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Double Cyclopolymerization of Functionalized Trienes Catalyzed by Palladium Complexes

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ABSTRACT: Pd−diimine complexes catalyze polymerization of 1,6,11-dodecatrienes having cyclic ester groups at the 4 and 9 positions to produce the polymers containing two *trans*-five-membered rings in the structural units. The doublecyclopolymerization of triene with cyclic acetal group yields the polymer with narrow molecular weight distribution (M_w/M_n = 1.20−1.66). The two five-membered rings in a monomer unit of these polymers are linked directly with racemo stereochemistry. Relative stereochemistry of the monomer units separated by ethylene spacer changes depending on the monomer and catalyst, and 91% syndioselectivity is obtained in the polymerization of the triene with cyclic acetal groups. Hydrolysis of the polymer containing cyclic acetal groups yields the polymer containing CH_2OH groups.

Introduction

Polymers with five- or six-membered rings along the polymer chain show unique optical and mechanical properties that are rarely observed in common polyolefins.[1] Cyclopolymerization of dienes catalyzed by early and late transition metal complexes affords these polymers from monomers without cyclic groups.[2] The cyclopolymerization catalyzed by late transition metal complexes has advantages in high selectivity in the cyclization, and produces the polymers with a regulated structure.[3] 1,1,1-Triallylethane was reported to undergo the cyclopolymerization in the presence of Ziegler catalyst to yield the polymer with a bicyclic group in the repeating unit via insertion of a vinyl group of the monomer into the metal−polymer bond and subsequent double cyclization.[4] The produced polymer, however, is not fully characterized and contains remnant vinyl groups due to imcomplete cyclization. Linear trienes having two vinyl and one vinylene groups may also undergo the double cyclopolymerization to yield the polymer having two cyclic groups in the repeating unit. Late transition metal complexes were known to catalyze tandem double and multiple cyclization of the polymers in spite of much lower reactivity of the vinylene group toward insertion than of the vinyl group into the metal−carbon bond. Widenhoefer reported the double cyclizative hydrosilylation of 1,6,11-dodecatriene having methoxycarbonyl groups catalyzed by Pd−phenanthroline catalyst to produce the bicyclic compounds functionalized by the silyl group. Stereochemistry of the product is regulated to trans,trans form in high selectivity.[5,6] The doublecyclopolymerization of analogous trienes has not been reported yet.

We have been engaged in the study of the cyclopolymerization of dienes catalyzed by the complexes of late transition metals such as Ni, Co, Fe, and Pd.[4,7−9] The dienes with polar functional groups are polymerized in the presence of Pd−diimine−BARF catalyst (Brookhart catalyst) (BARF = $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$).[7−9] The polymers of these dienes as well as their copolymers with ethylene or α-olefins exhibit variant properties depending on the functional groups and their density along the polymer chain.[9] This paper will show double-cyclizative polymerization of the linear trienes having the polar functional groups catalyzed by the Pd complexes.

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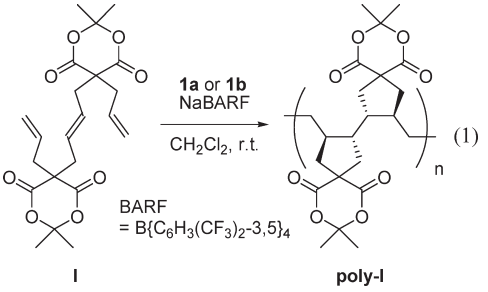
Results and Discussion

Chart 1 summarizes the trienes and Pd complexes **1a** and **1b** used in this study. 4,4,9,9-Tetracarboethoxy-1,6,11-dodecatriene (**II**) was prepared by Widenhoefer, and other trienes were newly prepared by using a similar procedure.

Catalysts formed in situ from the Pd complexes and NaBARF promoted the polymerization of 4,9-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5,5-diyl)-1,6,11-dodecatriene (**I**) according to eq 1. Table 1 summarizes results of the polymerization as well as that of trienes **II**−**VI**. The polymer of **I** contains two five-membered rings formed by successive cyclization of the olefinic groups. The structure was supported by the NMR results mentioned below.



Both Pd complexes **1a** and **1b** promote the cyclopolymerization in the presence of NaBARF. The catalytically active species are cationic Pd complexes formed in situ, similarly to the olefin polymerization as well as cyclopolymerization of dienes catalyzed by the Pd−diimine complexes. Poly-**I** showed GPC results (polystyrene standard) corresponding to M_n = 5100 and M_w/M_n = 1.51 (**1a**/NaBARF catalyst) and to M_n = 5500 and M_w/M_n = 1.49 (**1b**/NaBARF catalyst). The ^1H and $^{13}C\{^1H\}$ NMR spectra of the polymer contain the signals due to the five-membered rings along the polymer chain. The ^1H NMR spectra of the polymer contain the signals at δ 1.08−2.42 resemble to the signals of the polymer of isopropylidene diallylmalonate obtained by the cyclopolymerization catalyzed by the Pd complexes.

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Chart 1. Monomers and Catalysts Used in This Study

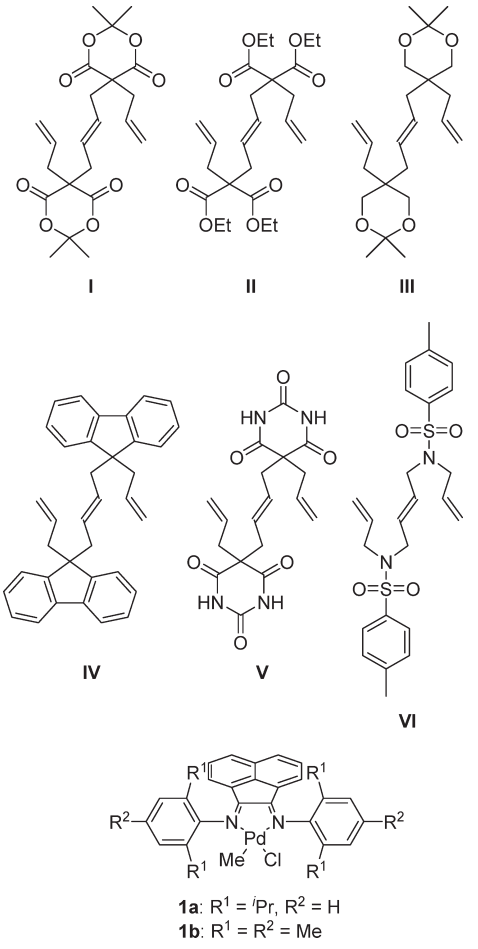


Table 1. Cyclopolymerization of 1,6,11-Dodecatrienes by Pd Complexes[a]

run	monomer	Pd complex	time/h	convn (%)[b]	M_n[c]	M_w/M_n[c]
1	**I**	**1a**	24	39	5100[e]	1.51[e]
2	**I**	**1b**	24	44	5500[e]	1.49[e]
3	**II**	**1b**	48	trace	1800[e]	1.49[e]
4	**III**	**1a**	1	75	8800[f]	1.66[f]
5	**III**	**1b**	1	quant.	13800[f]	1.29[f,g]
6	**IV**	**1a**	70	d	2300[e]	1.85[e]
7	**V**	**1b**	48	trace		
8	**VI**	**1a**	72	trace	1500[e]	1.20[e]

[a] Reaction conditions: Pd complex = 0.010 mmol, NaBARF = 0.012 mmol, [monomer]/[Pd] = 30, solvent = CH_2Cl_2 (0.5 mL), at room temperature. The monomer and Pd complexes are shown in Chart 1. [b] Determined by ^1H NMR. [c] Determined by GPC based on polystyrene standard. [d] Not determined. Most of the monomer remained unreacted. [e] $CHCl_3$ as eluent. [f] THF as eluent. [g] GPC suggested the presence of a minor fraction at the high molecular weight side.

No signals due to vinylic hydrogens are observed. The $^{13}C\{^1H\}$ NMR spectrum (Figure 1) shows quaternary carbon signal at δ 50.4 (d) which is close to the corresponding signals of the polymer of isopropylidene diallylmalonate (δ 51.1). Three CH_2 carbon signals are observed at δ 46.0, 39.0, and 30.7. The first and third signals are assigned to CH_2 carbons c and a in Figure 1 because the polymer of isopropylidene diallylmalonate shows the CH_2 carbon signals in the five-membered ring and of the ethylene spacer at similar positions (δ 45.8 and 31.5, respectively).

The other CH_2 carbon in the five-membered ring (j) is attached to the CH carbons that connect two five-membered rings and gives rise to the $^{13}C\{^1H\}$ NMR signal at δ 39.0. Signal of the CH

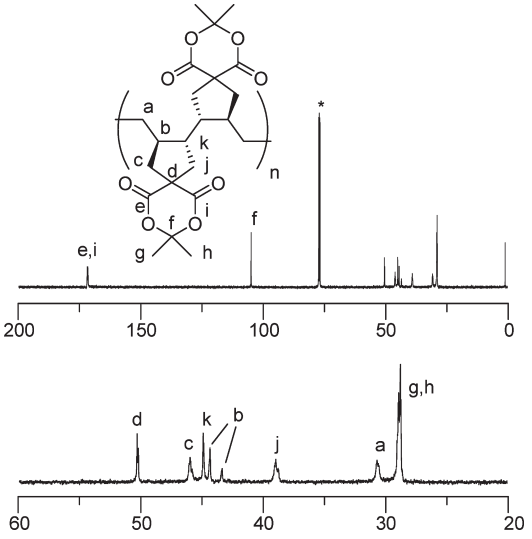


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of poly-**I** obtained by **1b**/NaBARF catalyst (Table 1, run 2).

carbon (k) appears at δ 45.0. The other CH carbon (b) shows the signals at δ 43.4 and 44.4, and the ^1H NMR signals of the corresponding CH hydrogens (δ 1.90) show correlation peaks with the ^1H NMR signals due to ethylene group attached to the five-membered ring. Appearance of the CH carbon signals suggests relative stereochemistry of the trans-five-membered rings along the polymer, as mentioned below.

Parts i and ii of Chart 2 show possible stereoisomers of the repeating units. Since the signal due to CH carbon (k) is observed as a single peak at δ 45.0, either of the racemo and meso repeating unit is formed by the successive intramolecular cyclization of the diene molecule during the polymerization. We assigned the racemo isomer to the product based on the following reasons. Calculation (GIAO method) of $^{13}C\{^1H\}$ NMR chemical shift indicates appearance of the CH carbon peak of the recemo and meso model compounds at δ 45.4 and 50.8, respectively. Actual peak position of the produced polymer (δ 45.0) is close to the former position.

Scheme 1 shows the mechanism of the double cyclization of the monomer during the polymerization. Insertion of a vinyl group into the Pd-polymer bond and subsequent cyclization via intramolecular insertion of the vinylene group yield an alkylpalladium species **A** having a trans-fused five-membered ring. Further insertion of remaining vinyl group into the Pd-CH bond forms two cyclopentane groups with racemo chemistry smoothly (path i in Scheme 1). Formation of the two five-membered rings with meso stereochemistry requires formal stereochemical inversion around the carbon attached to Pd of intermediate **A**, giving **C**, prior to the second cyclization. This process should involve shift of the Pd center of **A** to yield the cyclopentylpalladium species **B** via β-hydrogen elimination and reinsertion of the resulted olefin into the Pd−H bond and similar reactions to regenerate the Pd species ***C*** with opposite stereochemistry around the Pd−CH carbon to **A**. Formation of the racemo polymer end should take place much more smoothly than that of the meso structure, which is consistent with the selective formation of the two cyclopentane rings with racemo stereochemistry.

Parts iii and iv of Chart 2 show two stereochemical structures of the five-membered rings separated by an ethylene spacer. They correspond to two $^{13}C\{^1H\}$ NMR peaks of the CH carbon (b in Figure 1) (δ 43.4 and 44.4). Since the isotactic polymer of isopropylidene diallylmalonate shows its CH carbon signal at a higher magnetic position (δ 46.7) than that of the syndiotactic isomer (δ 47.0), these two signals are also assigned to racemo-isotactic

Scheme 1. Plausible Mechanism of Polymerization

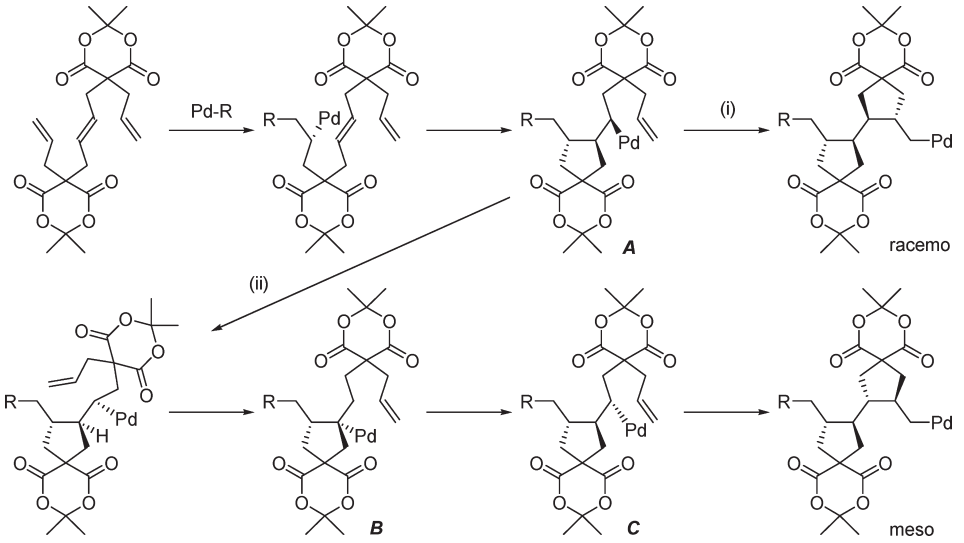
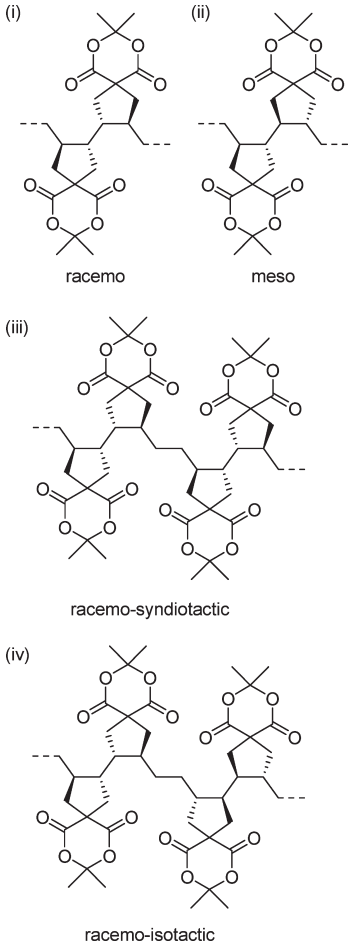


Chart 2. Tacticity of Intermolecular Double Cyclization



(δ 43.4) and racemo-syndiotactic (δ 44.4) isomers, respectively. Comparison of the peak intensity revealed that the polymers obtained by **1a**/NaBARF and by **1b**/NaBARF contained the two isomers with 67:33 and 34:66 ratios, respectively.

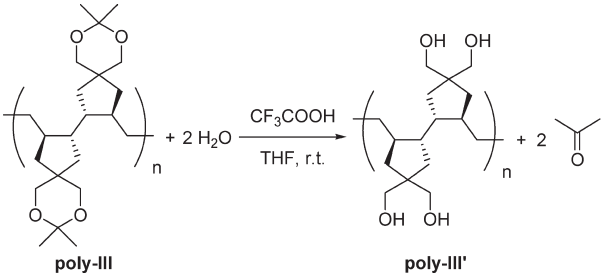
Reaction of 1,6,11-dodecatriene with diethyl malonate groups **II** in the presence of **1a**/NaBARF and **1b**/NaBARF catalysts did not cause its polymerization and resulted in recovery of the monomer in high yield. It is contrasted with the results that similar diester underwent cyclohydrosilylation with organosilanes catalyzed by Pd-phenanthroline complex.

Dodecatriene with cyclic acetal groups **III** undergoes the doublecyclopolymerization catalyzed by **1a**/NaBARF to produce the polymer having molecular weight higher than poly-**I** (M_n = 8800, M_w/M_n = 1.66). The reaction using **1b**/NaBARF catalyst produces the polymer with M_n = 13800 (M_w/M_n = 1.29).[10] The $^{13}C\{^1H\}$ NMR spectrum contains the signals at δ 33.2, 39.2, 40.6, 42.7. The signal positions are simlar to the polymer with trans-five-membered rings obtained from the corresponding diene (δ 33.5, 39.5, 40.4, and 45.7).[7−9]

Figure 2 shows the $^{13}C\{^1H\}$ NMR spectra of poly-**III**. CH carbon signals at δ 42.1, 42.7, and 44.2 are assigned to carbons b and k analogously to the corresponding signals of poly-**I**. The results suggest that the polymer contains racemo-isotactic and racemo-syndiotactic structures and no meso structures shown for poly-**I** in Chart 2. The polymer formed by the reaction using **1a**/NaBARF contains racemo-syndiotactic structure in high selectivity (91%), while the polymer obtained from **1b**/NaBARF is composed of racemo-isotactic and racemo-syndiotactic structures in 41:59 ratio.

Other 1,6,11-dodecatrienes in Chart 1, **IV**−**VI**, do not undergo smooth polymerization even in the presence of the Pd catalyst. The product of the reaction of **IV** catalyzed by **1a**/NaBARF is obtained in a low yield, and its GPC results suggest averaged molecular weights corresponding to the pentamer of the monomer. **V** and **VI** do not form the polymer even after prolonged reaction time in the presence of the Pd catalyst.

Acetal groups of poly-**III** undergo hydrolysis in the presence of water and a small amount of CF_3COOH to produce the polymer with hydroxyl groups poly-**III′**, as shown in eq 2.



(2)

The reaction proceeds in THF/H_2O (1:0.35) solvent, and deprotection of the polymer is completed in 20 h at room

Table 2. Solubility of Polymers.[a]

polymer	hexane	ether	$CHCl_3$	CH_2Cl_2	EtOAc	THF	DMF	DMSO	MeOH	H_2O
poly-**I**[b]	I	I	S	S	S	S	S	S	I	I
poly-**I**[c]	I	I	S	S	S	S	S	S	I	I
poly-**III**[b]	I	I	S	S	SS	S	S	S	I	I
poly-**III**[c]	I	I	S	S	SS	S	S	S	S[e]	I
poly-**III′**[d]	I	I	SS	S	I	I	SS	S	S	I

[a] Solubility of 5 mg of polymer in 1 mL of solvent. I: Insoluble. S: Soluble. SS: Sparingly soluble. [b] Obtained by **1a**/NaBARF. [c] Obtained by **1b**/NaBARF. [d] Obtained by hydrolysis of poly-**III** formed by **1a**/NaBARF. [e] Partial hydrolysis took place during NMR measurement.

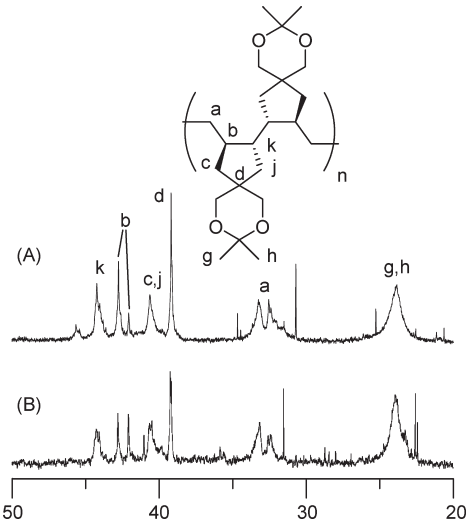


Figure 2. $^{13}C\{^1H\}$ NMR spectra of poly-**III** obtained by (A) **1a**/NaBARF and (B) **1b**/NaBARF catalysts ((A) in $CDCl_3$, 55 °C, (B) in $CDCl_3$, 50 °C).

temperature. The ^1H NMR spectrum of the polymer shows signals due to CH_2O hydrogens at δ 3.22, and no signals due to acetal groups.

Solubility of the polymers before and after the above hydrolysis is summarized in Table 2. Poly-**III** is insoluble in polar solvents such as MeOH, while the polymer after the hydrolysis is soluble in MeOH.

All the polymers do not show glass transition temperature in the region of 0−170 °C, and showed T_g (temperature of 5% weight decrease) at 168 °C (poly-**I**), 160 °C (poly-**III**), and 186 °C (poly-**III′**), respectively.

In summary, 1,6,11-dodecatrienes **I** and **III** undergo the Pd complex-catalyzed cyclopolymerization to produce polymers with unique structures. Dienes with a cyclic acetal group undergoes living cyclopolymerization, while the triene monomer with the same functional group, **III**, affords the polymer with narrow molecular weight distribution. Trienes with other functional groups **II** and **IV-VI** do not undergo the polymerization, although the diene with the same functional groups were reported to undergo the cyclopolymerization. The produced polymers in this study contain two neighboring trans-five-membered rings with racemo stereochemistry in each repeating unit with high stereochemistry.

Experimental Section

General Method. All manipulations of air- and water-sensitive compounds were carried out with standard high-vacuum or Schlenk techniques. NMR spectra were recorded on a Varian Mercury 300 and JEOL JNM-500 spectrometers. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were referenced to the signals of solvents. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder. Gel permeation chromatography (GPC) measurement was conducted at 40 °C on a JASCO high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV−vis detector (254 nm), using $CHCl_3$ as eluent at a flow rate of 1.0 mL min^{-1} with Shodex-806 L column (molecular range: 10^2 - 10^7), or on a TOSOH HLC-8020 high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV−vis detector (254 nm), using THF as eluent at a flow rate of 0.6 mL min^{-1} with TSKgel Super HM-L (molecular range: 10^2−10^7) and Super HM-M (molecular range: 10^2−10^7) column. Molecular weights were calculated relative to polystyrene standards. DSC was recorded on Seiko DSC 6200R. T_g was determined as onset temperature. TGA was recorded TG/DTA 6200R (in N_2, 5 °C min^{-1}).

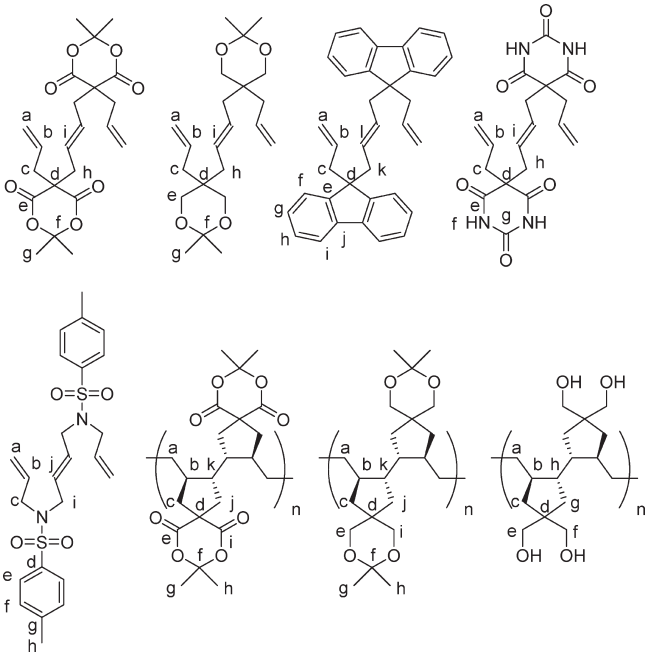
Materials. Dry CH_2Cl_2 used for the polymerization and reagents used for the preparation of monomers and Pd complexes were purchased and used as received. $CDCl_3$ was dried over CaH_2, vacuum-transferred, and degassed by repeated freeze−pump−thaw cycles was used for kinetic studies. Diimine ligands,[11] Pd complexes,[11] and NaBARF[12] were synthesized according to the literature method.

Synthesis of 4,9-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5,5-diyl)-1,6,11-dodecatriene (I). *trans*-1,4-Dibromo-2-butene (0.214 g, 1 mmol) and dry acetone (8.6 mL) were added to a 25 mL Schlenk flask containing 5-allyl-2,2-dimethyl-1,3-dioxane-4,6-dione (0.368 g, 2 mmol)[8] and K_2CO_3 (0.824 g, 6 mmol), and the mixture was refluxed for 13 h. Water was added to the reaction mixture, and the organic phase was extracted with $CHCl_3$, washed with brine and dried over $MgSO_4$. Volatile fractions were removed and the residue was chromatographed on silica gel (hexane/ethyl acetate = 5/1, R_f = 0.40) to afford 4,9-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5,5-diyl)-1,6,11-dodecatriene (**I**) as a white solid (0.294 g, 0.70 mmol, 70% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 5.66 (m, 1H, H_b), 5.50 (s, 1H, H_i), 5.20 (m, 2H, H_a), 2.70 (m, 4H, H_c and H_h), 1.68 (s, 6H, H_g). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 168.3 (C_e), 131.0 (C_b), 129.0 (C_i), 121.4 (C_a), 105.9 (C_f), 54.9 (C_d), 42.8 (C_c or C_h), 41.7 (C_c or C_h), 29.9 (C_g). Assignment of the NMR signals is based on the formula in Chart 3. Anal. Calcd (found) for $C_{22}H_{28}O_8$: C, 62.85 (62.88); H, 6.71 (6.74).

Synthesis of 4,9-(2,2-Dimethyl-1,3-dioxan-5,5-diyl)-1,6,11-dodecatriene (III). Concentrated H_2SO_4 (2.1 μL) was added to a 25 mL Schlenk flask containing 4,4,9,9-tetrahydroxymethyl-1,6,11-dodecatrinene (1.00 g, 3.52 mmol),[5] dry acetone (4.4 mL), and trimethyl orthoformate (3.1 mL, 28.2 mmol), and the mixture was refluxed for 14 h. sat. $NaHCO_3$ aq. was added to the reaction mixture and organic phase was extracted with ether and was washed with brine. After dried over $MgSO_4$, volatile fractions were removed and the residue was chromatographed on silica gel (hexane/ethyl acetate = 5/1, R_f = 0.55) to afford 4,9-(2,2-dimethyl-1,3-dioxan-5,5-diyl)-1,6,11-dodecatriene (**III**) as a pale yellow oil (0.649 g, 1.78 mmol, 51% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 5.72 (m, 1H, H_b), 5.41 (s, 1H, H_i), 5.06 (m, 2H, H_a), 3.51 (s, 4H, H_e), 2.06 (m, 4H, H_c and H_h), 1.35 (s, 6H, H_g). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 133.0 (C_b), 128.3 (C_i), 118.2 (C_a), 97.8 (C_f), 67.1 (C_e), 36.6 (C_c or C_h), 35.5 (C_d), 35.3 (C_c or C_h), 23.7 (C_g). Assignment of the NMR signals is based on the formula in Chart 3. Anal. Calcd (found) for $C_{22}H_{36}O_4$: C, 72.49 (72.25); H, 9.95 (10.04).

Synthesis of 4,9-Fluorenylidene-1,6,11-dodecatriene (IV). *n*-Butyllithium (1.6 M hexane solution, 3.6 mL, 5.8 mmol) was added dropwise to a 50 mL Schlenk flask containing

Chart 3



9-allylfluorene (1.00 g, 4.85 mmol) and dry THF (13 mL) at 0 °C, and the mixture was slowly warmed to room temperature and was stirred for 2 h. The reaction mixture was cooled to 0 °C, and *trans*-1,4-dibromo-2-butene (0.52 g, 2.43 mmol) was added and the mixture stirred at room temperature for 6 h. Water was added to the reaction mixture and organic phase was extracted with ether and was washed with brine. After dried over $MgSO_4$, volatile fractions were removed and the residue was chromatographed on silica gel (hexane/ethyl acetate = 50/1, R_f = 0.40) to afford 4,9-fluorenylidene-1,6,11-dodecatriene (**IV**) as a white solid (0.342 g, 1.38 mmol, 57% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.3 Hz, 2H, H_i), 7.36−7.22 (m, 6H, H_f, H_g, H_h), 5.11 (m, 1H, H_b), 5.06 (ddt, 1H, H_l), 4.72 (m, 2H, H_a), 2.39 (m, 4H, H_c and H_k). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 149.6 (C_e), 140.5 (C_j), 133.9 (C_b), 127.0 (C_g), 126.8 (C_h), 123.6 (C_f), 119.7 (C_i), 117.1 (C_a), 54.0 (C_d), 42.4 (C_c or C_k), 42.2 (C_c or C_k). Anal. Calcd (found) for $C_{36}H_{32}$: C, 93.06 (93.29); H, 6.94 (6.56). Assignment of the NMR signals is based on the formula in Chart 3.

Synthesis of 4,9-(2,4,6-Trioxo-1,3-pyrimidin-5,5-dinyl)-1,6,11-dodecatriene (V). DMSO solution (64 mL) of NaH (0.56 g, 23.2 mmol) was added dropwise to a 200 mL round-bottomed flask containing 4,4,9,9-tetracarboethoxy-1,6,11-dodecatriene (**II**)[5] (2.5 g, 5.53 mmol) and urea (3.32 g, 55.3 mmol), and the mixture was stirred at room temperature for 12 h. Water and ether were added to the reaction mixture and aqueous phase was acidified by HCl(aq). Organic phase was extracted with ether, washed with brine, and dried over $MgSO_4$. Volatile fractions were evaporated to afford 4,9-(2,4,6-trioxo-1,3-pyrimidin-5,5-dinyl)-1,6,11-dodecatriene (**V**) as a white solid (1.41 g, 3.63 mmol, 66% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.3 (br, 2H, H_f), 5.47 (m, 1H, H_b), 5.18 (s, 1H, H_i), 5.01 (m, 2H, H_a), 2.42 (m, 4H, H_c and H_h). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 172.0 (C_e), 131.3 (C_b), 128.2 (C_h), 120.2 (C_a), 55.0 (C_d), 41.6 (C_c). Assignment of the NMR signals is based on the formula in Chart 3.

Synthesis of 4,9-[(4-Methylphenyl)sulfonyl]-4,9-diaza-1,6,11-dodecatriene (VI). *N*-Allyl tosylamide (0.727 g, 3.44 mmol) and *trans*-1,4-dibromo-2-butene (0.368 g, 1.72 mmol) were added to a 50 mL round-bottomed flask containing K_2CO_3 (1.90 g, 13.8 mmol) and acetonitrile (35 mL) and the mixture was refluxed for 13 h. Water was added to the reaction mixture, and the organic phase was extracted with ether, washed with brine, and dried over $MgSO_4$. Volatile fractions were removed and the residue was chromatographed on silica gel (hexane/ethyl acetate = 5/1, R_f = 0.30) to afford 4,9-[(4-methylphenyl)-sulfonyl]-1,6,11-dodecatriene (**VI**) as a white solid (0.675 g, 1.42 mmol, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.5 Hz, 1H H_e), 7.23 (d, J = 8.5 Hz, 1H, H_f), 5.48 (m, 1H, H_b), 5.33 (s, 1H, H_j), 5.03 (m, 2H, H_a), 3.65 (m, 4H, H_c and H_i), 2.35 (s, 3H, H_h). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.3 (C_g), 137.1 (C_d), 132.5 (C_b), 129.7 (C_f), 129.1 (C_j), 127.1 (C_e), 119.0 (C_a), 49.5 (C_c or C_i), 47.9 (C_c or C_i), 21.5 (C_h). Assignment of the NMR signals is based on the formula in Chart 3. Anal. Calcd (found) for $C_{24}H_{30}N_2O_4S_2$: C, 60.73 (60.53); H, 6.37 (6.41).

Polymerization of 4,9-(2,2-Dimethyl-1,3-dioxan-5,5-diyl)-1,6,11-dodecatriene (III). Typically, NaBARF (0.012 mmol, 10.6 mg) was added to a 25 mL Schlenk flask containing a CH_2Cl_2 solution (0.5 mL) of Pd complex **1b** (0.01 mmol, 5.7 mg) under Ar. After several minutes of stirring, 4,9-(2,2-dimethyl-1,3-dioxan-5,5-diyl)-1,6,11-dodecatriene (**III**, 109.3 mg, 0.30 mmol) was added, and the reaction mixture was stirred at room temperature. The portion of the reaction mixture was taken out from the flask and subjected to ^{1}H NMR and GPC analysis to determine conversion of **III** and molecular weight of poly-**III** (1 h, quant. conversion). The reaction mixture was poured to hexane, and precipitate was dissolved in CH_2Cl_2 and reprecipitated from hexane to afford poly-**III** as white powder (74 mg, 68% yield, M_n = 13800, M_w/M_n = 1.29). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.56 (br, 4H, H_e and H_i), 1.91 (br, 4H, H_c and H_j), 1.52 (br, 1H, H_a), 1.39 (br, 7H, H_g, H_h, and H_k), 1.12 (br, 1H, H_a), 0.95 (br, 4H, H_c and H_j). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 97.7 (C_f), 70.4 (C_e or C_i), 70.0 (C_e or C_i), 44.2 (C_k), 42.7 (C_b), 42.1 (C_b), 40.6(C_c and C_j), 39.2 (C_d), 33.2, 32.5 (C_a), 23.8 (C_g and C_h).

I was polymerized similarly (24 h, 26 mg, yield: 21%, M_n = 5100, M_w/M_n = 1.51). Poly-**I**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.52 (br, 1H, H_c), 2.17 (br, 3H, H_j and H_k), 1.90 (br, 2H, H_b and H_c), 1.72 (s, 6H, H_g and H_h), 1.65 (br, 1H, H_a), 1.08 (br, 1H, H_a). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.0 (C_e and C_i), 105.0 (C_f), 50.4 (C_d), 46.0 (C_c), 45.0 (C_k), 43.4, 44.4 (C_b), 39.0 (C_j), 30.7 (C_a), 28.9 (C_g and C_h).

Assignment of the NMR signals is based on the formula in Figure 1 and Chart 3.

Hydrolysis of Poly-III. Trifluoroacetic acid (0.1 mL) was added to a 25 mL Schlenk flask containing THF (8.5 mL), water (3.0 mL), and poly-**III** (588 mg) and the mixture was stirred at room temperature for 20 h. $CHCl_3$ (10 mL) was added to the reaction mixture and the volatile fraction was evaportated to afford poly-**III′** as pink powder (450 mg, 77%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.22 (s, 4H, H_e and H_f), 1.62−0.83 (m, 8H, H_a, H_b, H_c, H_g, and H_h). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 67.8 (C_e or C_f), 67.2 (C_e or C_f), 46.8 (C_d), 45.0 (C_c), 43.4 (C_b or C_h), 42.4 (C_b or C_h), 39.2 (C_g), 32.6 (C_a), 31.7 (C_a).

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