Polymer Chemistry

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Effect of amino group modification at allyl position of methacrylamides on polymerization and polymer pH-/thermo-responsiveness†

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With an interest in β-amino acid derivative polymers containing a carbon backbone, the polymerization of *N*-*n*-propyl α-(aminomethyl)acrylamide (**4b**) and *N*-isopropyl α-(aminomethyl)acrylamide (**4b**) were investigated. The synthesis of **4** was achieved within many fewer steps than reported by using selective acylation and subsequent conjugate substitution of α-(chloromethyl)acryloyl chloride. **4** hardly homopolymerized, but copolymerization with *N*-substituted acrylamides afforded polymers with various compositions. Surprisingly, substitution with amino groups increased the hydrophobicity of the polymers and lowered the cloud point (T_c). Nevertheless, polymers containing the amino monomers as major components exhibited significantly higher T_c in 1 M HCl aq than those in water. Thus, in order to give clear pH responsiveness, it is necessary to use **4** as a major monomer.

Introduction

Vinyl polymers containing repeating units derived from α-amino acids have long attracted attention as macromolecules that exhibit properties different from those of polypeptides.[1–5] These vinyl polymers were often investigated as biocompatible materials similar to polypeptides,[6–8] while they were also studied as polymer materials utilizing carboxy and amino groups for pH- and temperature-responsive materials[7,9–14] and polymer electrolytes.[15] In typical examples, amino or carboxy groups of α-amino acids were used as reactive sites to link the carbon backbones.[1–11] On the other hand, poly(α-dehydroalanine) [**poly(1)**] is a vinyl polymer with a carbon backbone composed of two sp³ carbons in alanine units, of which amino and carboxy pendants remain active (Scheme 1A). Because of its structural features, **poly(1)** has long been a target for synthesis.[10,16–19] However, **poly(1)** cannot be synthesized directly from **1**, as the monomer isomerizes to an imine form by tautomerism. Therefore, the synthesis has only recently been achieved.[15] In contrast, **3a**, an unsaturated naturally occurring β-amino acid, is stable enough to be handled.[20–22] Thus, we investigated the radical polymerization of the corresponding ester **3b** and found that the polymer **poly(3b)** was pH- and temperature-responsive (Scheme 1B).[23] Unfortunately, this polymerization suffered from a side reaction between the amino pendants of the polymer and the ester of the unreacted monomer. For this reason, the structures of the obtained polymers were sensitively dependent on the polymerization conditions. To avoid
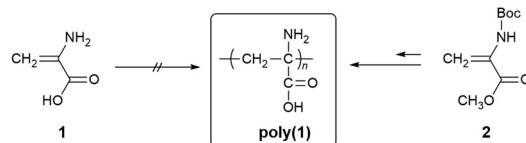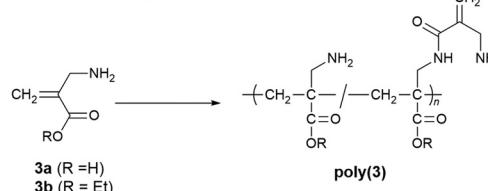
Scheme 1 Examples of polymers of amino acid derivatives composed of a vinyl polymer backbone. A: Poly(α-dehydroalanine) reported in ref. 14. B: Our previous work in ref. 22. C: This work.
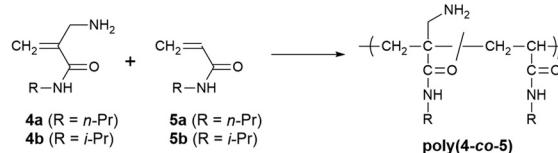
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the side reaction of ester–amide exchange, we have newly designed **4**, which is a derivative of **3a** but has an acrylamide structure (Scheme 1C). As is well known, acrylamides with appropriate *N*-substituents exhibit temperature responsiveness.[24] Furthermore, the polymer of **4** was expected to be pH responsive due to the amino pendants. Herein, we describe the synthesis and polymerization of **4** and the stimulus responsiveness of the polymer.

Results and discussion

Monomer synthesis

In our previous report,[22] **3** was synthesized in a three-step reaction starting with the Morita–Baylis–Hillman (MBH) reaction of ethyl acrylate and formaldehyde. A similar reaction was performed with *N*,*N*-diethyl acrylamide, but the resulting monomer, **9**, exhibited poor polymerizability (Scheme 2).[25] In analogy with common *N*,*N*-dialkyl methacrylamides, the acrylic skeleton of **9** cannot maintain a planar structure due to the steric repulsion between the *N*-substituents and the α-substituent, resulting in a twisted conjugated system with poor reactivity.[26] Therefore, the methacrylamide with one less *N*-substituent, **4**, was interesting, although its synthesis was not achieved due to the low reactivity of **5** in the MBH reaction (Scheme 2: Route A). For this reason, Zhuang *et al.* synthesized

6 in six steps starting from **9** (Route B);[27] if **4** is synthesized through this route, the required overall reaction steps are eight. Since Route B was too long, an alternative route consisting of four steps from *tert*-butyl acrylate (**11**) was investigated (Route C).

One of the key reactions of Route C was the conversion of **12** to **13**, because **12** is active in both acyl and conjugate substitution reactions. Although our previous work showed a preference for acyl substitution,[28] conjugate substitution with residual primary amines affording **14** was also expected. Therefore, in our first examination, conjugate substitution was promoted as a reaction to be aimed at rather than a side reaction to be avoided. **12** was added neat at 25 °C over 1 min into a solution of a large excess (10 molar equiv.) of *n*-propylamine (Table 1, entry 1). The ^{1}H NMR spectrum of the products suggested the production of **14a**, although a series of signals assignable to **15a** were also observed (Fig. S1A†). This implied the conjugate substitution of **13a** and **14a** as a side reaction. To suppress this reaction, a solution of **12** in CHCl₃ (0.50 M) was added dropwise to a solution of *n*-propylamine (2.0 M) over 100 min. Furthermore, in order to increase the selectivity of the acyl substitution reactions, the temperature was lowered to −20 °C (entry 2, Fig. S1B†) or −40 °C (entry 3, Fig. S1C†), resulting in a suppressed yield of **15a** (*ca.* 5%). However, the selective synthesis of **14a** or purification were not achieved. Thus, isopropylamine (entry 4, Fig. S2B†) and *tert*-butylamine
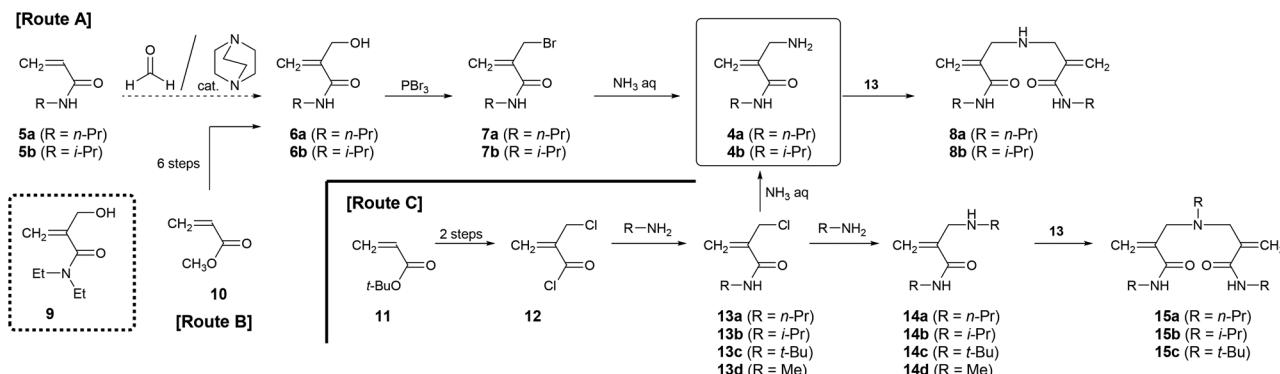
Scheme 2 Synthetic routes of **4** and possible side reactions.

Table 1 Synthesis of allyl-functionalized acrylamides from **12** and primary amines

Entry[a]	Amine	(Equimol.)	Temp. [°C]	Time [h]	Composition[b] [%]		
					13	**14**	**15**
1[c]	*n*-PrNH₂	10	25	18		79	21
2	*n*-PrNH₂	10	−20	18		94	6
3	*n*-PrNH₂	10	−40	18		95	5
4	i-PrNH₂	10	−20	18		97	3
5	*t*-BuNH₂	10	−20	18		>99	Trace
6	*n*-PrNH₂	1.0[d]	−20	22	100		
7	i-PrNH₂	2.0	−40	23	100		

[a] A solution of **12** in CHCl₃ (0.50 M) was added dropwise to a solution of *n*-propylamine (2.0 M) over 100 min. [b] Estimated from ^{1}H NMR spectra. [c] **12** was added to a 6.4 M solution of *n*-propylamine in CH₂Cl₂. [d] Et₃N (1.0 equimol.) was added.

(entry 5, Fig. S2A†) were examined as bulky amines to reduce the nucleophilicity of the secondary amino group of **14**. Notably, *tert*-butylamine was effective, and **14c** was obtained with high selectivity (99.5%, entry 5). Unfortunately, the radical polymerization of **14c** using 2,2′-azoisobutyronitrile (AIBN) in 1,4-dioxane (0.5 M) at 60 °C did not afford a polymeric product. The poor polymerizability of **14c** was anticipated due to the large steric hindrance of the *tert*-butyl group. Thus, **4** was synthesized as a monomer with less steric hindrance.

As mentioned above, for the synthesis of **4**, **12** must undergo only an acyl substitution reaction with a primary amine and be selectively converted to **13**. The key was found unexpectedly during a study of the synthesis of **14d**. We first attempted to synthesize **14d** with methylamine. Since methylamine was commercially available only in aqueous solution, it was extracted in advance with chloroform, and **12** was added dropwise to the organic layer at −40 °C. The ^{1}H NMR spectrum of the reaction mixture confirmed only signals of unreacted **12** and **13d**, suggesting no formation of **14d**. This was probably due to the incomplete extraction of methylamine, which made the feeding ratio of methylamine lower than planned. In other words, it was suggested that only the acyl substitution reaction proceeded selectively when **12** reacted with a primary amine at less than the stoichiometric ratio in a chloroform solution at −40 °C. Therefore, *n*-propylamine was selected as a primary amine that can be accurately weighed, and two molar equivalents to **12** were reacted (Table 1, entry 6). In addition to one molar equivalent of triethylamine required for the acyl substitution reaction, an excess of one molar equivalent was used to capture the liberated hydrogen chloride. The ^{1}H NMR spectrum of the product suggested that **13a** was produced selectively (yield: 63%). Similarly, **13b** was synthesized from isopropylamine (entry 7, yield: 77%).

Next, the synthesis of **4a** was investigated by adding an excess amount of aqueous ammonia to the 1,4-dioxane solution of **13a** at 25 °C. In the ^{1}H NMR spectrum of the products (Fig. S4A†), a series of signals different from that of the main product **4a** was observed. From the chemical shift value and integrated intensity ratio, this suggested the formation of **8a**. **8a** is generated by the conjugate substitution reaction of **4a** and **13a**. A similar side reaction occurred in the synthesis of **14a**, although the formation of **15a** was suppressed at a lower temperature. Therefore, the reaction between **13a** and aqueous ammonia was carried out at 0 °C. Since unreacted **13a** remained after 5 h (Fig. S4B†), the reaction time was extended to 22 h, resulting in the selective synthesis of **4a** (Fig. S4C†). **14b** was also synthesized in the same way.

In the ^{1}H NMR spectrum of **14b**, three signals were observed at 6.6, 3.4 and 1.6 ppm, each with an integrated intensity of one hydrogen atom (Fig. 1A). The signal at 6.6 ppm showed a COSY correlation with the methine hydrogen signal at 4.1 ppm, suggesting assignment to the amide protons (Fig. S5†). The signals at 3.4 and 1.6 ppm showed a COSY correlation with each other and were assigned to protons of the amino group. The two separated signals for the
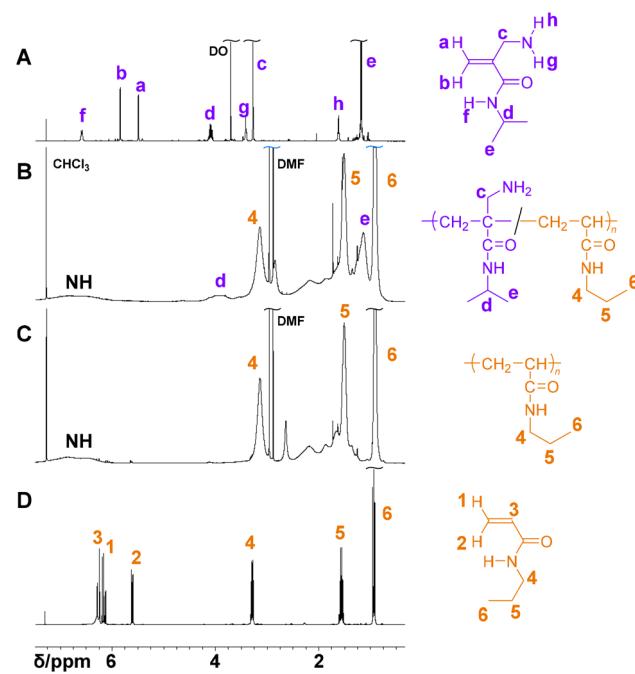

Fig. 1 ^{1}H NMR spectra of **4b** (A), **poly(4b-*co*-5a)** (Table 2, entry 10, B), **poly(5a)** (entry 12, C) and **5a** (D) (400 MHz, CDCl₃, 298 K).

amino protons suggest slow bond rotation. In order to understand this explanation, the stable conformation of **14b** was simulated using molecular mechanics and density functional theory (DFT). The results suggested that the hydrogen atom of the amide group and the nitrogen atom of the amino group formed a hydrogen bond in the most stable conformation (Fig. S6†).

Polymerization

The homopolymerization of **4** was conducted using AIBN in *N*,*N*-dimethyl formamide (DMF) at 65 °C for 24 h. However, neither **4a** (Table 2, entry 13) nor **4b** (entry 1) yielded a polymer.[29] As a control experiment, *N*-isopropyl acrylamide (**5b**, entry 7) and *N*-*n*-propyl acrylamide (**5a**, entry 12) were polymerized, respectively, resulting in polymer formation as expected. In other words, the lack of progress of the homopolymerization of **4** was not attributed to a technical cause. Therefore, the copolymerization of **4b** and **5b** was investigated at various feeding ratios (entries 2–6). Although all entries yielded polymers, it was difficult to evaluate the polymer composition from the ^{1}H NMR spectrum due to the structural similarity of **4b** and **5b** (Fig. S7†). Therefore, combinations of monomers with different *N*-substituents were investigated. For example, an equimolar mixture of **4b** and **5a** was used for copolymerization (entries 8–12). In the ^{1}H NMR spectrum of the product, clearly separated signals originating from the two *N*-substituents were observed (Fig. 1B). The signal of the *N*-methine proton of the isopropyl group around 4 ppm and that of the methylene proton of the *n*-propyl group around 3.1 ppm were typical examples. However, these signals were so

Table 2 Radical (co)polymerization of **4** and **5** in DMF at 60 °C using AIBN as an initiator

Entry	M1 (**4**)	M2 (**5**)	Feed [mol%]		Conv.[a] [mol%]		Yield [%]	Comp.[a] [mol%]		M_n[b]	$Đ$[b]	T_c[c] [°C]	
			4	5	4	5		4	5			H₂O	1 M HCl aq
1	**4b**	**5b**	100	0			0						
2	**4b**	**5b**	75	25	98	92	57			13 700	2.40	21	31
3	**4b**	**5b**	20	80	>99	>99	68			21 500	3.72	23	25
4	**4b**	**5b**	15	85	>99	>99	53			40 000	2.48	49	26
5	**4b**	**5b**	10	90	>99	94	26			19 200	2.48	33	29
6	**4b**	**5b**	5	95	>99	94	40			18 700	2.36	30	30
7	**4b**	**5b**	0	100		>99	30			35 800	1.49	(32)[d]	29
8	**4b**	**5a**	80	20	51	2.3	11	75	25	4700	1.61	12	30
9	**4b**	**5a**	50	50	93	66	8.7	52	48	6200	1.73	14	26
10	**4b**	**5a**	20	80	>99	90	74	26	74	16 000	1.85	20	17
11	**4b**	**5a**	10	90	>99	78	64	13	87	16 400	2.43	21	20
12	**4b**	**5a**	0	100		>99	35	0	100	20 100	1.48	23	18
13	**4a**	**5b**	100	0			0						
14	**4a**	**5b**	50	50	95	74	7.8	60	40	4480	1.63	16	28
15	**4a**	**5b**	20	80	>99	>99	9.4	28	72	23 800	2.43	23	19
16	**4a**	**5b**	10	90	>99	>99	39	8	92	28 400	2.28	27	26

[a] Determined by ¹H NMR spectrometry. [b] Determined by size-exclusion chromatography [poly(methyl methacrylate) standards, 0.5 wt% Libr solution in DMF, 40 °C]. [c] Cloud points defined as the temperature at which the transmittance at 589 nm became 50% in the heating process. [d] Ref. 30.

broad that accurate calculation of the integrated intensity was difficult. Therefore, the composition was estimated from the signals of the terminal methyl group of the *n*-propyl group at 0.8–1 ppm and that of the two methyl groups of the isopropyl group at 1–1.4 ppm. As a result, the molar fraction of **4b** units was estimated to be 52%, roughly matching the feeding ratio of 50%. Fig. 2A shows the growth of monomer conversions at each reaction time. Both monomers were consumed at approximately the same rate until 5 h when the conversion of **5a** reached 50%. Since **4b** was not homopolymerized, the monomer conversions implied alternating copolymerization. The tertiary carbon radical derived from **4b** is more stable than the secondary carbon radical derived from **5a** due to the large hyperconjugation effect. Therefore, propagating radicals preferentially attack **4b**. However, it is thermodynamically difficult for the **4b**-derived radical to attack **4b** to form a homo-sequence, probably due to the steric hindrance of the substituents. Therefore, **4b** hardly homopolymerizes. On the other

hand, **5a**, the sterically less hindered monomer, can be attacked, resulting in an alternating sequence of **4b**–**5a**. This interpretation alone cannot explain the fact that **4b** continues to be consumed in the later stages of the reaction while the conversion of **5a** remains almost unchanged. A possible scenario is as follows: In the later stages of the reaction when the monomer concentration becomes lower, the termination reaction occurs before the **4b**-derived radical propagates to **5b**. However, it is difficult to draw definitive conclusions from this result alone. As the feeding ratio of **4b** increased, the number average molecular weight tended to decrease. This is an expected result because **4b** does not homopolymerize. In entry 6, the feed ratio and conversion of **5a** were 20% and 2%, respectively, but the molar fraction of **5a** units in the copolymer was 25%. As the yield implies, not all products were recovered in this experiment. Considering that **4b** hardly homopolymerized, it could be understood that the product recovered as a precipitate was the polymeric component containing a large amount of **5a** units.

Similar copolymerization was performed for **4a** and **5b**. Monomer conversion monitoring in copolymerization with equimolar mixtures suggested preferential consumption of **4a** (Fig. 2B). **4a** is less sterically hindered by the *N*-substituent than **4b**, while **5b** has greater bulkiness than **5a**. Consequently, the order of polymerization rates was expected to be as follows: **4a** > **4b** > **5a** > **5b**. In fact, the difference in consumption rate between **4a** and **5b** was significant compared to the combination of **4b** and **5a**.

pH-/thermo-responsiveness

The transmittances at 589 nm (sodium D-line) of the aqueous solution of the prepared polymers were measured with rising temperature. The cloud point (T_c) was evaluated as the point at
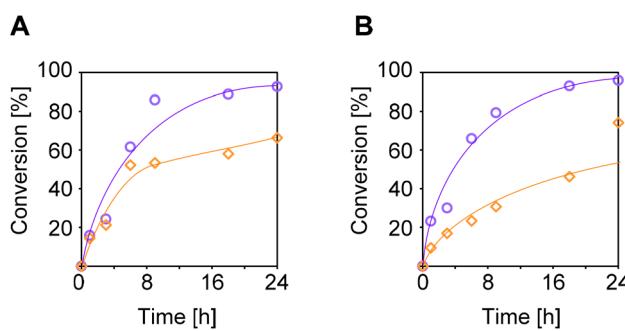
Fig. 2 Time *vs.* conversion plots for the copolymerization of an equimolar feeding ratio of **4** and **5**. A: For the copolymerization of **4b** (purple circles) and **5a** (orange diamonds). B: For the copolymerization of **4a** (purple circles) and **5b** (orange diamonds).

which the transmittance of the polymer aqueous solution became half before and after the change in the heating process (Fig. 3A). The homopolymer of **5a** exhibited a thermo-response with a lower critical separation temperature (LCST), and the T_c was 23 °C (entry 12). T_c decreased linearly with an increasing mole fraction of **4b** in the polymer (entries 8–12, Fig. 3C). Our previous study using an *N,N*-disubstituted acrylamide with a hydroxy pendant showed a linear trend of increasing T_c with increasing hydroxy content.[25] Since the amino group is a hydrophilic group as well as the hydroxy group, the decrease in T_c by copolymerization was contrary to our expectations. Amino groups have stronger properties as hydrogen-bond acceptors than hydroxy groups. In fact, as mentioned above, conformational analysis of **4b** by ^{1}H NMR spectroscopy and DFT calculations suggested that the nitrogen atom of the amino group forms a hydrogen bond with the hydrogen atom of the amide bond. Therefore, it was speculated that the amino group functioned as an acceptor for intramolecular hydrogen bonds and had the effect of lowering T_c.

A similar experiment was performed in 1 M HCl aq (Fig. 3B). For the copolymers with 0–26 mol% **4b** content, the T_c in 1 M HCl aq were lower than those in pure water (entries 10–12, Fig. 3C). In contrast, the T_c of the copolymers with 52 and 75 mol% **4b** content were drastically increased from those in pure water. In these copolymers, the ammonium pendant groups function as a strong hydrophilic group and inhibit the association of polymer chains by electric repulsion, resulting in a much higher T_c than expected. On the other hand, in order to actualize the effect of such an amino group, it is

necessary to prepare a copolymer with **4a** content of at least 52 mol%. A similar trend was observed for copolymers of **4a** and **5b** (Fig. 3D).

Conclusions

The polymerization of **4** was investigated from an interest in polymers of β-amino acid derivatives. **4** was synthesized in a four-step reaction starting from *tert*-butyl acrylate. Although optimizations of reaction conditions were required, the reaction steps were significantly reduced from the conventional synthesis method using a protection/deprotection protocol. The intermediate, **13**, is also attractive as a precursor of various allylic-modified methacrylamides because it exhibits activity in conjugate substitution reactions. Although **4** is an *N*-monosubstituted methacrylamide, the homopolymerization did not afford a polymeric product. Since the reactivity of (meth)acrylamide is known to vary greatly depending on temperature, solvent, and catalyst,[31–33] the polymerization of **4** still needs further investigation. For the copolymer of **5**, the incorporation of **4** was effective at increasing the hydrophilicity in acidic solution, but it was necessary to use **4** as the main component. Rather, copolymers with low **4** content were more hydrophobic than the homopolymer of **5**. This result was in contrast to copolymers bearing hydroxy groups. These facts suggest that the hydrogen-bond acceptability of the amino groups affected the hydrophobicity of the polymer.

Although various functional polymers have been reported for α-functionalized acrylates,[34] acrylamides have hardly been studied. As shown here, modification at the α-position does not simply reflect the properties of the functional group, such as hydrophilicity and hydrophobicity, in the polymer. Therefore, the chemistry of α-functionalized acrylamide has the potential to produce unexpected materials and functions.

Author contributions

Y. K. supervised this study and wrote a draft of this article. N. C. conducted all experiments on **4a**, **4b** and the polymers. K. I. examined the synthesis of **14**, **15** and **13d**. Y. A. helped all experiments as a post-doc researcher.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements
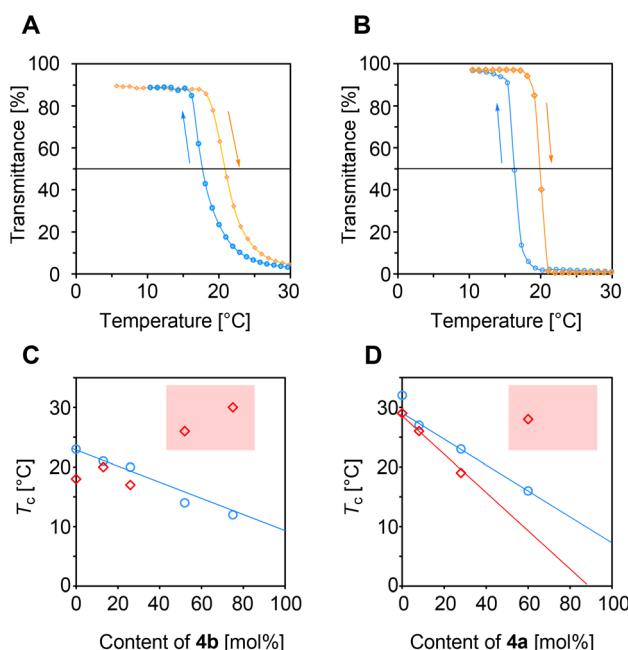
Fig. 3 Changes in transmittance of **poly(4b-*co*-5a)** (entry 11) in H$_2$O (A) and 1 M HCl aq (B). Plots of the mole fraction of **4** *vs.* T_c in H$_2$O (blue circles) and 1 M HCl aq (red diamonds) for **poly(4b-*co*-5a)** (C) and **poly(4a-*co*-5b)** (D).

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29 Although other monomers (**14a–d**) have low purity, polymerizations using AIBN were also investigated. Some phenomena implying polymerization, *e.g.* the increase of viscosity of the reaction mixture and the broad ^{1}H NMR signals with a small diffusion coefficient in DOSY spectra, were observed. However, no peak in high molecular weight region ($>10^3$) was observed by size exclusion chromatography (SEC) using chloroform as an eluent.

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