methyl}} / 3) \quad (1)$$

where A_{phenyl} is the integral area of protons from phenyl group in PMI unit and A_{methyl} is integral area of proton from methyl group in ODVE unit in copolymer. The calculated y/x ratio was about 1.8, which indicated that there existed much more PMI unit in the structure of copolymer, and this kind of results has been reported previously [36,40]. ^{13}C NMR spectrum of copolymer in CDCl_3 and the assignments of resonances for different protons in copolymer were shown in Fig. 2c. It can also be confirmed from the ^{13}C NMR spectrum that the synthesized polymer was a copolymer of PMI and ODVE, but we could not obtain any information about the monomer sequence in polymer chain because of very weak intensity of peaks for backbone carbons.

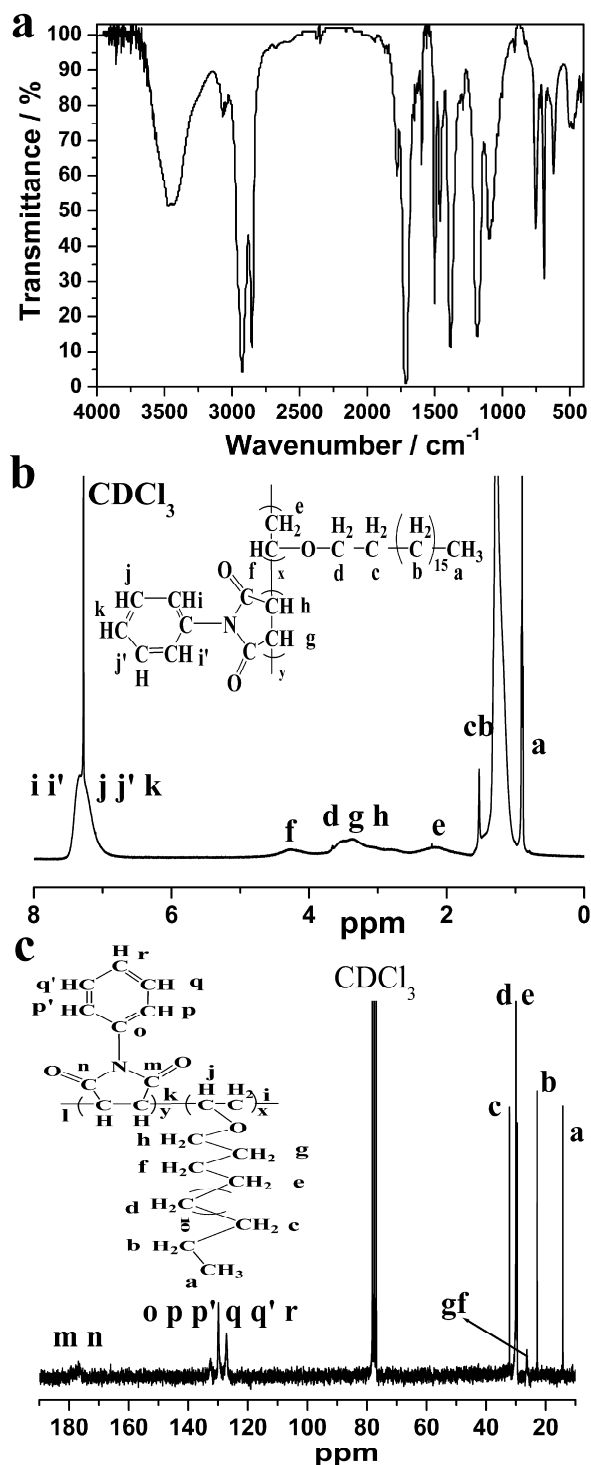


Fig. 2 (a) FT-IR spectrum, (b) ^1H NMR spectrum (600 MHz) in CDCl_3 , and (c) ^{13}C NMR spectrum (50 MHz) in CDCl_3 .

UCST-type thermoresponsive behavior of polymer solution

The thermoresponsive behavior of polymer solution was characterized by the scattered light intensity of polymer solution at different temperature at a fixed angle 90° in the measurement of SLS. The I_s of polymer solution in DMF decreased with increasing the temperature and remained constant with a small value (Fig. 3a) as the polymer solution was heated, and after that the cooling process was carried out. As the temperature is below a critical solution temperature (51°C in Fig. 3a), the I_s of polymer solution increased abruptly, and the critical temperature during the cooling process is defined as the temperature of cloud point (T_{cp}), e.g. point A in Fig. 3a. At low temperature (20°C in Fig. 3a) the polymer solution in DMF was turbid and above T_{cp} the polymer

solution was transparent (60 °C in Fig. 3a), which indicated that the polymer solution exhibited upper critical solution temperature (UCST) type behavior in DMF. Furthermore, the transition between the turbid and transparent state was reversible.

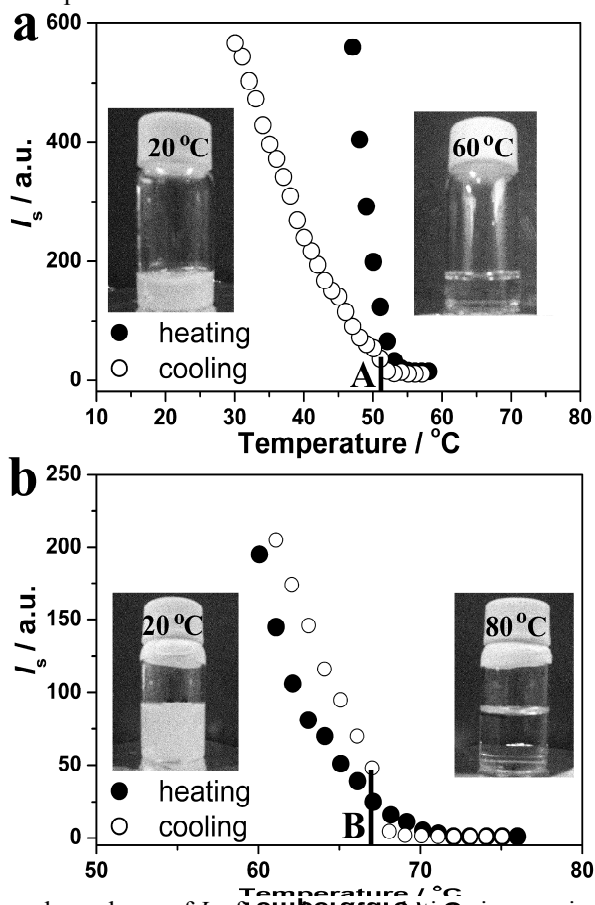


Fig. 3 Temperature dependence of I_s of copolymer solutions in organic solvent. (a) 1wt.% polymer solution in DMF, (b) 0.1 wt.% polymer solution in 1-butanol. The temperature at which photograph was taken is indicated in the graph.

Similar to the solution in DMF, polymer solution in 1-butanol also exhibit reversible UCST-type behavior. The I_s of polymer solution in 1-butanol also exhibited temperature dependence and T_{cp} defined during cooling process was a little higher, e.g., point B (67 °C) in Fig. 3b. The transition of polymer solution state between turbid (20 °C in Fig. 3b) and transparent (80 °C in Fig. 3b) was also reversible.

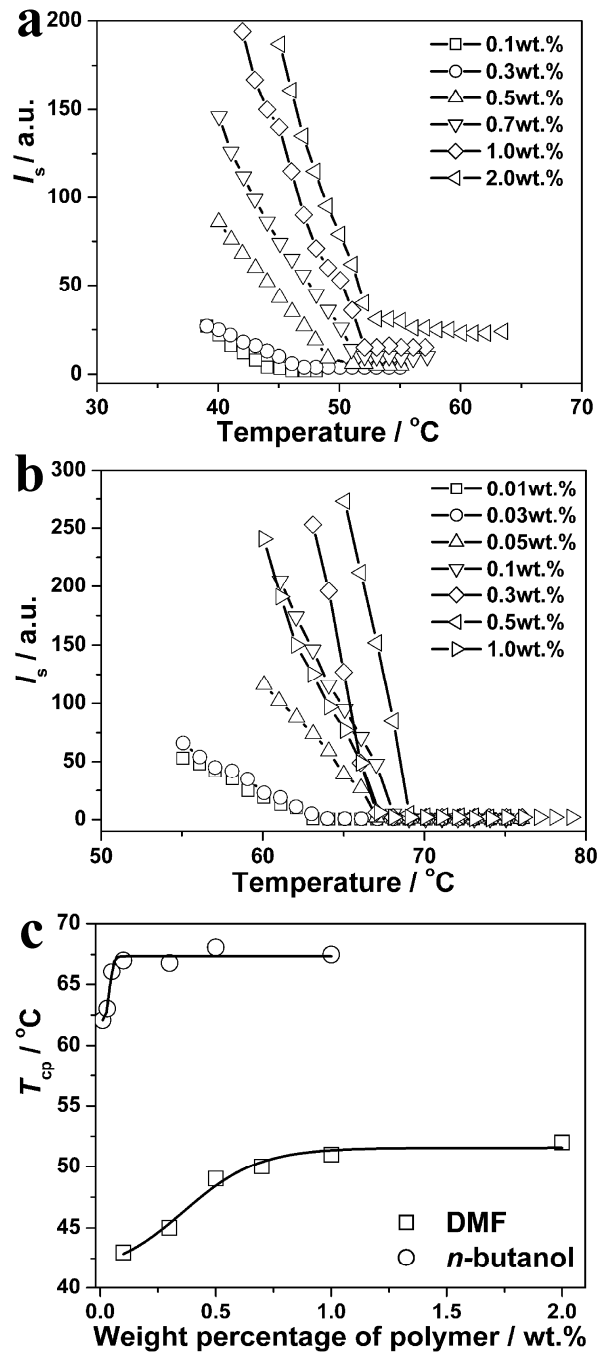


Fig. 4 (a) Temperature dependence of I_s of copolymer solutions in DMF. (b) Temperature dependence of I_s of copolymer solutions in 1-butanol. Polymer concentration is indicated in graph (a) and (b). (c) T_{cp} of polymer solution at different polymer concentration.

The I_s of polymer solution at different polymer concentration at different temperature during cooling process was shown in Fig. 4a (DMF) and 4b (1-butanol). The T_{cp} of polymer solution at different polymer concentration was shown in Fig. 4c. It can be seen that the phase behavior of polymer solution in DMF and 1-butanol was UCST-type and T_{cp} of polymer solution in 1-butanol was higher than that of in DMF. In experiments, polymer solution became much more turbid visually after phase separation in 1-butanol than in DMF with same polymer concentration. It can be deduced that for this polymer DMF owns better solvent quality than 1-butanol.

Effect of solvent and co-solvent on UCST-type thermoresponsive behavior

In preliminary experiments, this copolymer can be dissolved in some nonpolar and weak polar solvents such as diethyl ether, toluene, chloroform, 1,2-dichloroethane, dichloromethane,

1,4-dioxane, cyclohexane, and benzene. This polymer can not dissolve in some strongly polar solvents such as methanol, ethanol, isopropanol, acetone, EG, and DMSO. Distinct from polymer solution in DMF, polymer can be dissolved in DMAc rather than exhibit UCST-type phase behavior. Although polymer solution in 1-butanol can exhibit reversible UCST-type behavior, polymer in methanol, ethanol, and propanol can not be dissolved even above the boiling point of used solvent. In general, it seemed that some polar especially strongly polar solvents were non-solvent for this polymer, and some nonpolar or weak polar solvents were solvent for this polymer. In some proper solvent such as DMF, 1-butanol, 1-hexanol, 1-octanol or in some mixed solvents, polymer can exhibit UCST-type behavior.

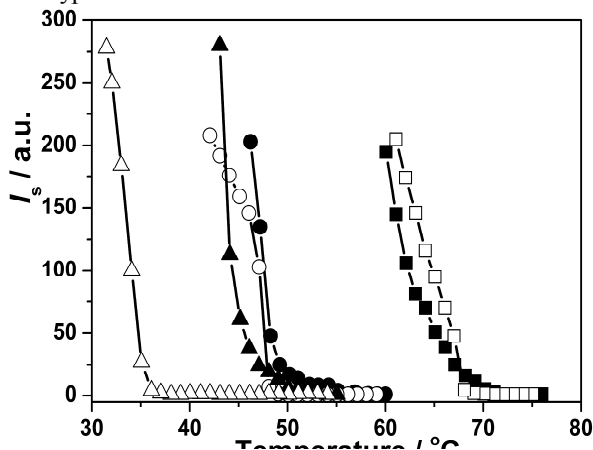


Fig. 5 Temperature dependence of I_s of copolymer solutions in different alcohols. Triangle: 1-octanol, circle: 1-hexanol and square: 1-butanol. The solid and hollow symbols stand for heating and cooling process respectively.

Thermoresponsive behavior of polymer in some selected *n*-alkyl alcohols was also investigated, and the I_s of polymer solution at different alcohols during heating and cooling processes are shown in Fig. 5. It can be seen polymer in all selected alcohols can exhibit UCST-type behavior. The value of T_{cp} of polymer solution during cooling processes in these selected alcohols was as follows: 1-butanol > 1-hexanol > 1-octanol, and the decreasing order of T_{cp} in alcohols was in accordance with the decreasing order of solvent polarity. So for this polymer some higher alcohols owned better solvent quality than some lower alcohols especially at higher temperatures. Compared with thermoresponsive behavior of polymer solution in 1-hexanol and 1-butanol, curve of I_s versus temperature in 1-octanol presented a distinct discrepancy between cooling and heating processes. This discrepancy may be attributed to that the dissolution of the polymer in viscous solvent took longer time in heating process, which causes the delay of the decrease of I_s .

Effect of addition of co-solvent on thermoresponsive behavior of polymer solution in DMF was investigated, and results are shown in Fig. 6. Polymer can dissolve in toluene, so toluene as a good solvent was added into the polymer solution in DMF. In the added toluene range shown in Fig. 6a, polymer solution in mixed solvent of DMF and toluene can exhibit UCST-type behavior. T_{cp} of polymer solution decreased with increase in toluene as shown in Fig. 6c. The decreasing in T_{cp} may be attributed to stronger interaction between polymer and good solvent. Because polymer can not dissolve in EG, EG was considered as a nonsolvent and added to the polymer solution in DMF. In experimental added EG range shown in Fig. 6b, polymer solution in mixed solvent of DMF and EG can also exhibit UCST-type behavior as shown in Fig. 6b, and T_{cp} of polymer solution increased with increasing EG as shown in Fig. 6c. With increasing EG, the solvent quality of the mixed solvent became poor and the polymer would be soluble only at higher temperature resulting in increasing in T_{cp} .

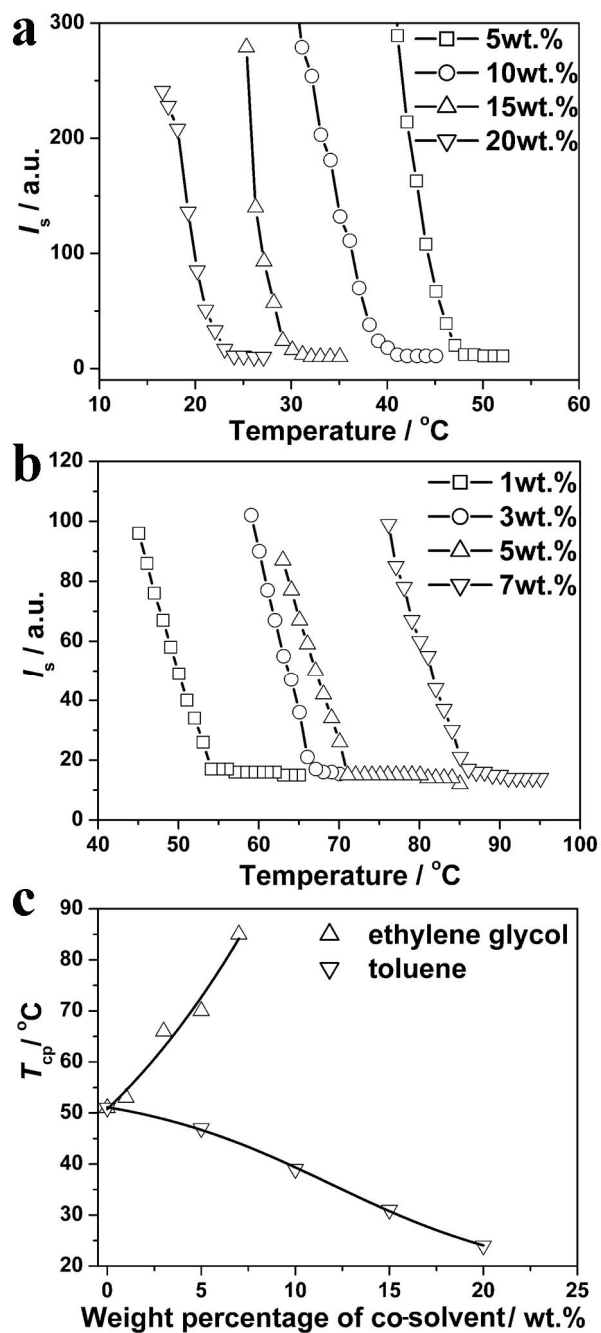


Fig. 6 Temperature dependence of I_s of copolymer solutions in DMF mixed with (a) toluene and (b) EG. (c) T_{cp} of copolymer solution with different weight percentage of co-solvent in mixed solvent. The polymer concentration is 1.0 wt.%. The weight percentage values of co-solvent in mixed solvent are indicated in graph (a) and (b).

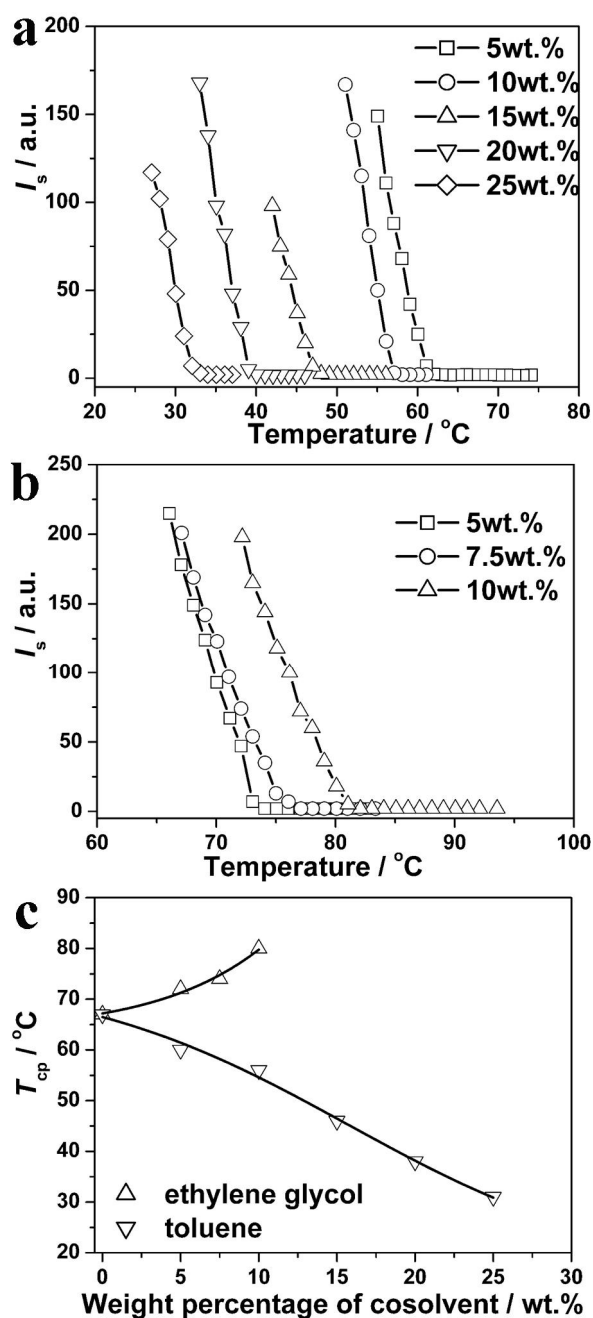


Fig. 7 Temperature dependence of I_s of copolymer solutions in 1-butanol mixed with (a) toluene and (b) EG. (c) T_{cp} of polymer solution with different weight percentage of co-solvent in mixed solvent. The polymer concentration is 0.1 wt.%. The weight percentage values of co-solvent in mixed solvent are indicated in graph (a) and (b).

Effect of co-solvent on thermoresponsive behavior of polymer solution in 1-butanol was also studied, and results are shown in Fig. 7. At the experimental added co-solvent range, polymer solution can exhibit UCST-type behavior in mixed solvent of co-solvent and 1-butanol as shown in Fig. 7a and 7b. Similar to situation of addition of co-solvent in DMF, the addition of toluene as good solvent decreased the T_{cp} and addition of EG as nonsolvent increased the T_{cp} , as shown in Fig. 7c.

As mentioned above, T_{cp} of the polymer solution can be changed by addition of proper co-solvent conveniently, which presents an easy way to tune the T_{cp} of polymer solution. Addition of co-solvent usually can tune the solvent quality and based on the changes in solvent quality, some very useful applications can be obtained in the field of polymer science and supramolecular chemistry.

High resolution ^1H NMR spectra of copolymer in DMF- d_7 at different temperatures

Although many measurements can be used for studying the thermoresponsive behavior of polymer solutions, NMR is a good choice for investigating mechanism of the thermoresponsive behavior of polymer in molecular level [41]. High resolution ^1H NMR measurement was made, and ^1H NMR spectra of polymer at different temperatures and assignments of resonances to various protons in the copolymer were shown in Fig. 8a. At low temperatures, e.g., 20 °C, 25 °C and 30 °C the signals of protons from phenyl group and most of protons from *n*-octadecyl group can be recognized and the shape line of related protons seemed broaden, while the signals of protons from the backbone of the copolymer did not appear. These phenomena of ^1H NMR signals at low temperatures indicated that the mobility of polymer segments in DMF- d_7 was restricted at low temperatures resulting in broadened and poorly resolved spectra. With increasing the temperature the peaks of protons from methyl and methylene groups became sharp and intensity of these peaks became large, and similar tendency for peaks of protons from phenyl group was also observed. Furthermore, at higher temperature (e.g. above 55 °C) the signals of protons from the backbone of copolymer chain can be recognized and the shape line of all protons seemed resolved better than that at lower temperatures, which indicated that the mobility of polymer segments increased. However, compared to ^1H NMR spectrum in CDCl_3 (Fig. 2b), the ^1H NMR spectrum of copolymer in DMF- d_7 seemed a little poorly resolved, which may indicate that chloroform was a better solvent than DMF for polymer even at high temperatures.

The half-height width (HW) of proton peaks from methyl group (peak at 0.92 ppm) and phenyl group (peak from 7.6 to 7.1 ppm) at different temperature in DMF- d_7 is shown in Fig. 8b. The behavior of HW of proton peaks from methyl group with increasing the temperature can be divided into two stages by a critical temperature (CT) such as point A in Fig. 8b. It can be seen that the HW decreased sharply at the first stage (from 20 to 50 °C) and then remained almost constant (from 55 to 70 °C) at the second stage. The tangent intersection of those two stages can be defined as CT and the value of CT was about 52.5 °C, which was close to the T_{cp} (51 °C) of polymer solution in DMF in Fig. 4c. It is well-known that the HW can reveal the mobility of related polymer segments and narrower HW indicates better mobility of related polymer segments. So it can be deduced that the mobility of methyl group increased with increasing temperature. In view of phase separation at lower temperatures visually, the decreasing mobility of methyl group can be attributed to the aggregation of pendent alkyl chain below T_{cp} .

The behavior of HW of proton peaks from phenyl groups with increasing temperature can be also divided into two stages by another CT such as point B in Fig 8b. Below CT (e.g., from 20 to 30 °C), the HW decreases much more steeply than that at higher temperature than CT (e.g. from 35 to 70 °C). The extrapolation value of CT is about 32 °C, which is lower than the CT value (52.5 °C) of methyl groups. The existence of two different CTs can be attributed to those two independent motion units. *N*-Phenyl maleimide group and vinyl ether group can be considered as polar groups which should own proper interaction with polar DMF. On the other hand, the pendent alkyl chain is a nonpolar group, so the phase separation of copolymer can be attributed to the aggregation of nonpolar long pendent alkyl groups in polar DMF solvent. Even after the aggregation of the alkyl chain below T_{cp} , the mobility of the phenyl group is almost unchanged, because the polar main chain is solvated in polar DMF. Further decrease of temperature causes more strong segregation of the alkyl chain, which decreases the mobility of the main chain in the end at lower temperature than T_{cp} .

So according to the high resolution ^1H NMR spectra at different temperatures in DMF- d_7 , the probable mechanism of thermoresponsive behavior could be described as follows. At high temperatures the polymer chain can be dissolved well in DMF resulting in a homogeneous transparent polymer solution. As the temperature decreases to a critical temperature, the solvent quality of DMF becomes poor for polymer especially for pendent long alkyl groups and the poor solvent condition leads to the aggregation of alkyl chain at T_{cp} resulting in phase separation. After phase separation, the mobility of the alkyl chain decreases gradually with decreasing temperature, as shown in the gradual broadening of methyl peak in ^1H NMR spectrum. However, the phenyl group does not reveal such a drastic decrease in mobility until 32 °C, because the solvent quality for the main chain is still good even below T_{cp} .

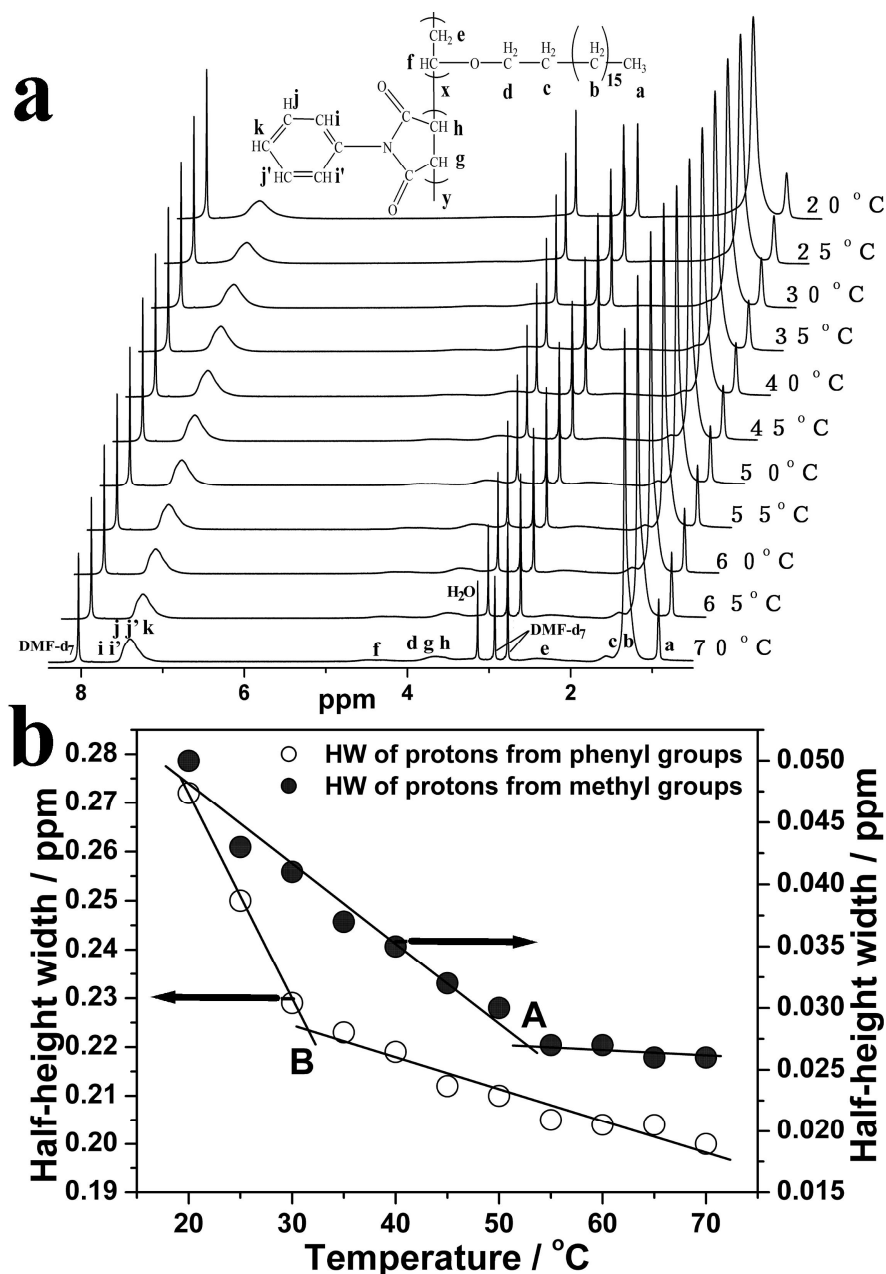


Fig. 8 (a) ¹H NMR of polymer in DMF-d₇ at different temperatures. (b) Half-height width of peak of protons at different temperatures.

Conclusion

Comb-like copolymer of *N*-phenyl maleimide (PMI) and *n*-octadecyl vinyl ether (ODVE) was synthesized by conventional free radical solution polymerization. **The synthesized copolymer contained more units of PMI than that of ODVE.** The copolymer can exhibit UCST-type behavior in DMF, 1-butanol and other proper organic media, in both heating and cooling scans reversibly. The cloud point of polymer solution in organic media can be tuned conveniently by adding proper certain co-solvent, and the good solvent decreased the cloud point while the nonsolvent increased the cloud point. The high resolution ¹H NMR spectrum in DMF-d₇ indicated that decreasing the temperature leads to aggregation of the pendent long alkyl chain and phase separation at the cloud point, after that, the decrease in mobility of polymer main chain occurred at lower temperature.

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Figure captions

Fig. 1 (a) Scheme for synthesis and chemical architecture of copolymer. (b) GPC graph of synthesized copolymer.

Fig. 2 (a) FT-IR spectrum (b) ^1H NMR spectrum (600 MHz) in CDCl_3 (c) ^{13}C NMR spectrum (50 MHz) in CDCl_3

Fig. 3 Temperature dependence of I_s of copolymer solution in organic solvent. (a) 1wt.% polymer solution in DMF, (b) 0.1 wt.% polymer solution in 1-butanol. The temperature at which photograph was taken is indicated in the graph.

Fig. 4 (a) Temperature dependence of I_s of copolymer solutions in DMF. (b) Temperature dependence of I_s of copolymer solutions in 1-butanol. Polymer concentration is indicated in graph (a) and (b). (c) T_{cp} of polymer solution at different polymer concentration.

Fig. 5 Temperature dependence of I_s of copolymer solutions in different alcohols. Triangle: 1-

octanol, circle: 1-hexanol and square: 1-butanol. The solid and hollow symbols stand for heating and cooling process respectively.

Fig. 6 Temperature dependence of I_s of copolymer solutions in DMF mixed with (a) toluene and (b) EG. (c) T_{cp} of polymer solution with different weight percentage of co-solvent in mixed solvent. The polymer concentration is 1.0 wt.%. The weight percentage values of co-solvent in mixed solvent are indicated in graph (a) and (b).

Fig. 7 Temperature dependence of I_s of copolymer solutions in 1-butanol mixed with (a) toluene and (b) EG. (c) T_{cp} of polymer solution with different weight percentage of co-solvent in mixed solvent. The polymer concentration is 0.1 wt.%. The weight percentage values of co-solvent in mixed solvent are indicated in graph (a) and (b).

Fig. 8 (a) ^1H NMR of polymer in DMF- d_7 at different temperatures. (b) Half-height width of peak of protons at different temperatures.