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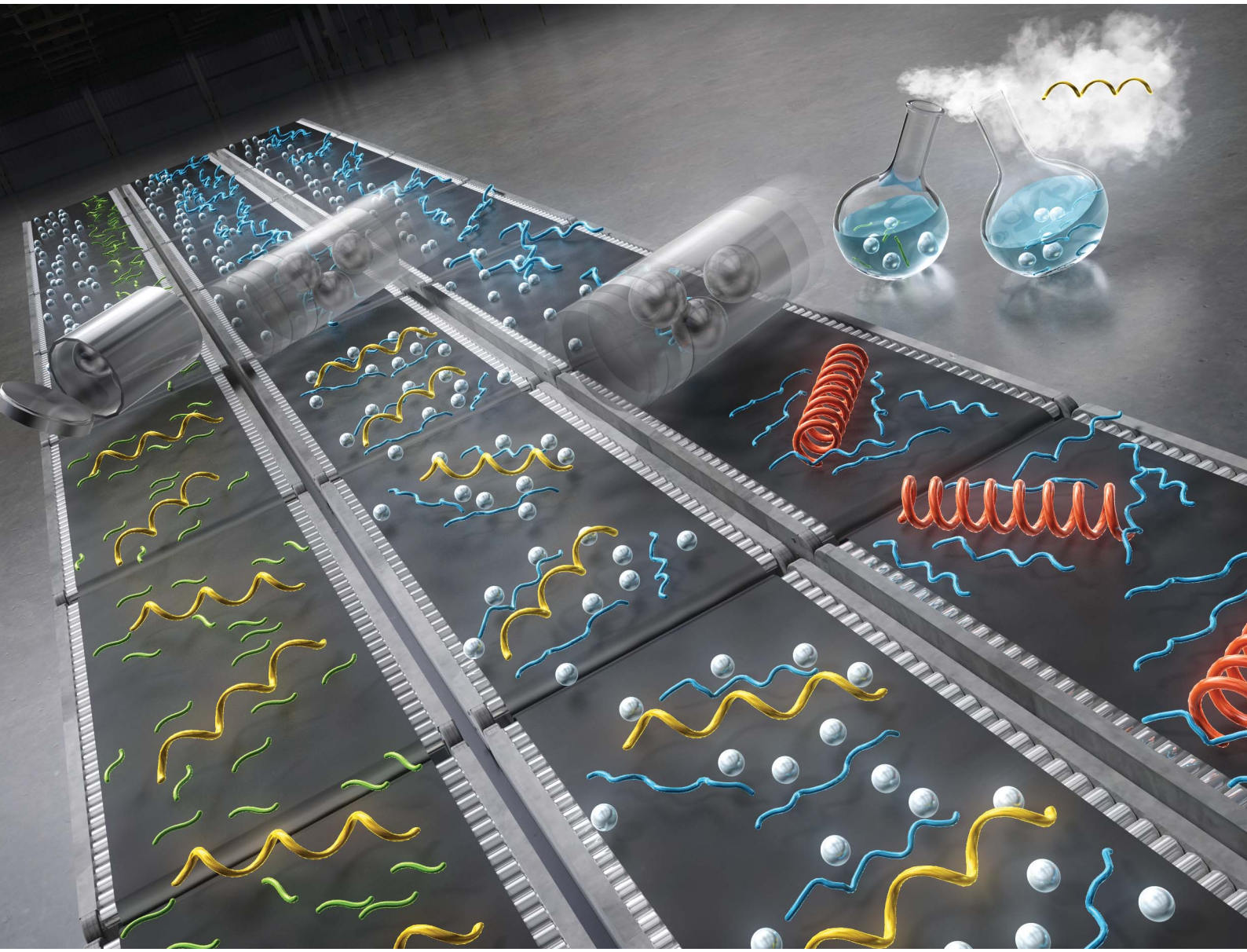

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PAPER

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Helical-structure transition and color changes in aromatic polyacetylenes under mechanochemical conditions: effect of the additive-alcohol chain length

Haruki Ikushima [a] and Yasuteru Mawatari *[ab]

This study investigates the control of higher-order polymer structures through mechanochemical (MC) synthesis, focusing on poly(2-ethynylnaphthalene) (**P2EN**) as a model helical poly(arylacetylene). The products of MC synthesis using linear alcohols (C1–C22) as additives were compared with those of conventional solution synthesis using these alcohols as solvents. Interestingly, the polymer color, which depends on helical conformation, is directly influenced by the carbon-chain length of the alcohol additive in MC synthesis. Short-chain alcohols produce yellow **P2EN** with extended helices (the *cis-transoid* structure), whereas long-chain alcohols yield red **P2EN** with contracted helices (the *cis-cisoid* structure). This structure-dependent color variation is exclusive to MC synthesis; solution polymerization consistently produces yellow **P2EN** with extended helices, regardless of the alcohol used. The results of this study suggest that under MC conditions, localized heat and pressure facilitate transitions from metastable *cis-transoid* to stable *cis-cisoid* conformations through specific high-affinity polymer/additive interactions. Thus, MC synthesis with appropriate additives can direct the synthesis of polymers with thermodynamically stable higher-order structures. The proposed approach offers an environmentally friendly method for controlling the conformation (and material properties) of polymers, potentially enabling the green industrial production of functional polymer materials.

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Introduction

In mechanochemical (MC) synthesis, chemical reactions are induced by mechanical energy. Recently, owing to its solvent-free nature, MC synthesis has attracted significant attention in green chemistry.[1–4] To establish this method as a major synthesis technique alongside solution synthesis, investigating the advantages specific to MC synthesis, such as improved reactivity and the ability to form unique structures, is vital. The neat grinding (NG) method, which uses no additives, involves mild reaction conditions[5] and improved reactivities of poorly soluble compounds.[6] Various additive methods are being investigated for reactivity improvements that cannot be ensured by using NG alone. Liquid-assisted grinding (LAG), which involves grinding with small amounts of liquid, is a commonly used method involving additives that can be used to control reaction pathways, improve reactivity,[7] promote post-polymerization polymer modification, and suppress polymer-chain cleavage caused by mechanical stimulation.[8] Ion- and liquid-assisted grinding (ILAG), which involves grinding with catalytic amounts of ionic salts and liquid additives, enables the quantitative and selective conversion of bismuth salicylate into various forms.[9] Ionic liquid-assisted grinding (IL-AG) improves the rate of fluorination for aromatic and 1,3-dicarbonyl compounds.[10] Polymer-assisted grinding (POLAG), which involves grinding with organic polymers, improves the efficiency of the solid-state cross-coupling of insoluble aryl halides[11] and various other reactions, such as regioselective oxidative Heck coupling.[12] Moreover, these additives can control the higher-order structures of products, such as the structures of metal–organic frameworks (MOFs) and the polymorphs of cocrystals. Friščić *et al.* reported on the structural control of products in the ILAG-based synthesis of MOFs.[13] Hasa *et al.* showed that polymorphs can be structurally controlled by tuning the number of monomer units of polyethylene glycol added during the cocrystallization reaction of caffeine and glutaric acid.[14] Although numerous studies investigate improvements in polymerization,[15,16] the effect of additives on the higher-order structures of polymers remains largely unexplored to date. Controlling the higher-order structure of polymers, which significantly affects their functionality as materials, is extremely important.

[a]*Graduate School of Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan. E-mail: mawatari@muroran-it.ac.jp*

[b]*The Center for Rare Earths Research, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, Japan*

Previous studies have focused on controlling the higher-order structures of aromatic-substituted polyacetylenes (PAAs), a type of synthetic helical polymer.[17–22] On polymerizing monomers in solution with the catalyst [Rh(norbornadiene)Cl]$_2$-NEt$_3$, the polymerization proceeds *via* a coordination-insertion mechanism[23] (Fig. 1A), producing polymers with *cis*-configured geometric structures in the main chain.[24–26] The secondary structure of these polymers comprises a helix, and their color varies with the solvent used, likely owing to different degrees of helix elongation and contraction in different solvents.[27–30] Specifically, poly(2-ethynylnaphtalene) (**P2EN**) is obtained as a yellow powder consisting of an extended helical structure called *cis-transoid* (*ct*) when synthesized in ethanol, and as a red powder consisting of a contracted helical structure called *cis-cisoid* (*cc*) when synthesized in toluene (TOL) (Fig. 1B).[31] Furthermore, upon immersion in TOL, **P2EN** powder with a metastable extended helical structure undergoes solid-state helical contraction, transitioning to a relatively stable contracted helical structure (Fig. 1B). As changes in the secondary structure of this polymer are accompanied with a visual color change, **P2EN** was selected for examining the effects of additives on secondary-structure changes in MC reactions.

A recent study demonstrated the MC polymerization of phenylacetylene-based monomers using the [Rh(norbornadiene)Cl]$_2$-NEt$_3$ catalyst system.[32] The MC polymerization of 4-methoxycarbonylphenylacetylene, with the solid linear alcohol 1-hexadecanol as an additive, yields polymers without significantly decreasing both the *cis* content of the main chain and molecular weight of the polymer, indicating that the presence of additives is essential for the MC synthesis of aromatic polyacetylenes with high *cis* content in the main chains that can easily isomerize under pressure. Based on this research, to expand the range of applicable monomers for MC polymerization using the [Rh(norbornadiene)Cl]$_2$-NEt$_3$ catalyst system, the MC polymerization of **2EN**, a naphthylacetylene-based monomer, was attempted. Using 1-hexadecanol as an additive produces a red powder, whereas LAG with EtOH, a liquid alcohol used in conventional solution polymerization, yields a yellow powder. Thus, in the MC synthesis of **P2EN**, the choice of additive influences the polymer color control, *i.e.*, the formation of higher-order structures.

This study demonstrated the MC synthesis of **P2EN** using linear-alcohol additives with carbon numbers within 1–22 and examined the relationship between the carbon chains of the additives and the color difference depending on the helical structure of the synthesized **P2ENs**. Interestingly, when linear alcohols with different carbon numbers were used as additives in the MC synthesis of **P2EN**, the color of the synthesized polymers varied from yellow to red depending upon the carbon number (Fig. 1C). Furthermore, to investigate whether this phenomenon is specific to MC synthesis, the MC synthesis of **P2EN** was compared with solution synthesis using heat-melted alcohols as solvents. The color-control of polymers produced by the MC synthesis of **P2EN** through the choice of additives comprises a new strategy for higher-order polymer-structure modulation through additive selection in MC synthesis.

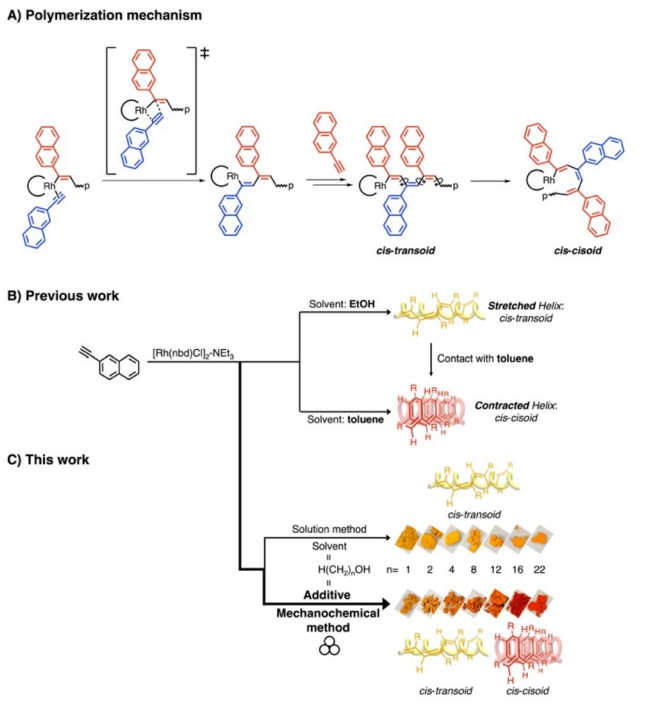

Fig. 1 (A) Rh-catalyzed polymerization mechanism of **2EN**. (B) Control of *cis-transoid* or *cis-cisoid* formation by polymerization-solvent selection, and *cis-transoid* to *cis-cisoid* transition on contact with toluene. (C) Control of *cis-transoid* or *cis-cisoid* formation by modulating the carbon number of the additive alcohol in MC synthesis.

Results and discussion

Synthesis method-dependent color of polymers

MC polymerization was conducted using linear alcohols with different carbon numbers as additives. A high *cis* content is required for helical structure formation, which is the origin of the color variation observed for **P2EN**. The MC polymerization of 4-methoxycarbonylphenylacetylene using only monomers, Rh catalysts, and Et$_3$N results in the formation of polymers with a low molecular weight and *cis* content.[32] Interestingly, the addition of 1-hexadecanol (C_{16}OH), a solid alcohol that does not participate in the reaction, to the MC polymerization system suppresses the decrease in molecular weight and *cis–trans* isomerization. In this study, MC polymerization using C_{16}OH and EtOH, which is commonly used as a solvent in conventional solution synthesis, as additives resulted in the formation of red (Table 1, entry 6) and yellow (Table 1, entry 2) polymers, respectively. The Raman spectra of these polymers, as described in subsequent section, shows a high *cis* content. Therefore, similar to solid additives, liquid additives function as cushions that suppress *cis*-to-*trans* isomerization. The colors of polymers synthesized using linear alcohols with different carbon numbers as additives differed. Therefore, the MC polymerization of **2EN** was attempted using various linear alcohols with carbon numbers within 1–22 as additives to clarify the relationship between the carbon number of the linear alcohol used as an additive and the color of the resulting polymer (Table 1,

Table 1 Polymerization results of **2EN**[a]

Entry	P2EN	Polymerization temp. (°C)	$H(CH_2)_nOH$	Yield (%)	Color
1	**P1(M)**[b]	—	1	88	
2	**P2(M)**[b]	—	2	96	
3	**P4(M)**[b]	—	4	94	
4	**P8(M)**[b]	—	8	93	
5	**P12(M)**[b]	—	12	91	
6	**P16(M)**[b]	—	16	97	
7	**P22(M)**[b]	—	22	75	
8	**P1(S)**[c]	60	1	98	
9	**P2(S)**[c]	75	2	99	
10	**P4(S)**[c]	75	4	97	
11	**P8(S)**[c]	75	8	98	
12	**P12(S)**[c]	75	12	99	
13	**P16(S)**[c]	75	16	96	
14	**P22(S)**[c]	75	22	99	
15	**PN(M)**[b]	—	—	77	

[a] Reaction time of 30 min. [b] Conditions of the MC method: molar ratio of (**2EN**/Rh cat./Et_3N) = 100/1/50. The weight of the **2EN** and additive are 300 and 600 mg, respectively. [c] Conditions of the solution method: [**2EN**] = 0.2 mol L^{-1}, molar ratio of [**2EN**]/[Rh cat.]/[Et_3N] = 100/1/50.

entry 1, 3, 4, 5, and 7). Regarding polymer abbreviations, the numbers represent the carbon number of the linear alcohol used as an additive or solvent, and "N" signifies cases where no additive was used. Additionally, for synthesis methods, MC synthesis is represented as "(M)" and solution synthesis as "(S)". **P1(M)** is yellow; **P4(M)**, **P8(M)**, and **P12(M)** are orange; and **P22(M)** is almost the same red as **P16(M)**. When hydrocarbons with carbon chains similar to those of the added alcohols were used as additives, the colors of the resulting polymers were almost identical. According to the literature, polymers derived from **2EN** show variations in color depending on the type of polymerization solvent used in solution polymerization.[31] However, in this study, the use of various alcohols as additives in solution synthesis resulted in yellow polymers in all cases (Table 1, entry 8–14). Interestingly, only in MC polymerization did the difference in the carbon number of the alcohol additive manifest as a difference in the color of **P2EN**. In contrast, **PN(M)**, generated by NG without additives, was brown, which is distinct from the other polymers (entry 15 in Table 1 and Fig. S1). **PN(M)** is the only compound soluble in several organic solvents such as $CHCl_3$, THF, and toluene because of its extremely low M_n and *cis* content (Table S1), *i.e.*, pressure-induced chain scission and isomerization to the *trans* structure, as indicated by the GPC trace in Fig. S1 and the Raman spectra shown in Fig. 3.

The absorption maxima (λ_{max}) in diffuse reflective UV–vis (DR UV–vis) spectra of **P1(M)**, **P2(M)**, **P4(M)**, **P8(M)**, and **P12(M)** were observed at ~450 nm, while those of **P16(M)** and **P22(M)** were observed at ~500 nm (Fig. 2). In the case of previous **P2EN**, the λ_{max} of the *ct* and *cc* forms are observed at 445 and 510 nm, respectively.[31] Therefore, the observed data suggest the formation of the *ct* structure for **P1(M)**, **P2(M)**, **P4(M)**, **P8(M)**, and

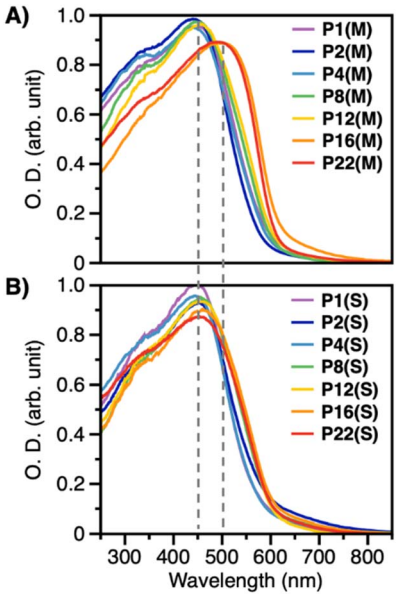

Fig. 2 DRUV–vis spectra of **P2ENs** synthesized by (A) the MC method and (B) the solution synthesis observed on alumina powders.

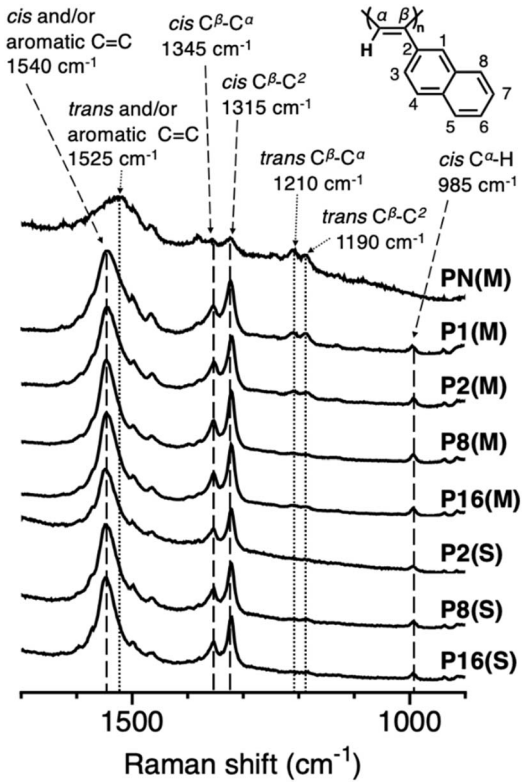

Fig. 3 Resonance Raman spectra of **P2ENs** synthesized by the MC method and solution synthesis.

P12(M), and *cc* structure for **P16(M)** and **P22(M)**. Notably, the λ_{max} of all solution-synthesized polymers was ~450 nm, indicating the formation of *ct* structures. Interestingly, the λ_{max} for **P8(S)–P22(S)**, obtained through solution synthesis using alcohols with relatively long alkyl-chain lengths as solvents, remained unchanged at 445 nm; however, the absorption intensity near 530 nm increased slightly. These spectral features indicate the slight formation of the *cc* structure, which likely imparts a slight redness to the polymer. Therefore, in solution synthesis, as the alkyl-chain length of the solvent increases, the hydrophobic interactions between the solvent and polymer molecules become stronger, resulting in the partial formation of the relatively stable *cc* structure. This tendency is remarkably pronounced in MC synthesis, suggesting that **P16(M)** and **P22(M)** produce large amounts of the *cc* structure.

Raman study

The *cis* content in the geometric structure of the main chain of the substituted polyacetylenes was estimated using solution-state ^{1}H-NMR measurements. Because all **P2ENs** other than **PN(M)** are insoluble in common organic solvents, resonance Raman spectra were measured to qualitatively evaluate the geometric structure of the main chain, and each peak was assigned based on the literature (Fig. 3).[31,33] In the spectrum of **PN(M)** without additives, intense peaks assigned to the *trans* structure were observed, while the peak assigned to *cis* C^{α}–H (at 985 cm^{-1}) was not observed. Additionally, because only **PN(M)** is soluble in organic solvents, its ^{1}H-NMR spectrum was measured (Fig. S2), and its *cis* content was calculated to be 10%, indicating that the majority of the main chain is in the *trans* structure. According to the literature, **P2EN** synthesized in EtOH shows a *cis* content of 22% when heat-treated at 200 °C for 1 min. The results of this study indicate that the energy generated by the ball-milling process used in this study likely exceeds the energy generated by heat treatment at 200 °C for 1 min.[31] Notably, the Raman spectra of **P2ENs** obtained by MC synthesis and solution synthesis with additives contained intense peaks assigned to the *cis* structure, indicating that the majority of the main chain is in the *cis* structure. For these **P2ENs**, differences are observed in the peak-intensity ratio of the peak at 1210 cm^{-1} (attributed to *trans* C^{β}–C^{α}) to that at 1345 cm^{-1} (due to *cis* C^{β}–C^{α}); **PN(M)**, **P1(M)**, **P2(M)**, and the other samples show approximate peak-intensity ratios of 1, 0.4, 0.2, and 0.1, respectively. This result suggests that using additive alcohols with a high carbon number in MC synthesis can effectively suppress the *cis*-to-*trans* isomerization of the polymer main chain. In resonance Raman spectroscopy, peaks from components with absorption bands near the irradiation wavelength, in this case 532 nm (corresponding to the *trans* form), were enhanced.[34,35]

DSC study

The DSC traces of **P2ENs** were measured at a heating rate of 10 °C min^{-1} under Ar (Fig. 4). The trace shows two exothermic peaks at around 210 °C and 235 °C in all polymers. According to previous reports, these exothermic peaks can be attributed to the thermal *cis*-to-*trans* isomerization of the *ct* and *cc* structures, which comprise extended and contracted helical structures, respectively.[31] However, the exothermic peak position observed in this study (near 235 °C) is at a lower temperature than that reported

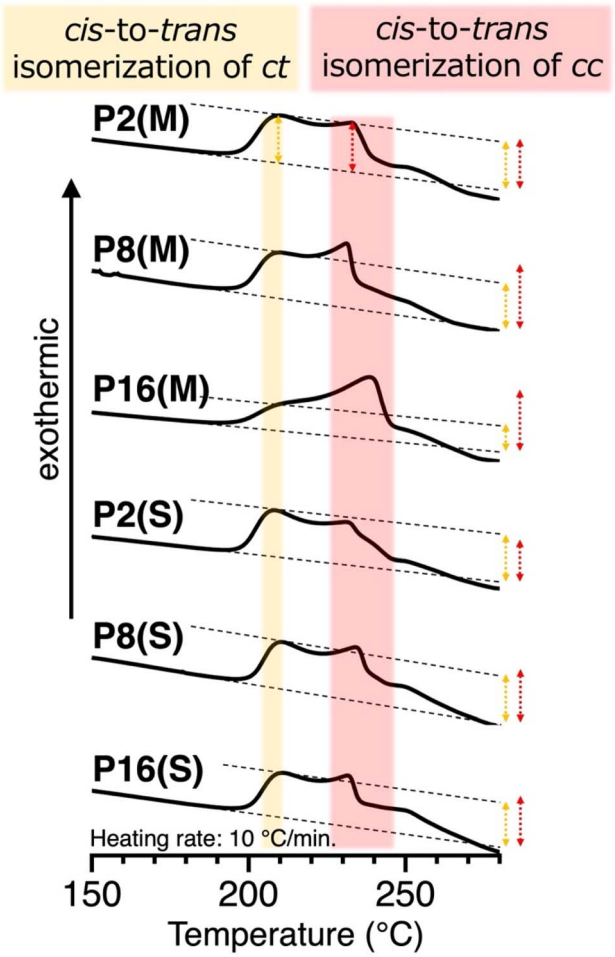

Fig. 4 DSC traces of **P2ENs** observed under Ar.

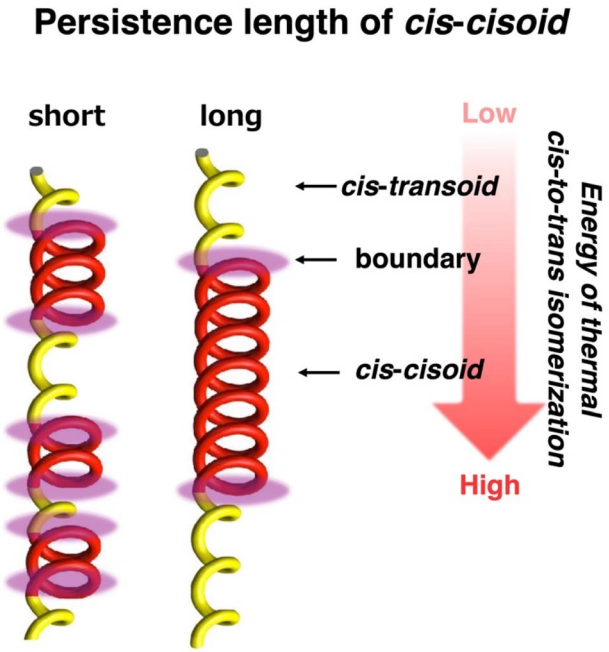

Fig. 5 Relationship between the persistence length of *cc* and the energy of *cis*-to-*trans* isomerization.

previously (247 °C). The *cis*-to-*trans* isomerization energy required for units located inside the *cc* sequence is expected to be greater than that required for units near the boundary with the *ct* structure (Fig. 5) because the highly regular π-stacking between the naphthyl groups of side chains formed by units inside the *cc* sequence hinders the rotational motion of the naphthyl groups, triggering *cis*-to-*trans* isomerization. Therefore, the shift of this peak to a lower temperature indicates a higher proportion of low-regularity chains between the naphthyl groups, *i.e.*, in the boundary regions with *ct*. Thus, the appearance of the exothermic peak at around 235 °C indicates that the *cc* shows a relatively short persistence length. This hypothesis is validated by the XRD pattern of **P2ENs**; the peak intensity at 3.4 Å (corresponding to the distance between naphthyl groups in the side chains of *cc*) is extremely weak (Fig. S3). To represent the ratio of *cc* to *ct* in the polymer, the *cc* ratio was defined (R_{cc} = peak intensity near 235 °C/peak intensity at 210 °C), which is ∼1.0 for **P2(M)**, **P2(S)**, **P8(S)**, and **P16(S)**, 1.4 for **P8(M)**, and 2.2 for **P16(M)**. While the R_{cc} of all solution-synthesized **P2ENs** is almost the same, the R_{cc} of MC-synthesized **P2ENs** increases with increasing carbon number of the alcohol additive. Interestingly, even the spectrum of **P16(M)**, which is a red sample, contains an exothermic peak attributed to the *cis*-to-*trans* isomerization of *ct* at approximately 210 °C. Notably, the spectrum of red *cc* **P2EN** synthesized in TOL does not contain an exothermic peak at 210 °C. Since the majority of **P16(M)** was confirmed to be *cc* with some *ct*, the *ct* formed through polymerization likely transitioned to *cc* under continuous MC conditions. This phenomenon is likely because the method used in this study differs from previously reported methods of *cc* formation, which involve polymerization using solvents with high affinity for the polymer, immersion to the solvents, or the heat-treatment of *ct*-formed polymers.[31]

Transition from *ct* to *cc* in the MC synthesis environment

To investigate the effect of the MC synthesis duration on the R_{cc} of the produced polymer, polymers were synthesized at reaction times of 5, 1, and 1/6 min (Table 2). Surprisingly, a yellow

Table 2 Polymerization results of **2EN** at various reaction times[a]

Entry	**P2EN**	$H(CH_2)_nOH$	Ball-milling time (min)	Yield (%)	Color
1	**P16(M)-5**	16	5	69	
2	**P16(M)-1**	16	1	39	
3	**P16(M)-1/6**	16	1/6	20	

[a] Mechanochemical method: molar ratio of (**2EN**/Rh cat./Et_3N) = 100/1/50. The weight of the **2EN** and additive are 300 and 600 mg, respectively.

sample is synthesized within 10 s (**P16(M)-1/6**). On increasing the reaction time, the redness of the polymers gradually increases, with orange and red samples synthesized within 5 and 30 min, respectively (**P16(M)-5** and **P16(M)**, respectively) (entry 1 in Table 2 and entry 6 in Table 1, respectively). This time-dependent change suggests an increase in the R_{cc} of the polymer during MC synthesis.

The R_{cc} of **P16(M)-1/6**, **P16(M)-1**, and **P16(M)-5** determined from DSC are 0.9, 1.3, and 1.6, respectively (Fig. 6). Thus, the R_{cc} increases with increasing reaction time, indicating that the *ct* formed though polymerization transitions to *cc* under continuous MC conditions. Additionally, the exothermic peak attributed to the thermal *cis*-to-*trans* isomerization of *cc* was observed at 240 °C in all cases, indicating that the persistence length of *cc* remained constant, regardless of the reaction time.

Interestingly, in solution synthesis, alcohols with different carbon numbers do not produce polymers with different R_{cc} values (entry 8–14 in Table 1), indicating that contact with long-chain alcohols is not the only reason for the *ct* to *cc* transition of **P16(M)**. Compared with ambient temperature and pressure conditions, the unique environment generated during MC synthesis, including localized heat and pressure, likely enhances the affinity between long-chain alcohol and polymer molecules. Consequently, long-chain alcohols can interact strongly with polymers frozen in the metastable *ct* structure, thereby undergoing facile transition to the stable *cc* structure. Moreover, on ball-milling **P2(S)**, previously synthesized in EtOH, with 1-hexadecanol for 30 min, the sample becomes slightly reddish and the R_{cc} hardly increases. Thus, for facile *ct* to *cc* transition, polymer chains should be placed in an MC-synthesis environment with numerous long-chain alcohol molecules in close proximity.

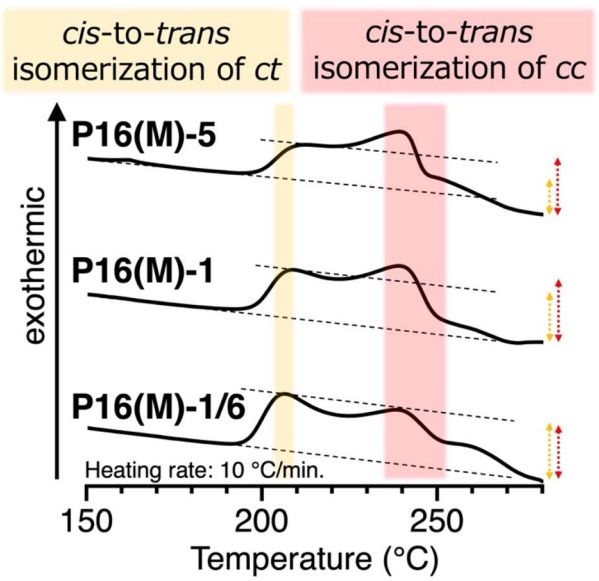

Fig. 6 DSC traces of P2ENs synthesized at various polymerization times observed under Ar.

Conclusions

In this study, **P2EN** was synthesized *via* MC synthesis using linear alcohols with carbon numbers ranging from 1 to 22 as additives and solution synthesis using the same linear alcohols as polymerization solvents. MC synthesis using linear-alcohol additives with a small carbon number resulted in the formation of yellow-powder **P2EN** comprising the ct structure with an extended helix, whereas using additives with a high carbon number resulted in red-powder **P2EN** comprising the cc structure with a contracted helix. This result is specific to MC synthesis; in conventional solution synthesis, yellow-powder **P2EN** containing extended helices is formed in all cases with no selectivity. Under MC conditions where localized heat and pressure occur, polymers frozen in metastable structures likely transition to stable structures owing to interactions with additives that show a high affinity toward the polymer. This study indicates that the use of additives with a high affinity for polymers in MC synthesis leads to the formation of stable higher-order structures. The additive-based control of higher-order structure formation through MC synthesis is also expected to be possible for other polymers. Controlling the higher-order structure of polymers enables the performance control of polymer materials. Therefore, this study confirms the high potential applicability of MC synthesis, which is more environmentally friendly than conventional solution methods, in industrial polymer-material manufacturing processes.

Author contributions

H. I.: conceptualization, funding acquisition, investigation, methodology, project administration, validation, visualization, and writing – original draft. Y. M.: conceptualization, resources, supervision, and writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: **https://doi.org/10.1039/d5mr00102a**.

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