Macromolecular Research, Vol. 21, No. 1, pp 114-117 (2013)
DOI 10.1007/s13233-012-0190-3

www.springer.com/13233
pISSN 1598-5032 eISSN 2092-7673

Notes

Ring-Opening Metathesis Polymerization of Dicyclopentadiene and Tricyclopentadiene

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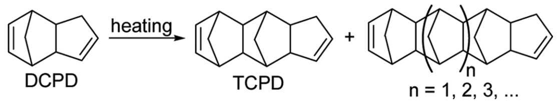
Received November 28, 2011; Revised January 19, 2012; Accepted April 22, 2012

Introduction

Over the past few decades, cyclo-olefin polymers (COPs) prepared by ring-opening metathesis polymerization (ROMP) and subsequent hydrogenation have received considerable attention because of their attractive properties such as high transparency, low fluorescence, and low birefringence, which are suitable for use as optical-grade materials.[1-4] Nippon Zeon commercialized COPs with names of Zeonor and Zeonex.[5] The cyclo-olefin monomers are Diels-Alder adducts of cyclopentadiene such as norbornene (NB), phenylnorbornene, dicyclopentadiene (DCPD), and 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene (DMON). The glass transition temperature (T_g) is modulated in the range 75-160 ºC by choosing the appropriate monomer.[6,7]

Cyclopentadiene is a major constituent in the C5-stream of naphtha cracking. Up to now, most C5-streams have not been used as sources of chemicals, but have instead been incinerated as energy sources. Cyclopentadiene is transformed to dicyclopentadiene (DCPD) through its spontaneous Diels-Alder addition reaction. When DCPD is heated, tricyclopentadiene (TCPD) and higher oligocyclopentadienes are formed through successive Diels-Alder reactions (eq. (1)).[8,9] By stopping the Diels-Alder oligomerization at an appropriate time (~17 h' heating under reflux), a mixture containing ~40 wt% TCPD is attainable, which is fractionated through vacuum distillation. The distillate is composed of four stereoisomers. The major isomer amounts to ~80% of the total, and can be isolated by recrystallization in ethanol. Previously, we reported preparations of ethylene copolymers (COCs) of TCPD and its partially hydrogenated compound HTCPD.[8,10,11] In this work, we report the preparation of a new COP employing TCPD as the monomer. The COP, prepared using solely DCPD, exhibits a low T_g of ~100 ºC.[12-15] By further addition of bulky TCPD, we can increase T_g to a more attractive region. An advantage of the COP preparation is that the fed cyclo-olefin monomer can be fully converted to the polymer. In ethylene/cyclo-olefin copolymerizations, full conversion of the fed cyclo-olefin is practically impossible because of the drift in monomer concentrations during the polymerization, and so recovery of the unreacted bulky monomers may be problematic.



(1)

Experimental

DCPD/TCPD Ring-Opening Metathesis Polymerization. The total amount of *endo*-DCPD and single-isomeric TCPD was fixed at 19 mmol. The amounts of DCPD and TCPD corresponding to the mole fractions in Tables I and II were measured in a glove box and added to a bomb reactor (50-mL size). Cyclohexane (weight=4 times the total weight of DCPD and TCPD) is added to make a 20 wt% solution. 1-Octene (0.106 g, 0.943 mmol) was added as a chain-transfer agent. The reactor was assembled, brought out from the glove box, and immersed in an oil bath at 80 ºC. An activated catalyst was prepared by mixing $W(=NPh)(2,6\text{-}Me_2\text{-}phenolate)_4$ (14.4 mg, 0.189 mmol) and *n*-BuLi (0.378 mmol) in cyclohexane (0.5 mL) for 15 min. The activated catalyst was fed into the system with a syringe under inert conditions. After stirring the mixture for 4 h, 2-propanol (10 mL) was added to quench the reaction. The solid precipitate was collected by filtration. The collected polymer was washed with diethyl ether, and the isolated polymer was dried under vacuum for 12 h at 40 ºC. The ^{1}H NMR spectra of the polymers were obtained at 25 ºC after dissolution in 1,2-$C_6D_4Cl_2$.

Hydrogenation Reactions. The hydrogenation reaction was conducted directly after ROMP, without isolation of the ROMP product. After ROMP, an activated catalyst prepared by mixing $Ni(acac)_2$ (29 mg, 0.11 mmol) and triisobutylaluminum (87 mg, 0.44 mmol) in cyclohexane (9.5 g) [or $(Cy_3P)_2Cl_2Ru(H)(Cl)(CO)$ (27 mg, 0.038 mmol) in cyclohexane (6 g) for Table I] was injected under inert conditions using a syringe. The reactor was pressurized to 35 bar. Hydrogenation is carried out at 80 ºC for 6 h (or at 160 ºC for 17 h for the ruthenium catalyst). Afterwards, the reactor was cooled to ~60 ºC and the remaining hydrogen gas was vented off. 2-Propanol (10 mL) was added to precipitate the solid,

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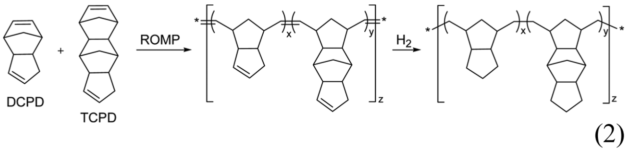
which was collected by filtration. The collected polymer was stirred in diethyl ether for an hour to wash the polymer. The isolated polymer was dried under vacuum for 12 h at 70 °C. The ^{1}H NMR spectra of the polymers were obtained at 25 °C after dissolution in 1,2-$C_6D_4Cl_2$.

Results and Discussion

Several catalytic systems such as $WCl_4/Et_2Al(OEt)$, MoO (2,6-Me_2-phenlate)$_4$/*n*-BuLi, and Grubbs' ruthenium catalyst have been reported to be able to perform ROMP of DCPD.[12,14,16,17] DCPD bears two types of double bond: one is of the norbornene-type and the other is of the cyclopentene-type. The former is more reactive than the latter, and hence, if the proper polymerization conditions are employed, ROMP of DCPD is possible without touching the cyclopentene-type double bond. The catalytic system of W(=NPh)(2,6-Me_2-phenolate)$_4$/*n*-BuLi was reported to polymerize *endo*-DCPD without crosslinking.[14] Tricyclopentadiene (TCPD) also has the same two types of double bond as DCPD. ROMP of single-isomeric TCPD is realized in cyclohexane without crosslinking using the same catalyst W(=NPh)(2,6-Me_2-phenolate)$_4$/*n*-BuLi employed in ROMP of DCPD, but stirring is stopped within several minutes through the formation of a thick viscous solution. The isolated polymer exhibits a very high T_g (254 °C). The most attractive COP resins are those with T_g in the range 130-160 °C. COPs exhibiting such T_g values can be prepared through ROMP of a mixture of *endo*-DCPD and single-isomeric TCPD and the subsequent hydrogenation reaction (eq. (2) and Table I).

Typically, ROMP is carried out in cyclohexane to dissolve the TCPD and DCPD. The total amount of TCPD and DCPD is fixed as 19 mmol, and cyclohexane is added to make a 20 wt% solution. The catalyst W(=NPh)(2,6-Me_2-phenolate)$_4$ (0.019 mmol), activated with two equivalents of *n*-BuLi, is fed to the solution at 80 °C. 1-Octene (50 equivalents to the catalyst) is added as a chain-transfer agent to lower the molecular weight. In the absence of 1-octene, a very high-molecular-weight polymer is generated, which hampers full conversion because of the stirring problem. A very thick, viscous solution is obtained in 4 h, and almost full conversion (80%-100%) of the monomer to the polymer is achieved under the typical polymerization conditions. The viscosity of the polymer solution increases upon increasing the [TCPD]/[DCPD] ratio. When the TCPD mole fraction exceeds 50 mol%, stirring stops in the early stages (within 10 min). From a practical point of view, TCPD distillate as a mixture of four stereoisomers is a more attractive monomer than the single-isomeric TCPD obtained through recrystallization. When the isomeric mixture of TCPD is fed as the monomer instead of the single-isomeric TCPD in ROMP, the formation of a gel is inevitable.



(2)

Generally, the polymers obtained from ROMP are thermally unstable because of the presence of double bonds, which cause facile oxidative degradation or crosslinking.[18] The hydrogenation reaction is carried out immediately after ROMP without isolating the polymer bearing these double bonds. Grubbs' metathesis catalyst, $(Cy_3P)_2Cl_2Ru(=CHOEt)$, was reported to be effective for the hydrogenation of the double bonds in the polymer backbone formed by ROMP of DCPD alone.[14] However, when the same Grubbs' catalyst is employed for hydrogenation of the polymers obtained by ROMP of a mixture of DCPD and TCPD, some part of the polymers becomes a gel.

We suspect that Grubbs' catalyst brings about the metathesis reaction of the appended cyclopentene-type double bonds on the TCPD unit, thus causing crosslinking. When a ruthenium complex $(PCy_3)_2ClRu(CO)(H)$,[19] which cannot act as a metathesis catalyst, is employed in the hydrogenation reaction, all the double bonds in the backbone and in the

Table I. Polymerization Results of DCPD and TCPD[a,b]

Entry	DCPD (mol%)	TCPD (mol%)	Yield (%)	T_g (°C) before Hydrogenation[c]	T_g (°C) after Hydrogenation[c]	M_w ($\times 10^{-3}$)[d]	M_w/M_n
1	100	0	90	151	105	495	2.3
2	90	10	92	163	113	328	3.5
3	80	20	92	181	120	230	2.8
4	70	30	99	194	130	252	3.6
5	65	35	99	199	146	260	2.8
6	60	40	97	202	155	273	2.7

[a]Polymerization conditions: sum of DCPD and TCPD=19 mmol, cyclohexane solvent=4 times total weight of DCPD and TCPD, catalyst= W(NPh)(2,6-Me_2-phenolate)$_4$ (14.5 mg, 0.019 mmol), [Cat]:[*n*-BuLi]:[1-octene]=1:2:50, 80 °C, 4 h. [b]Hydrogenation conditions: catalyst= $(PCy_3)_2Cl_2Ru(H)(Cl)(CO)$ (27.5 mg, 0.038 mmol) in cyclohexane (10 g), H_2=35 bar, 160 °C, 17 h. [c]Glass transition temperature determined on DSC. [d]Determined on GPC using the polystyrene standard.

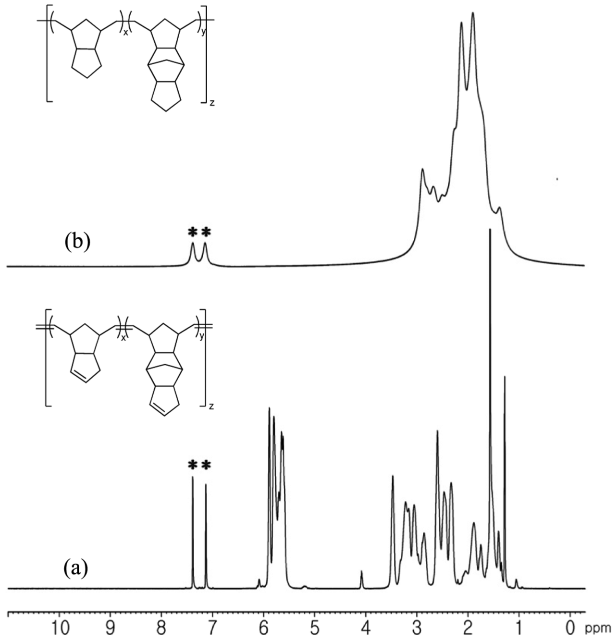


Figure 1. The ^{1}H NMR spectra of DCPD/TCPD polymers before hydrogenation (a) and after hydrogenation (b) (*signals from 1,2-dichlorobenzene-d_4).

appended cyclopentene units are hydrogenated under rather harsh conditions (35-bar H_2, 160 °C, 17 h).

Through the hydrogenation reaction process, the solution viscosity increases and some cyclohexane is additionally added at the time of feeding of the hydrogenation catalyst. Complete hydrogenation can be confirmed by the disappearance of the vinyl signals at 5.5-6.0 ppm in the ^{1}H NMR spectrum of the hydrogenated polymers (Figure 1).

The T_g values of the polymers are increased by the increase in the TCPD mole fraction in the feeding (Table I and Figure 2). When the TCPD mole fraction is 40 mol%, T_g of the polymer before hydrogenation is as high as 202 °C. Under N_2-flow, the T_g of the ROMP-product before hydrogenation is observable using DSC.

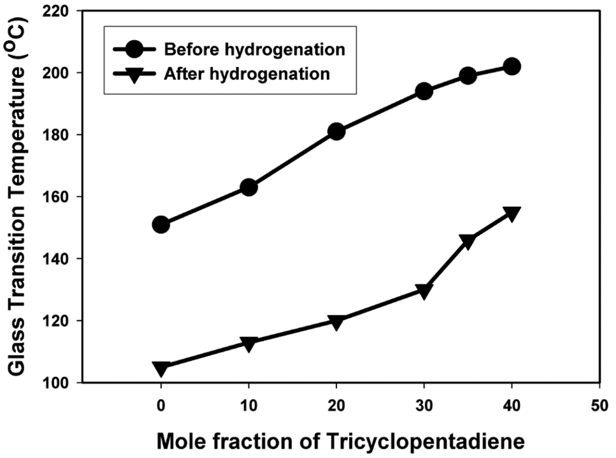


Figure 2. Relationship between T_g and TCPD content.

After hydrogenation, T_g is significantly lowered to 155 °C. The same amount of T_g lowering (~50 °C) is observed for other polymers obtained with different TCPD mole fractions (Figure 2).

The molecular weights obtained by using 50 equivalents of 1-octene are in the range 230,000-330,000 (M_w), which are too high compared with commercial COPs. In order to lower the molecular weight, the amount of chain-transfer agent (1-octene) is increased to 100, 125, and 150 equivalents at fixed TCPD mole fractions of 20 or 35 mol%, for which COPs with T_g values of 125 or 145 °C, respectively, are obtained (Table II). Increasing the amount of 1-octene lowers the molecular weight. At a TCPD mole fraction of 20 mol%, the molecular weight decreases from 199,000 to 132,000 upon increasing the amount of 1-octene from 100 to 150 equivalents (entries 1-3). At a TCPD mole fraction of 35 mol%, the molecular weight decreases from 231,000 to 176,000 upon increasing the amount of 1-octene from 100 to 150 equivalents (entries 4-6).

Employing the homogeneous Ru catalyst in the hydrogenation reaction causes some problems. It is not easy to remove the catalyst residue after hydrogenation, and yellowish poly-

Table II. Polymerization Results of DCPD and TCPD with Variation of the Amount of 1-Octene[a,b]

Entry	DCPD (mol%)	TCPD (mol%)	1-Octene[c] (eq)	Yield (%)	T_g^d (°C)	M_w ($\times10^{-3}$)[e]	M_w/M_n
1	80	20	100	91	126	199	3.1
2	80	20	125	95	128	185	3.2
3	80	20	150	90	124	132	2.9
4	65	35	100	89	143	231	3.2
5	65	35	125	92	144	212	3.1
6	65	35	150	94	147	176	3.3

[a]Polymerization conditions: sum of DCPD and TCPD=19 mmol, cyclohexane solvent=4 times the total weight of DCPD and TCPD, catalyst= W(NPh)(2,6-Me$_2$-phenolate)$_4$ (14.5 mg, 0.019 mmol), [Cat]:[*n*-BuLi]=1:2, 80 °C, 6 h. [b]Hydrogenation conditions: catalyst=Ni(acac)$_2$ (29 mg, 0.114 mmol) activated with Al(iBu)$_3$ (87 mg, 0.44 mmol) in cyclohexane (10 g), H_2=35 bar, 80 °C, 6 h. [c]Mole ratio of [1-octene]/[cat]. [d]Glass transition temperature determined on DSC after hydrogenation. [e]Determined on GPC using the polystyrene standard.

mers are isolated. Ruthenium is very expensive, so there are also problems with production costs. A nickel-based catalytic system was developed by Zeon. Nickel acetylacetonate (Ni(acac)$_2$) activated with triisobutylaluminum (Al(iBu)$_3$) is able to hydrogenate the ROMP product of DCPD.[20] Complete hydrogenation is realized at a lower temperature of 80 $^{\circ}$C and a shorter reaction time of 6 h. The hydrogenation reaction proceeds directly after ROMP without isolation of the ROMP product. The vinyl signals at 5-6 ppm disappear completely from the ^{1}H NMR spectrum after hydrogenation (Figure 1), and the isolated polymer is not yellowish but white.

Conclusions

Ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) and tricyclopentadiene (TCPD) is performed using a catalytic system of W(=NPh)(2,6-Me$_2$-phenolate)$_4$/*n*-BuLi. After polymerization, the double bonds not only in the polymer backbone but also in the cyclopentene-type ring are hydrogenated using the catalytic system, (PCy$_3$)$_2$Cl$_2$Ru(H)(Cl)(CO) or Ni(acac)$_2$/triisobutylaluminium. Glass transition temperature (T_g) of the amorphous polymer is controlled by the mole ratio of DCPD and TCPD. As the content of TCPD unit is increased from 0 to 40 mol%, the T_g increases in the range of 100 °C~155 °C.

Acknowledgments. This work was supported by the Energy Efficiency and Resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Knowledge Economy (2007-M-CC24-P-04-3-030) and by Priority Research Centers Program (2010-0028294) through the NRF grant funded by the MEST of Korean government.

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