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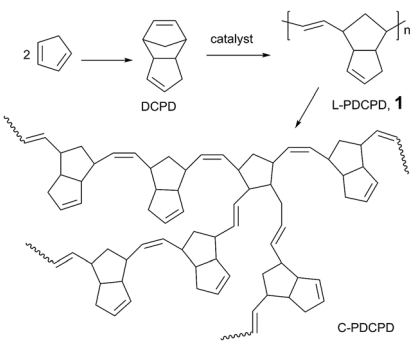
ROMP of acetoxy-substituted dicyclopentadiene to a linear polymer with a high T_g†

Laijiang Gong, Kun Liu, Encai Ou, Feng Xu, Yanbing Lu, Zhao Wang, Tao Gao, Zhongkui Yang and Weijian Xu*

A polydicyclopentadiene derivative was obtained *via* ring-opening metathesis polymerization (ROMP) of acetoxy-substituted dicyclopentadiene (AcO-DCPD) using the Grubbs 1st generation catalyst. Analyses of the polymer microstructures indicate that polymers are linear. The glass transition temperatures (T_g) of the linear polymers range from 136 °C to 159 °C, which are much higher than that of linear polydicyclopentadiene.

Polydicyclopentadiene (PDCPD) is formed through ROMP of dicyclopentadiene (DCPD) using a variety of transition-metal-based metathesis catalysts.[1–6] To date, the reaction mechanism for endo-DCPD which is illustrated in Scheme 1 has been widely accepted.[4,5] DCPD contains two different carbon–carbon double bonds: norbornene-type and cyclopentene-type. Both of them are capable of binding with the catalyst to undergo metathesis. Consequently, in the ROMP either both or one of the double bonds from DCPD can be involved.[2] In the first case a crossed-linked PDCPD (C-PDCPD) is the product while in the second case linear PDCPD (L-PDCPD) can be obtained.[3] Furthermore, different cross-linking reaction mechanisms of DCPD due to an olefin addition reaction have also been reported.[6] Up to now, with most of the catalytic systems, the polymerization is very fast and gives crossed-linked PDCPD, so that the reaction can be only applied in reaction injection molding (RIM) techniques for manufacturing of impact-resistant and tough molded parts.[7–9] Considering the L-PDCPD's good thermal stability, good solubility and the promising application in copolymerization, to polymerize DCPD into L-PDCPD will be of value.[10,11] However, only a few of studies[3,12–15] in ROMP of DCPD involving selectively ring-opening of the norbornene ring in DCPD to L-PDCPD have been reported. Furthermore, most of them employed certain selective binary catalytic systems instead of well-defined catalysts.[1] It has been demonstrated that the main advantages of the well-defined catalysts compared to the binary catalytic ones are the relatively high catalyst stability, the elimination of co-catalyst or activators, and the lack of side reactions resulting from the high Lewis acidity of the older systems.[16,17]

Therefore, the method to obtain linear PDCPD derivative by using Grubbs' 1st generation catalyst (G1) has been devised (crossed-linked PDCPD will be obtained with G1 (ref. 5)). A feasible way to get linear PDCPD derivative is to selectively inactivate the cyclopentene-type double bond of DCPD. It is well known that the driving force for ROMP is the release of the ring strain energy. Higher ring strain energy usually leads to higher reactivity toward ROMP.[18] As an electron-withdrawing group, the acetoxy group has a large stabilizing effect on the rings due to the anti-π double bond.[19] It has also been reported that[20] the acetoxy group could lower the activity of ROMP of acetoxy-substituted cycloolefin (Scheme 2a and b). For example, no polymerization was observed with acetoxy-substituted cyclopentene (Scheme 2d) using Grubbs 2nd generation catalyst even if cyclopentene can be polymerized under the same conditions.[21]



Scheme 1 Reaction scheme of ROMP for endo-DCPD.

State Key Laboratory for Chemo/Biosensing and Chemometrics, Hunan University, Changsha, 410082, P. R. China. E-mail: weijianxu59@gmail.com; gonglaijiang@126.com; Fax: +86-0731-88821549; Tel: +86-0731-88821749

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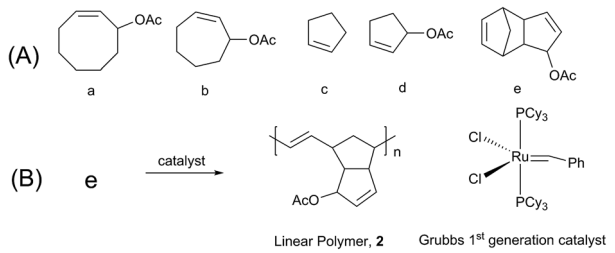

Scheme 2 (A) Molecule structure: (a) 3-acetoxy-cyclooctene, (b) 3-acetoxy-cycloheptene, (c) cyclopentene, (d) 3-acetoxy-cyclopentene, (e) AcO-DCPD; (B) the synthesis of linear polymer and the Grubbs 1st generation catalyst (G1).

In this communication, the acetoxy group was introduced to the active methylene of the DCPD to lower the activity of the cyclopentene-type ring.[18–20] Then we successfully obtained linear acetoxy-substituted PDCPD (PAD) by ROMP of AcO-DCPD involving selectively ring-opening of norbornene-type ring (Scheme 2B). Evidence for the success of linear PAD synthesis was provided by using a variety of characterization techniques, including ^{1}H NMR, ^{13}C NMR and ^{1}H–^{13}C HMQC.

Synthesis of acetoxy-dicyclopentadiene

The AcO-DCPD was synthesized referring to the modified Mironov's method.[22] To a solution of 50 g of DCPD in 110 mL of acetic anhydride, 30 mL of acetic acid and 40.2 g of SeO_2 were added. The mixture was stirred at room temperature for 24 h. After cooling, the mixture was filtered through a celite pad, diluted with H_2O and extracted with 100 mL of hexane three times. The extract was separated by distillation. Yield: 35.2 g (49%). The structures of the AcO-DCPD were characterized by ^{1}H NMR spectrum (Fig. 1). ^{1}H NMR ($CDCl_3$): δ = 6.06 (1H, dd, J = 5.4, 2.4 Hz), 5.84–5.89 (1H, m), 5.83 (1H, dd, J = 5.4, 2.4 Hz), 5.55 (1H, dt, J = 5.9, 1.8 Hz), 4.92–4.95 (1H, m), 3.33–3.40 (1H, m), 3.88 (1H, br s), 2.80 (1H, br s), 2.57 (1H, dq, J = 6.9, 2.2 Hz), 2.03 (3H, s), 1.57 (1H, d, J = 8.4 Hz), 1.38 (1H, d, J = 8.4 Hz).

Table 1 AcO-DCPD conversion at different catalyst loading; CH_2Cl_2 solution; [M] = 1.15 mmol; catalyst: Grubbs 1st catalyst; T = 0 °C

Entry	[M]/[Cat.][a]	Yield[b] (%)	M_w (kDa)	M_n (kDa)	M_w/M_n	T_g (°C)
#1	70	96.0	29.0	22.3	1.24	136.4
#2	130	96.1	53.7	34.2	1.48	137.5
#3	350	95.8	69.2	46.0	1.45	141.1
#4	900	95.9	80.7	58.6	1.37	146.8
#5	1700	91.3	223.2	115.4	2.01	152.7
#6	3850	87.5	619.0	274.1	2.44	159.1

[a] Monomer (AcO-DCPD) to catalyst ratio. [b] Isolated yield of polymer.

Synthesis of PAD from AcO-DCPD

All the experiments were performed at 0 °C in a Schlenk flask with a magnetic stirrer. The catalyst was first dissolved in dichloromethane and rapidly recrystallized using dry nitrogen flow to obtain the catalyst in smaller and more soluble form, in order to accelerate the dissolution of the catalyst powder.[23] In the glove box, estimated amount of G1 (2.0 mg mL^{-1} in CH_2Cl_2) was added into 10 mL Schlenk flasks by pipettor. Then the flasks were sealed with airtight stoppers, taken out of the glove box and cooled down to 0 °C under continuous stirring. Five minutes later, 0.20 g AcO-DCPD was added by a 1.0 mL Hamilton glass syringe under N_2 atmosphere. After 4 h the reaction mixtures were quenched with ethyl vinyl ether and stirred for additional 15 min. The solvent was removed and the product was dried under vacuum. Yields are given in Table 1.

The successful synthesis of linear PAD

The PAD can be easily dissolved in several solvents (CH_2Cl_2, $CHCl_3$, THF and toluene) at room temperature. This means that the PAD may be linear. The NMR studies were fully carried out for a sample (entry #3). The analysis of ^{13}C NMR spectrum indicates that only four kinds of signals at a high field region (138.0 ppm, 132.0 ppm, 131.2 ppm, 130.6 ppm) are C=C carbons while a higher signal at 170.5 ppm is C=O carbon

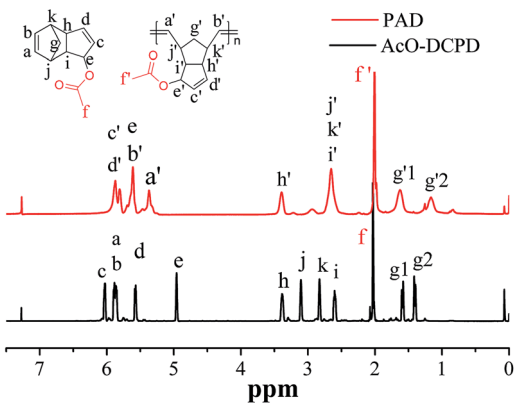

Fig. 1 ^{1}H NMR spectrum of AcO-DCPD (in $CDCl_3$).

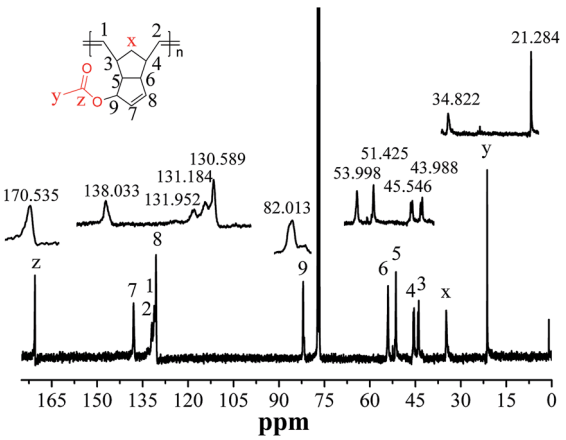

Fig. 2 ^{13}C NMR spectrum of PAD (in $CDCl_3$).

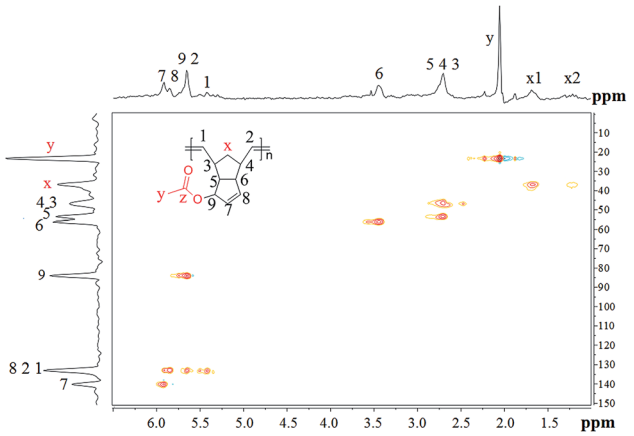

Fig. 3 $^{1}H-^{13}C$ HMQC spectrum of PAD (in $CDCl_3$).

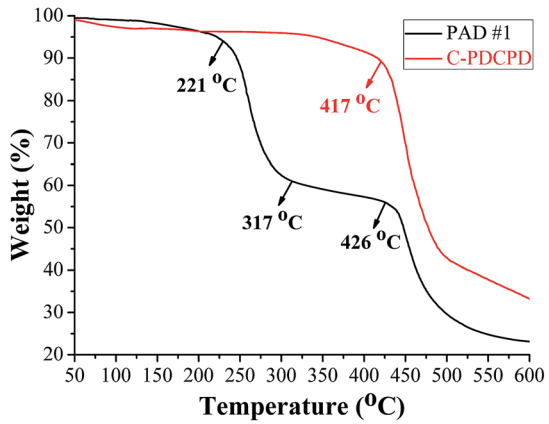

Fig. 4 TG curves of the PAD #1 and C-PDCPD (C-PDCD was prepared under the same condition as the PAD #1).

(Fig. 2). This has also proven the obtainment of the linear PAD. The structure of PAD was also characterized by $^{1}H-^{13}C$ HMQC (Fig. 3).

Through the analysis of the $^{1}H-^{13}C$ HMQC spectrum, the ^{1}H NMR signals are assigned unambiguously. The acetoxyl group proton signals are clearly observed around 2.0 ppm as a singlet. In the ^{1}H NMR of the PAD, five signals existed in the region of the double bond, while only four signals in the ^{1}H NMR of the AcO-DCPD (Fig. A, ESI†). The signal at 5.6 ppm can be easily assigned to a methane proton labelled with "9" in the $^{1}H-^{13}C$ HMQC spectrum (Fig. 3 carbon 9). As a result, there are only four kinds of signals labelled with C=C carbons in the ^{1}H NMR spectra. This is the additional evidence in support of the product of the linear PAD. Other signals are assigned one by one in Fig. 3. From the above, the structure of PAD is proved to be linear by using analogous experiments.[3,11]

Thermogravimetric analyses of PAD

The thermal stability of PAD was studied by TGA (Fig. 4). The onset degradation temperatures (T_d) are defined by the temperatures of 5% weight loss in TGA curves. It's quite obvious

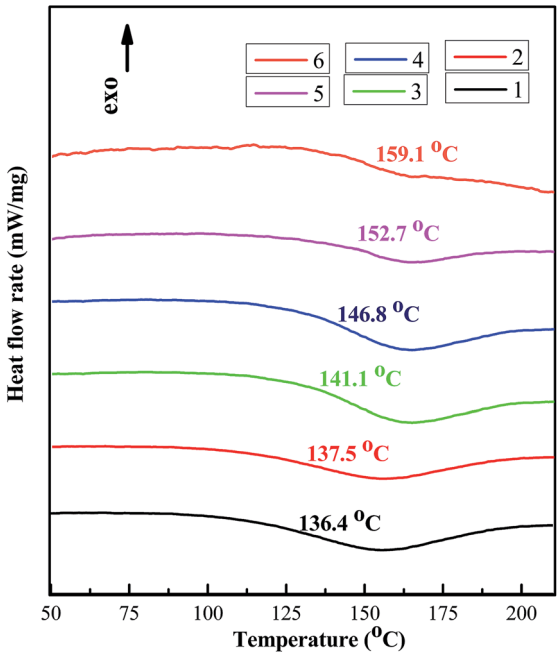

Fig. 5 Determination of T_g of PADs by differential scanning calorimetry (DSC).

that the PAD displays two degradation steps and the first degradation step loses nearly 32% weight (from 221 °C to 317 °C), which is attributed to the degradation of acetoxy unit (in conformity with the weight percentage of acetoxy group in PAD). The other one begins around 426 °C which is similar to cross-linked PDCPD.[24,25]

DSC analyses of PAD

The thermal transition temperatures of PAD is examined by DSC analyses. Note that the PAD is amorphous, which only exhibits a sharp T_g without any melting temperature (Fig. 5). A range of T_g values has been reported for PDCPD that depends on and characterizes the amount of cross-linking. For reference, DSC measurements of linear PDCPD yielded a T_g of 53 °C.[26] As would be expected, T_g is dependent on several parameters, including comonomer, molecular weight, and functionality. In this communication, the measured T_g range of 136 °C to 159 °C (T_g values are compiled in Table 1 and Fig. 5) for the PAD obtained in our experiments indicates more excellent thermal performance than the L-PDCPD. As mentioned before, the only difference between the PAD and the L-PDCPD is whether to be substituted by acetoxy group. Hence, the acetoxy added to the chain of L-PDCPD should be responsible for the higher T_g values of the PADs.[27,28]

Conclusions

We successfully synthesized a derivative of DCPD, AcO-DCPD, which can be polymerized into acetoxy-substituted PDCPD using first well-defined ruthenium catalyst. The microstructures of the polydicyclopentadiene derivative were analyzed by ^{1}H

NMR, ^{13}C NMR and ^{1}H–^{13}C HMQC and proved to be linear.[14] The thermal stability of PAD is not good enough, because the onset of PAD degradation temperatures is around 220 °C. However, the T_g of the polymers obtained from AcO-DCPD range from 136 °C to 159 °C, which are much higher than that of L-PDCPD. PAD can be recycled easily with its good solubility and used as heat-resistant material instead of PDCPD.

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