Dynamics of the phase separation in a thermoresponsive polymer: accelerated phase separation of stereo-controlled poly(N,N-diethylacrylamide) in water

メタデータ	言語: English 出版者: ACS Publications 公開日: 2019-11-01 キーワード (Ja): 温度応答性高分子, 相分離ダイナミクス, レーザー温度ジャンプ法, 立体規則性, コイル-グロビュール相転移 キーワード (En): Thermoresponsive polymer, Phase separation dynamics, Laser T-jump technique, Tacticity, Coil-to-globule phase transition 作成者: 松本, 充央, 多田, 貴則, 麻生, 隆彬, 東海林, 竜也, 西山, 聖, 堀邊, 英夫, 勝本, 之晶, 坪井, 泰之 メールアドレス: 所属: Osaka City University, Osaka City University, Osaka City University, Hokkaido University, Osaka City University, Osaka City University, Osaka City University, Fukuoka University, Osaka City University, Hokkaido University
URL	https://ocu-omu.repo.nii.ac.jp/records/2020051

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Dynamics of the Phase Separation in a Thermoresponsive Polymer: Accelerated Phase Separation of Stereocontrolled Poly(*N,N*-diethylacrylamide) in Water

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Citation	Langmuir, 34 (45); 13690–13696
Issue Date	2018-10-26
Type	Journal Article
Textversion	author
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DOI	10.1021/acs.langmuir.8b02848

Self-Archiving by Author(s)
Placed on: Osaka City University

MATSUMOTO, M., TADA, T., ASOH, T.-A., SHOJI, T., NISHIYAMA, T., HORIBE, H., KATSUMOTO, Y., & TSUBOI, Y. (2018). Dynamics of the Phase Separation in a Thermoresponsive Polymer: Accelerated Phase Separation of Stereocontrolled Poly (*N,N*-diethylacrylamide) in Water. *Langmuir*. 34, 13690-13696. doi:10.1021/acs.langmuir.8b02848

Dynamics of the phase separation in a thermoresponsive polymer: accelerated phase separation of stereo-controlled poly(*N*,*N*-diethylacrylamide) in water

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ABSTRACT: We studied the dependence on tacticity of the dynamic phase separation behavior of thermoresponsive poly(*N*,*N*-diethylacrylamide) (PDEA) in an aqueous solution. Using a laser temperature-jump technique combined with transient photometry, we determined the time constants of the phase separation, and found that both atactic and isotactic-rich PDEAs had fast and slow phase separation processes (τ_{fast} and τ_{slow}). The fast process (τ_{fast}) was independent of the tacticity irrespective of the concentration. On the other hand, the slow process had a strong dependence on the tacticity. We found the slow phase separation process got considerably faster with increasing isotacticity in dilute solutions. This effect due to the tacticity of the PDEA is totally different from that for poly(*N*-isopropylacrylamide) and can be explained based on the difference between the hydrophobicity of atactic PDEA and that of isotactic-rich PDEA.

Introduction

In 1968, Heskins and Guillet reported the first demonstration of an aqueous solution of poly(*N*-isopropylacrylamide) (PNIPAM) exhibiting reversible phase separation with lower critical solution temperature (LCST).[1] Following this discovery, the fundamental features of PNIPAM were investigated by static/dynamic light scattering,[2–7] vibrational spectroscopy,[6,8–10] NMR spectroscopy,[11,12] calorimetry,[13–15] small-angle neutron scattering,[16,17] and so on. These numerous studies show that PNIPAM chains are homogeneously dissolved in water below the LCST taking hydrated random-coil structures. Upon heating above the LCST, the PNIPAM chains turn into globular structures accompanied by dehydration of the polymer chains (coil-to-globule phase transition). Subsequently, these dehydrated polymer chains (globules) aggregate with each other. Finally, the solution separates into water-rich and polymer-rich-domains due to hydrophobic interactions between the globules (phase separation). Until now, many researchers have synthesized a number of LCST-type thermoresponsive polymers such as poly(*N*-substituted acrylamide)s, poly(*N*-substituted methacrylamide)s, and poly(alkyl vinyl ether)s.[18,19]

In addition to PNIPAM, poly(*N*,*N*-diethylacrylamide) (PDEA) is another representative LCST-type thermoresponsive polymer. PDEA has an analogous chemical structure to PNIPAM, and both polymers have similar LCSTs. PDEA has been studied to understand the dependence of the phase separation behavior on the chemical structure.[20,21,30–38,22–29] For instance, Itakura et al. and Zhang et al. reported that PDEA partly formed precursory polymer aggregates in a dilute aqueous solution even below the LCST.[21,22] For PNIPAM, such precursory polymer aggregates have never been observed. Furthermore, Maeda et al. and Hashimoto et al. spectroscopically investigated PDEA and suggested that the side chains of PDEA were more hydrophobic than those of PNIPAM.[23,24] Not only these static properties but also the dynamic properties of the

phase separation behavior (phase separation dynamics) are important to further understand the effect of the side chains. Recently, we investigated the phase separation dynamics for PDEA using a method previously developed by us that combines a laser temperature-jump (T-jump) technique with transient photometry.[39] In a previous study we showed that the phase separation for PDEA is much faster than that for PNIPAM, and the phase separation mechanism for PDEA is partly different from that for PNIPAM.[40] Such obvious differences between PNIPAM and PDEA are due to interactions between the side chains and water molecules and/or between the side chains themselves (hydrophobic interaction).[41]

In the present study, we focused on the tacticity of PDEA. In 2000, Nakahama et al synthesized both highly isotactic and highly syndiotactic PDEA by anionic polymerization and found that highly syndiotactic PDEA did not dissolve in water.[42] Furthermore, Katsumoto et al. reported on the effect of the tacticity on the phase diagram and presented hydration structures for both aqueous PDEA solutions and thin PDEA films.[41,43] These studies indicate that isotactic-rich PDEA is more hydrophilic than atactic PDEA. Thus, the tacticity is a key factor for the thermoresponsive behavior of PDEA. We demonstrated the effect of the tacticity on the phase separation dynamics for PDEA and showed that the phase separation rate for PDEA can be controlled by modifying the tacticity.

Experimental Section

Materials.

N,*N*-dimethylformamide (DMF), acetone, and *n*-hexane were purchased from Nacalai tesque. Scandium(III) triflate ($Sc(OTf)_3$) and Ytterbium(III) triflate ($Y(OTf)_3$) were purchased from

Aldrich. Dimethyl sulfoxide-d_6 (DMSO-d_6) was purchased from Tokyo Chemical Industries. All these reagents were used as received. *N*,*N*-diethyl acrylamide (DEA) was purchased from Tokyo Chemical Industries and distilled under reduced pressure at 90 °C to remove the inhibitor. Methanol (special grade) and toluene (special grade) were purchased from Nacalai tesque and Wako Pure Chemical Industries, respectively, and they were distilled before use. α,α-azobis(isobutyronitrile) (AIBN) was purchased from Wako Pure Chemical Industries and was recrystallized from methanol. 1-Phenylethyl phenyldithioacetate (PEPD) was synthesized and identified according to the literature.[35]

Synthesis of Stereo-Controlled PDEA.

PDEA was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization in the presence of a Lewis acid catalyst.[43] DEA (3.3 g, 26 mmol) as a monomer, PEPD as a RAFT agent, AIBN as an initiator, and $Sc(OTf)_3$ or $Y(OTf)_3$ as a Lewis acid catalyst were all dissolved in a methanol/toluene mixture (1:1, v:v, 10 mL) (with a molar feed ratio of [DEA]/[PEPD]/[AIBN] = 1500/3/1). Polymerization was carried out at 60 °C under a nitrogen ambient (polymerization time = 8.0 h). These polymers were purified twice by reprecipitation from acetone to *n*-hexane. The tacticity of PDEA was controlled by changing the concentration of the Lewis acid catalyst (0–0.14 M).

Sample Characterization.

The weight-averaged molecular weight (M_w) and the polydispersity (M_w/M_n) of the PDEA samples were evaluated using size-exclusion chromatography (SEC) (Shimadzu system) equipped with a GPC K-806M column (Shodex). DMF (LiBr 10 mM) was used as an eluent with a flow rate of 1.0 mL min^{-1} at 40 °C. SEC chromatograms were calibrated using standard

polystyrene samples (Tosoh Co., TSKgel). The concentration of the sample solutions was 10 mg mL^{-1}. ^1H NMR spectra were recorded on a JEOL JNM-ECZ400S (400 MHz) in DMSO-d_6 at 130 °C to determine the tacticity of the samples (meso-diad content). The cloud point (T_c) of the sample solutions was determined on the basis of the temperature dependence of the optical transmittance.[40] Temperature-variable dynamic light scattering (DLS) by the sample solutions (0.10 wt%) was measured using an ELSZ-2000ZS (Otsuka Electronics Co.). The sample solutions were filtered (Advantec, 13CP045AS, pore size: 0.45 μm) before the DLS experiments. The data were analyzed by the CONTIN algorithm.

Laser T-jump Technique Combined with Transient Photometry.

Details of the laser T-jump technique have previously been described elsewhere and are briefly introduced here.[40] The sample solutions were kept at a temperature marginally lower (0.20–1.0 K) than T_c using a temperature controller and were irradiated with a single pulse of near-infrared nanosecond laser light (λ = 1200 nm), which was obtained by focusing a single 1064 nm laser pulse (fwhm ≈ 10 ns) into a Raman shifter ($Ba(NO_3)_2$ crystal) in an optical cavity. The laser irradiation transiently induced phase separation (temperature rise; ΔT = 1–1.5 K) by direct vibrational excitation of the water molecules. For the probe light, a continuous-wave green laser beam (λ = 532 nm) was coaxially introduced into the solutions with the heating light pulse. Transient changes in the optical transmittance of the probe light were monitored by the increase in turbidity of the solutions (due to the phase separation). The origin of the time scale (t = 0) is defined as the time when the heating pulse reaches the cell.

Results and Discussion

Characterization of the Samples.

The fundamental characteristics of the synthesized PDEA are summarized in **Table 1.** The molecular weights of these lie in a narrow range (M_w = 60000–74000 g mol^{-1}) with a low polydispersity index (M_w/M_n = 1.1–1.4), which allowed us to easily investigate the effects of the tacticity (**Figure S1** in the Supporting Information shows SEC traces of all samples). The meso-diad content (*m*) of the PDEAs ranged from 55 % to 90 %, determined from the methylene proton peaks of the polymer in the ^{1}H NMR spectra (see the details in the Supporting Information, **Figure S2**).[43] We denoted the PDEAs on the basis of the value of *m* (e.g., "*m55*" means PDEA with 55 % of *m*). Note that, *m55* is an atactic PDEA, and the others are stereo-controlled (isotactic-rich) PDEA. The value of T_c in the aqueous PDEA solution increased from about 30 °C to 40 °C with increasing values of *m* (*m55* to *m90*), indicating that the isotactic-rich PDEA was more hydrophilic than the atactic PDEA (**Figure S3** and **S4**). Such behavior is consistent with a report by Katsumoto and co-workers.[43]

Table 1. Characterization of synthesized PDEAs.

Entry	Name	M_w [a]	M_w/M_n [a]	*m*:*r* [b]	T_c [°C] [c]
1	*m55*	66000	1.4	55:45	31.1
2	*m58*	60000	1.1	58:42	32.4
3	*m64*	66000	1.2	64:36	33.4
4	*m70*	71000	1.4	70:30	34.0
5	*m90*	74000	1.1	90:10	39.9

[a] Determined by SEC in DMF containing 10 mM LiBr at 40 °C (polystyrene standards).; [b] Determined by ^{1}H-NMR spectra of each sample in DMSO-d_6 at 130 °C.; [c] Determined by the

transmittance curve. The sample concentration was 0.50 wt% and the heating rate was 0.2 °C/min.

DLS Measurements.

Figure 1 shows the hydrodynamic diameter (d_H) distribution for each sample in water at room temperature (polymer concentration was 0.10 wt%). We can clearly see two peaks in all these histograms. As in our previous work, the peak at smaller d_H (Peak-I) corresponds to individual single polymer chains, and the peak at larger d_H (Peak-II) is ascribed to polymer aggregates (pre-aggregates) arising from weak intermolecular interactions, such as the entanglement of polymer chains.[40] The average value of d_H for Peak-I increases from 10 nm to 19 nm with increasing isotacticity. This suggests that individual PDEA chains with higher isotacticity have relatively loose structures below T_c due to the sufficiently high level of hydration (higher hydrophilicity) compared with the lower isotacticity sample, which is in good agreement with the effect of the tacticity on T_c. This can be ascribed to the difference in the excluded volume effect in the polymer chains based on steric hindrance.[44] On the other hand, the average value of d_H for Peak-II is around 100–200 nm. The relative scattering intensity of Peak-II increases with increasing isotacticity, meaning that the number of pre-aggregates had increased. Note that, there was no effect due to the tacticity found in the values of d_H for Peak-II.

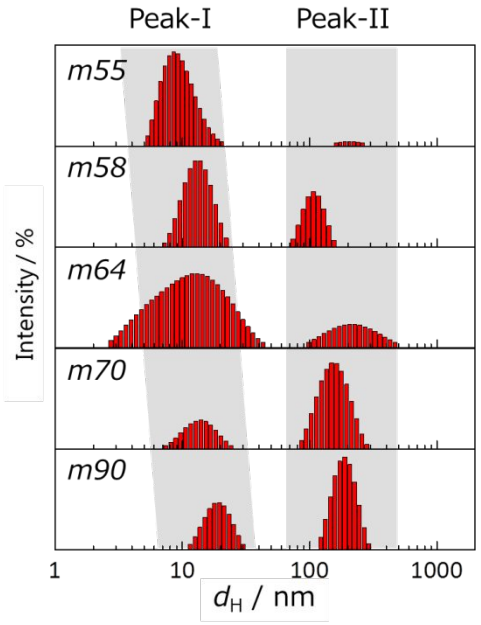

Figure 1. The d_H distributions for each PDEA, which have different tacticity, obtained by DLS experiments at room temperature. The polymer concentration was 0.10 wt%.

Figure 2 shows the temperature dependence of the d_H distributions for *m55* in water (polymer concentration was 0.10 wt%). In the histograms, we see three kinds of peaks: Peak-I (around 10 nm), Peak-II (from several tens of nanometers to a few hundred of nanometers), and Peak-III (around 1000 nm). Peak-I and Peak-II have already been described above in Figure 1. Peak-III is assigned to polymer-rich domains formed by phase separation. Below T_c, (25–30 °C), Peak-I and Peak-II are observed. The scattering intensity of Peak-II is significantly lower than that of Peak-I, meaning that there are hardly any pre-aggregates of PDEA in this temperature range. From 31 °C to 33 °C (around T_c), the scattering intensity of Peak-I decreases while that of Peak-II increases. When Peak-I had almost completely disappeared at 33 °C, Peak-III appears due to the phase separation. Above T_c (34–40 °C), only one peak (Peak-III) can be observed. The

value of d_H for Peak-III increases slightly with increasing solution temperature up to 36 °C due to further aggregation and then gradually decreases. Such behavior above 36 °C suggests that the polymer-chain globules in the aggregates had become more compact.[22] Peak-I, Peak-II, and Peak-III were observed also in isotactic-rich PDEA (*m70*, **Figure S5** in the Supporting Information). The size of the aggregate after phase separation for *m70* was somewhat larger than that for *m55*. This might be due to that the aggregate of highly isotactic PDEA has more water than that for atactic PDEA because of higher hydrophilicity (higher Tc). However, details are not discussed here. The corresponding correlation curves, which are row-data in DLS experiments, were shown in **Figure S6** in the Supporting Information.

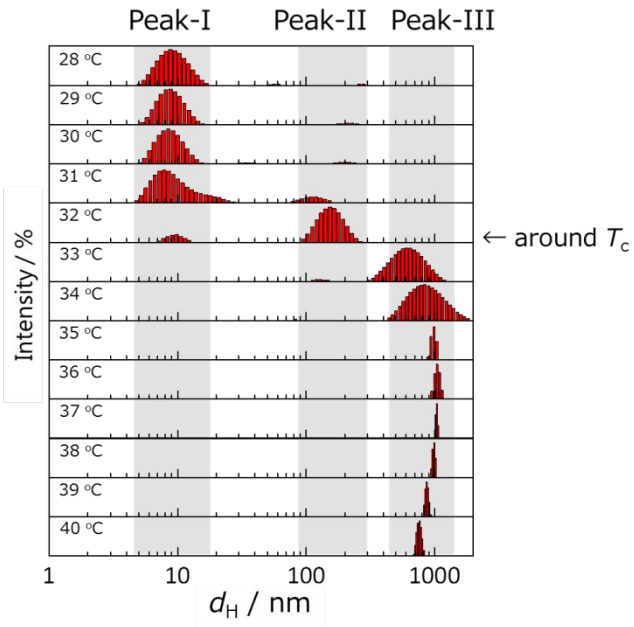

Figure 2. Temperature dependence of the d_H distributions for *m55* obtained by DLS experiments. The polymer concentration was 0.10 wt%. The waiting time after raising the temperature was 2 min.

Phase Separation Dynamics for Stereo-Controlled PDEA.

Figure 3 shows a representative transient decay curve of the optical transmittance obtained from the laser T-jump experiment (*m55*, 3.0 wt%), in which initial temperature was 29.2 °C (T_c was 29.7 °C). Immediately after the laser T-jump (t = 0 s), the optical transmittance rapidly decays from 100 % to 25 % in t = 200 ms due to the phase separation. After t = 200 ms, the optical transmittance gradually recovers and it finally reached 100 % at about t = 1 s because of cooling of the irradiated area in the sample solution. The decay curve was well fitted with a double exponential function,[40]

$$T(t) = A_{\text{fast}}\exp\left(-\frac{t}{\tau_{\text{fast}}}\right) + A_{\text{slow}}\exp\left(-\frac{t}{\tau_{\text{slow}}}\right) + B, \quad (1)$$

where τ_{fast} and τ_{slow} are time constants for the fast and slow phase separation, respectively. A_{fast} and A_{slow} are pre-exponential factors. B is a fitting constant corresponding to the minimum transmittance after the T-jump. Here, we define

$$f = \frac{A_{\text{fast}}}{A_{\text{fast}} + A_{\text{slow}}} \quad (2)$$

as the relative contribution of the fast phase separation component to the whole process. For Figure 3, we determined these parameters to be: τ_{fast} = 8.3 ms, τ_{slow} = 54 ms and f = 0.42.

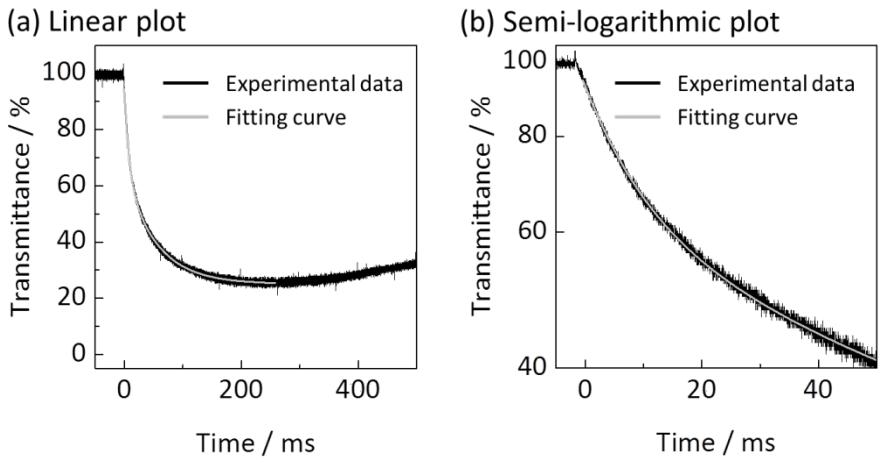

Figure 3. Representative transmittance curve (*m55*, 3.0 wt%). The origin of the time scale (t = 0 s) is the time when the heating pulse reaches the sample cell. The initial temperature before the T-jump was 29.2 °C (T_c was 29.7 °C). The black lines show the experimental data. The gray line is the curve with a double exponential function fitted to the data ($R^2 > 0.99$). (a) and (b) are linear and semi-logarithmic plots, respectively (same data).

In our previous study, we determined time constants of the phase separation for atactic PDEA and revealed that PDEA had two phase separation processes: a fast and a slow process.[40] We briefly describe the phase separation mechanism as follows. In the slow phase separation process, individual polymer chains (polymer globules) aggregate with each other by diffusion in solution. This is the normal phase separation process described in the introduction. In the fast phase separation process, the pre-aggregates undergo shrinkage accompanied by dehydration (coil-to-globule phase transition) without further aggregation. This causes an increase in refractive index because of an increase in averaged chain density and a decrease in water content .[45] Thus it should lead an increase in multiple light scattering resulting in a decrease of the light transmission. Such shrinkage behavior for physically crosslinked aggregates is similar

to the volume phase transition for chemically cross linked microgels in terms of time scale. However, details are not discussed here.[46] Note that, aggregation of each pre-aggregate would have negligible effects on the dynamics, because number of the pre-aggregates is significantly lower than that of individual polymer chains (less than 1%).

In the present study, we obtained τ_{fast}, τ_{slow}, and f for both atactic PDEA and isotactic-rich PDEA. As a representative example for isotactic-rich PDEA, the values for *m70* are plotted against polymer concentration (0.50–10.0 wt%) in **Figure 4**. τ_{slow} decreases from 110 ms to 20 ms with increasing polymer concentration, meaning that the slow phase separation process accelerates as the concentration is increased. On the other hand, the time constant for the fast process due to the pre-aggregates (τ_{fast}) remains at almost 10 ms irrespective of the polymer concentration. Note that the f values of all the samples are around 0.4 (0.23–0.69) irrespective of the concentration (Figure 4b), indicating that both the fast and slow processes make comparable contributions to the whole phase separation process. That is, the slow process is the rate-controlling step for the whole process. The concentration dependence of τ_{fast}, τ_{slow}, and f for atactic PDEA and other isotactic-rich PDEA are shown in **Figure S8** and **S9** in the Supporting Information. In the next section, we describe the effect of the tacticity on the phase separation dynamics for stereo-controlled PDEA.

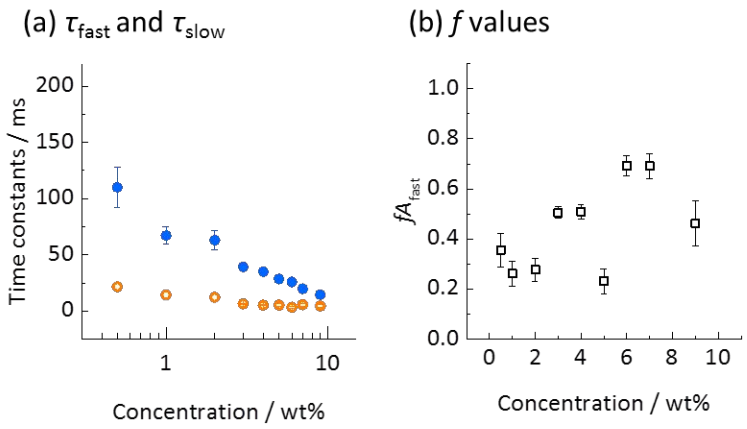

Figure 4. Dependences of the phase separation dynamics on concentration for *m70* (0.50–10 wt%). (a) The fast and slow time constants for the phase separation (τ_{fast} and τ_{slow}). (b) The relative contribution of the fast phase separation component (*f*). The orange open and blue closed circles show the average values of τ_{fast} and τ_{slow}, respectively. The black squares show the *f* value. The data were obtained by averaging over 30 laser T-jump experiments. The error bars show standard deviations.

Effect of Tacticity on the Phase Separation Dynamics.

To discuss the effect of the tacticity on the dynamics, τ_{fast} and τ_{slow} are plotted against the value of *m* of the samples in **Figure 5**, where the polymer concentrations are (a) 10 wt% and (b) 0.50 wt%. In the 10 wt% solution, τ_{slow} has little dependence upon the tacticity with $\tau_{slow} \approx 23$ ms on average (Figure 5a). Wintgens and Amiel reported that polymer chains of both PNIPAM and its derivatives formed physical networks like hydrogels in highly concentrated aqueous solutions around T_c.[47] Therefore, the phase separation dynamics for PDEA in the dense solution (10 wt%) can be understood using a theory for the volume phase transition of hydrogels, which is in good agreement with previous PNIPAM systems.[48] According to the Tanaka-Fillmore theory, the rate

of such swelling or shrinkage is proportional to the inverse of the cooperative diffusion coefficient that depends on the cross linking density of the polymer network: that is, the polymer concentration.[49,50] Note that the tacticity of the polymer chains has no relationship with the average cross linking density in the solution. In the dilute solution (0.50 wt%), τ_{slow} decreases from 250 ms to 80 ms as the value of *m* rises by 9%, and then remains constant with further increases in *m* (Figure 5b). Such behavior can be explained in terms of diffusion-controlled aggregation because the PDEA chains are homogeneously dissolved in water without intermolecular overlapping of the polymer chains in the dilute solution. This will be discussed in the later section. It is notable that higher temperature in isotactic-rich PDEA when the T-jump was applied had negligible effect on the dynamics, because the diffusion coefficient for each PDEA hardly depended on the temperature below the T_c (Figure S7 in the Supporting Information). Contrary to the slow process, the dynamics of the fast process are independent of the tacticity at any concentration ($\tau_{fast} \approx 10$ ms). In other words, a number of pre-aggregate was hardly reflected in the fast process. This is consistent with the mechanism where the fast phase separation for PDEA is originated from the shrinkage of the pre-aggregates without any further diffusion-aggregation. What is important point here is that the slow phase separation that is dominant in the whole system accelerated by modification of the tacticity.

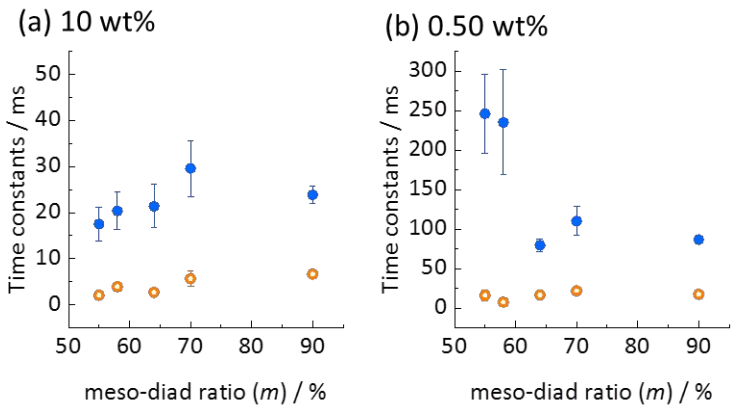

Figure 5. Effect of tacticity on τ_{fast} and τ_{slow} for PDEA. The polymer concentrations are (a) 10 wt% and (b) 0.50 wt%. The orange open and blue closed circles show the average values ofτ_{fast} and τ_{slow}, respectively. The data were obtained by averaging over 30 laser T-jump experiments. The error bars show standard deviations.

Stepwise Growth Model.

As described above, the phase separation for isotactic-rich PDEA was faster than that for atactic PDEA in the low concentration region. To understand the phase separation dynamics for this, we made a rough estimate of the growth rate of the polymer-rich domains using a stepwise (sequential) growth model based on diffusion-controlled aggregation.[51] **Figure 6a** shows a schematic illustration of this model. The calculation is based on the following assumptions: (1) in a dilute solution the domains grow by the collisions between a couple of adjacent polymer aggregates, (2) the mean square displacement of the aggregates is regarded as the average intermolecular distance between adjacent aggregates, and (3) the volume of the domain is equal to the sum of the volume of these two aggregates.

The diffusion time required for aggregation of the i^{th} step (t_i) is expressed by equation (3), which is derived from the Stokes-Einstein equation.[52,53]

$$t_i = \frac{3\,\pi\mu\ \ {r_i}^2}{4k_{\mathrm{B}}Td_{\mathrm{agg},i}} \tag{3}$$

where k_{B} is the Boltzmann constant, T is absolute temperature, μ is the viscosity of the solvent and $d_{\mathrm{agg},i}$ is the hydrodynamic diameter of a polymer aggregate, r_i is the diffusion distance, and t_i is the time required for the diffusion. The subscript "i" means the i^{th} step.

r_i was calculated as the average intermolecular distance between two adjacent aggregates, and thus is given by

$$r_i = \frac{d_{\mathrm{agg},i_3}}{d_{\mathrm{glo}}}\sqrt{\frac{M_w}{C_{\mathrm{poly}}N_{\mathrm{A}}}}\ \ (\text{when } i = 1,\ d_{\mathrm{agg},\,i}\ =\ d_{\mathrm{glo}}) \tag{4}$$

where d_{glo} is the hydrodynamic diameter of a single polymer globule, C_{poly} is the concentration by weight of the polymer, and N_{A} is Avogadro's number. According to the literature, PDEA chains with hydrated random-coil structures shrink by about 50 % after the phase transition.[29] Thus, we estimated the values of d_{glo} from the values of d_{H} obtained in the DLS measurements (Figure 1); for instance, d_{glo} for *m55* was 5 nm.

Combining equations (3) and (4), we obtained t_i for each step. As an example, we plot d_{agg} vs. total time ($t = \Sigma t_i$) for *m55* in **Figure 6b**. d_{agg} increases step-by-step with time. Here, we assumed that our laser T-jump system monitored the time when the diameter of the domains became about 200 nm (τ_{cal}) by taking into account the effect of the particle size on the optical transmittance in solution, which is based on our preliminary experiment (see details in the Supporting Information, **Figure S10**). Based on this assumption, we obtained τ_{cal} for all samples (0.50 wt%). All of the estimated values (τ_{cal}) and experimental values τ_{slow} are summarized in

Table 2. τ_{cal} decreases with increasing isotacticity from 250 ms to 90 ms and is close to τ_{slow}. Moreover, a number of collisions of polymer globules decreased with increasing the isotacticity. The most important point in our model is that the phase separation dynamics for the stereo-controlled PDEA can be explained by the hydrophobicity that is reflected in the size of polymer chains. Note that difference in diffusion coefficient for the stereo-controlled PDEA has a negligible effect on the whole phase separation dynamics. Except for 0.50 wt%, our diffusion-limited aggregation model hardly explained the dynamics in the highly concentrated polymer solution (e.g. 10 wt%). This should be due to the non-negligible overlapping effect of the polymer chains because the overlap concentration of the synthesized PDEA is about 1-2 wt%. It is notable that our model is inappropriate for τ_{fast} because the fast process does not need any further diffusion of the polymer chains. Altogether, we have thus successfully explained the mechanism that governs the acceleration in the phase separation of stereo-controlled PDEA using a simple model based on stepwise aggregation of the polymer chains.

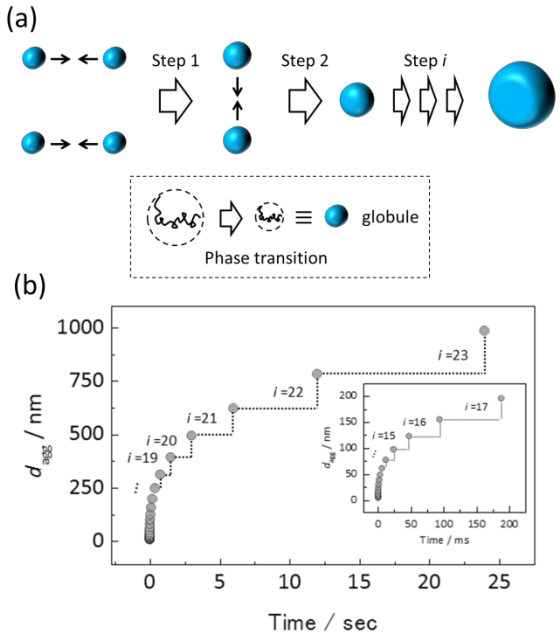

Figure 6. Stepwise Growth Model of a polymer-rich domain based on diffusion-limited aggregation of the polymer chains. (a) An illustration of the model. (b) Estimated growth-rate of a polymer-rich domain for m55. The inset shows an expanded view ranging from 0 ms to 200 ms.

Table 2. Summary of τ_{cal} and τ_{slow} for each sample.

	τ_{cal} / ms [a)]		τ_{slow} / ms [b)]
m55	190	(i = 17)	250
m58	120	(i = 16)	190
m64	130	(i = 16)	80
m70	76	(i = 15)	110
m90	50	(i = 14)	90

[a)] The growth rate of the PDEA-rich domain (the time when the domain became about 200 nm) estimated by a stepwise growth model based on diffusion-limited aggregation.; [b)] The time constant for slow phase separation of PDEA at 0.50 wt% determined by the laser T-jump experiments.

Summary and Conclusions

In summary, in this study we investigated the dependence of the phase separation dynamics of aqueous PDEA solutions on the tacticity of the PDEA. According to the cloud point and DLS measurements, the hydrophobicity of PDEA decreases as the meso-diad ratio in the polymer chains increases, by which the hydrodynamic diameter becomes larger. In the laser T-jump experiments for the dynamics, it was found that atactic and isotactic-rich PDEA have fast phase separation processes (10 ms) in addition to the slow (normal) processes (80–250 ms). The fast process is ascribed to the polymer aggregates formed even below the cloud point and is independent of the tacticity. The slow process strongly depends on the tacticity. The phase separation of highly isotactic PDEA is clearly faster than that of atactic PDEA (maximum acceleration of 2.5 times) in the dilute solution. We used a stepwise growth model for polymer aggregates to successfully demonstrate that the acceleration of the slow phase separation process originates from the difference in the hydrophobicity of the PDEA.

In conclusion, we can control the phase separation in PDEA by a slight modification of the tacticity in a dilute solution. This new insight shows that the sum of the small differences in the static properties derived from the primary structure (chemical structure and stereoregularity) have a strong effect on the dynamics. We hope that the present study will help to provide an understanding of this complex phase separation behavior.

ASSOCIATED CONTENT

Supporting Information.

Supporting data includes additional fundamental data about the synthesized polymers and other plots of the phase separation dynamics. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

M. M conducted all experiments and wrote the manuscript. Y. T. conceived and supervised the project. All authors discussed the results and commented on the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by JGC-S Scholarship Foundation, and JSPS KAKENHI Grant Numbers JP26288011, JP16K17922, and JP16H06506/JP16H06507 in Scientific Research on

Innovative Areas “Nano-Material Manipulation and Structural Order Control with Optical Forces”.

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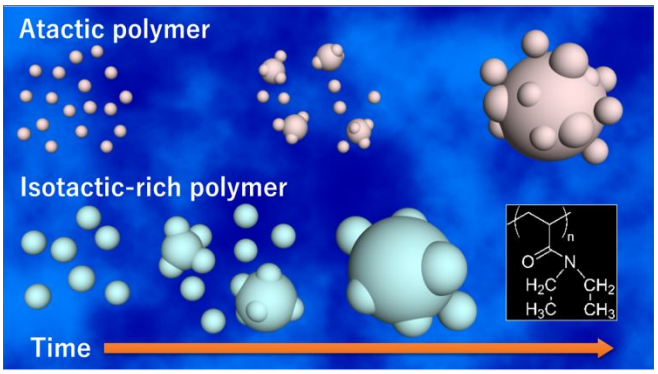
Table of Contents.



KEYWORDS: LCST, poly(*N*,*N*-diethylacrylamide), globule, microgel, phase transition