Ring-Opening Metathesis Copolymerization of Dicyclopentadiene and Cyclopentene Through Reaction Injection Molding Process

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ABSTRACT: Copolymer of dicyclopentadiene and cyclopentene (CPE) is synthesized through ring-opening metathesis polymerization using the second-generation Grubbs catalyst. The influences of monomer composition, catalyst concentration, and reaction temperature on gelification time and monomer conversion have been investigated. Furthermore, the reaction injection molding process is employed to produce the copolymer of dicyclopentadiene and CPE. It has been found that postcuring process is necessary to achieve 100% monomer conversion. The incorporation of a small amount of CPE into the copolymers can reduce the weight loss rate in the TGA process and improve the mechanical properties. The effects of CPE fraction, catalyst concentration, and postcuring temperature on thermal stability and mechanical properties are discussed. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2489–2493, 2012

Key words: dicyclopentadiene; copolymerization; Grubbs catalyst; ROMP; RIM

INTRODUCTION

The ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD), a by-product from naphtha crackers, has received many interests in recent years.[1,2] The ROMP products of DCPD are commercially available under the trade names of Telene®, Metton®, Prometa®, Metathene®, etc.[3] These products are generally lightweight with high glass transition temperatures (T_g) and excellent mechanical properties. Reaction injection molding (RIM) process of DCPD is usually employed to manufacture large size parts, such as heavy-truck hood, snowmobile hood, and large container.

The choice of catalyst is critical for the ROMP. In early years, the early transition metal catalytic systems were comparably cheap and, therefore, were often used in industrial applications. However, these catalysts also had problems owing to their air-instability, variable curing activity, and occasional requirement of solvent. In the recent years, a series of highly active carbene ROMP catalysts have been developed.[4] The "Schrock catalyst," molybdenum alkylidenes, combines rapid initiation with high propagation rates.[5] Although the field of metathesis polymerization is dominated for a long time by molybdenum alkylidenes, the true breakthrough is restricted by poor functional-group tolerance of Schrock catalysts and their sensitivity towards protic solvents and air. This restriction can be solved with the advent of Grubbs' catalyst and the related complexes for metathesis polymerization.[6] The polymerization using Grubbs' catalysts not only has rapid initiation and propagation rates, but also can perform well in protic media and under the conditions without rigorous exclusion of molecular oxygen. The Grubbs' catalysts show promise in developing ROMP thermosets for their extremely high activity even at sub-ambient temperatures.[7]

RIM process was first used in PU industry.[8] The mixtures of low viscosity materials are quickly injected into the mold. The product is obtained in a few minutes with the polymerization of monomers. RIM combines the polymerization and molding together, which has the advantages of high efficiency, low viscosity, low mold pressure, low tooling cost, etc.[9] For DCPD, it has the low viscosity for mixing.[10] However, it should be noticed the reaction rate of DCPD ROMP using Grubbs' catalysts is too rapid to ensure enough time to fill the mold.[11] The fast
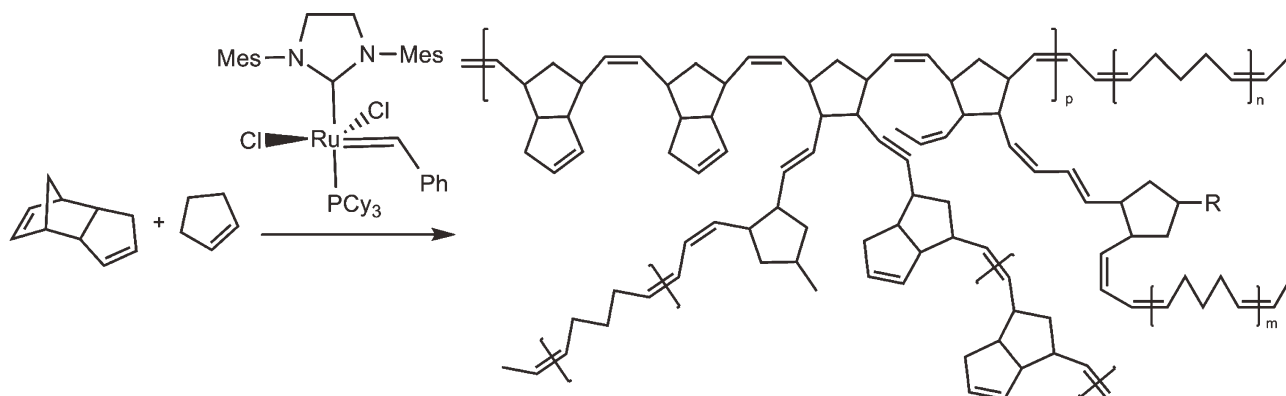
Scheme 1 Copolymerization of DCPD and CPE using the Grubbs catalyst

reaction need be retarded by adding an inhibitor[12] or by other means.[13,14] Most of researches are focused on the application of the latent Grubss catalysts, which exhibits no catalytic at room temperature but can be triggered quantitatively for a high active form to initiate the reaction. At the same time, another approach turns to search suitable comonomer to improve the properties. For example, Yoonessi et al.[15] synthesized highly delaminated poly(DCPD)/clay nanocomposites. The incorporation of 0.5 wt % clay increased T_g 13°C above that of the PDCPD, while 1 wt % clay led to the best mechanical properties. Jeong and Kessler[16] prepared norbornene-functionalized multi-walled carbon nanotube (MWNT)/DCPD nanocomposites. The tensile toughness was increased by more than 900% by using 0.4 wt % MWNTs. Henna et al.[17] turned to the field of renewable and sustainable feedstocks, and synthesized polymeric thermosetting resins using a commercially available vegetable oil derivative Dilulin as the comonomer.

To our best knowledge, few researches have reported to control the reaction process using the copolymerization of DCPD with other comonomer. In this article, we introduced cyclopentene (CPE), a low-stain comonomer,[18] into the ROMP system of DCPD to control polymerization process and yield good material properties.

EXPERIMENTAL

Materials

Grubbs' second generation catalyst, (1,3-Bis (2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro (phenylmethylene) (tricyclohexylphosphine) ruthenium, was purchased from Sigma-Aldrich, degassed and stored in the glove-box. CPE, provided by Aladdin Chemistry (Shanghai, China), was dried over anhydrous CaH_2 and distilled for 6 h before use. *Endo*-DCPD (98 wt %) stabilized with 100–200 ppm *p-tert*-butylcatechol was purchased from Aladdin Chemistry. DCPD was purified by vacuum distillation.

Polymerization

The DCPD and CPE copolymerization was achieved by the Grubbs catalyst. The polymerization was carried out in a 50-mL glass flask under atmospheric pressure. Before polymerization, the flask was evacuated and purged with nitrogen alternatively for three times. Sequentially, the purple Grubbs catalyst powder was added to the reactor in a glove box. The polymerization was started by adding the DCPD/CPE solution. After the gel was formed, the copolymerization was stopped by adding acidified ethanol. The reaction mixture was slowly poured into a dilute HCl/ethanol solution. The precipitated

TABLE I
Influence of Catalyst Concentration on DCPD and CPE Copolymerization[a]

Monomer/ CAT	Gelification time (min)	Conversion of CPE (%)	Conversion of DCPD (%)	Total Conversion (%)
30000/1	9	95.7	99.2	98.1
60000/1	16	97.7	98.9	98.5
120000/1	15	97.5	99.3	98.7
180000/1	42	99.8	99.9	99.9
240000/1	48	94.8	98.7	97.4

[a] Reaction temperature is 35°C; DCPD/CPE = 1/1.

TABLE II
Influence of Temperature on DCPD and CPE Copolymerization[a]

Temperature (°C)	Gelification time (min)	Conversion of CPE (%)	Conversion of DCPD (%)	Total Conversion (%)
35	17	83.9	98.7	97.9
50	5	85.3	99.6	98.8
60	3	83.1	99.8	98.9

[a] Monomer/CAT = 60,000; DCPD/CPE = 9/1.

polymer was filtered, washed with ethanol, and dried under vacuum at 120°C.

RIM

The RIM process of DCPD/CPE was accomplished with the same Grubbs' second generation catalyst. The catalyst powder and monomers were quickly mixed in a flask, which was evacuated and charged with nitrogen alternatively for three times before being used. Sequentially, the mixture was injected into a rectangular mold with the dimension of 25 × 25 × 0.4 cm³. The mold temperature was raised to 35°C and kept for 30 min. And then, the mold was rapidly heated to 160–200°C and kept for 30 min for the postcuring process.

Characterization

After the samples were soaked in toluene for 24 h, the solution were filtered with 0.22 μm filter paper and injected to gas chromatography to measure the fraction of residual monomer. Infrared spectra of copolymers were recorded on a Nicolet 5700 spectrophotometer. T_g of copolymers was measured through DSC analysis carried out at a heating rate of 10°C/min with a Perkin-Elmer DSC-7 instrument. Thermogravimetric analysis was conducted on a TA

Q200 instrument at a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Copolymerization of DCPD-CPE in reactor

CPE is a low-strain cyclic olefin, whose strain is as low as 2.9 kcal/mol.[19] As the ring opening process is promoted by the release of stain and the change of entropy from cyclic olefin to linear polymers,[18] the metathesis rate of CPE is expected to be lower than that of DCPD. The reaction scheme is shown as follows (Scheme 1):

Catalyst concentration affects the number of active sites generated in the system, and has a significant influence on the polymerization process. As listed in Table I, when the DCPD to CPE molar ratio is kept at 1/1 and the monomer to catalyst ratio is increased from 3000/1 to 240,000/1, the gelification time is increased from 9 to 42 min while the change of conversion is insignificant.

The temperature also has major influence on the DCPD and CPE copolymerization. In Table II, as the temperature is increased from 35 to 60°C, the gelification time is reduced from 17 to 3 min.

RIM of DCPD-CPE

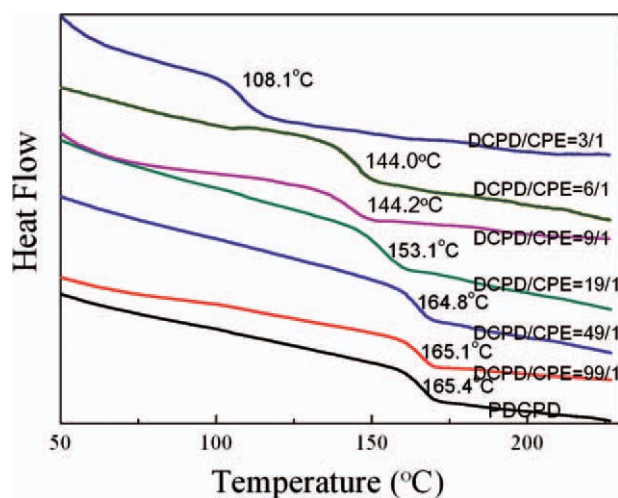The DCPD-CPE system is also used for the RIM process. The reaction system is exposed to air in the

Figure 1 DSC traces of the resulting poly(DCPD-co-CPE) with various monomer ratio by RIM process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
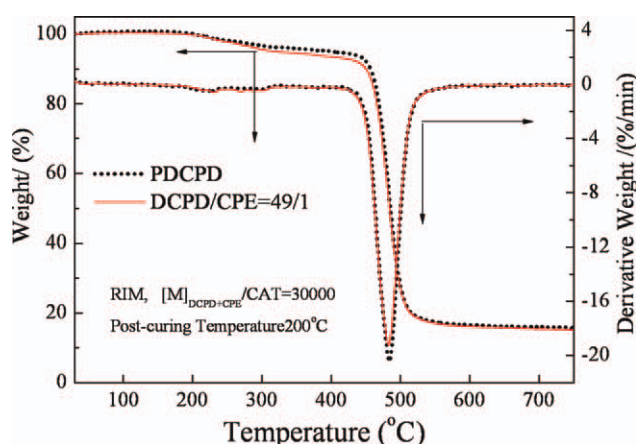

Figure 2 TG traces of the obtained poly(DCPD-co-CPE) and PDCPD by RIM process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
The Properties of Poly(DCPD-co-CPE) with Different Compositions by RIM Process

Properties	Units	PDCPD	DCPD/ CPE = 99	DCPD/ CPE = 49	DCPD/ CPE = 19	DCPD/ CPE = 9	DCPD/ CPE = 6	DCPD/ CPE = 3
Tensile modulus	Mpa	1790 ± 30	1790 ± 30	1820 ± 20	1660 ± 30	1530 ± 20	1470 ± 30	1410 ± 40
Tensile yield strength	Mpa	62.1 ± 2	65.2 ± 1	63.8 ± 1	55.5 ± 2	51.7 ± 1	43.3 ± 1	36.6 ± 1
Yield elongation	%	8 ± 0.2	11.7 ± 0.2	12.5 ± 0.2	10.9 ± 0.2	6.8 ± 0.1	6.2 ± 0.2	5.6 ± 0.2
Elongation at break	%	6.1 ± 0.5	27.2 ± 0.6	19.2 ± 0.5	10.9 ± 0.5	14.9 ± 0.5	9 ± 0.5	7.8 ± 0.5
Flexural modulus	Mpa	1780 ± 50	1730 ± 50	1850 ± 40	1730 ± 40	1440 ± 30	1400 ± 30	1310 ± 40
Flexural strength	Mpa	72.3 ± 2	77.7 ± 2	78.6 ± 2	72.7 ± 2	63.6 ± 1	58.1 ± 1	47.2 ± 1
Breaking displacements	mm	23.7 ± 0.5	22.3 ± 0.5	24.3 ± 0.5	23.6 ± 0.2	23 ± 0.5	22.9 ± 1	18.8 ± 1
Notched impact strength	KJ/m^2	4.42 ± 0.2	5.19 ± 0.2	4.76 ± 0.2	5.19 ± 0.2	4.44 ± 0.2	3.52 ± 0.2	4.99 ± 0.2
T_g	°C	165.4	165.1	164.8	153.1	144.2	144.0	108.1
ΔC_p	J/(g[a] °C)	0.1863	0.2204	0.1860	0.2188	0.1831	0.1626	0.1804

[a] The RIM process was taken under 35°C with [M]/CAT = 30,000 and the postcuring was under 200°C.

process, which is harmful for the polymerization.[20] The conversion of RIM sample obtained at 35°C is only 90% which is much lower than samples prepared in flask (35°C, 98%). Even reacted in flask, there are about 2% monomer not polymerized, which will degrade the mechanical properties significantly. Therefore, postcuring at a much higher temperature is necessary. The temperatures used for postcuring are 160, 180, and 200°C. After the postcuring procedure, the conversation of monomers is nearly 100%.

Figure 1 shows the DSC trace of RIM products with various initial monomer ratios. When the molar ratio of DCPD/CPE is higher than 49/1, the change in T_g is insignificant. But if the ratio of DCPD/CPE is lower than 49/1, T_g will be declined considerably. That is caused by the decrease of crosslinking degree.

Figure 2 shows the TGA trace of various RIM products. It can be seen that the weight loss is insignificant until 422°C. After 422°C, the weight loss rate increases dramatically. Moreover, the onset temperature is reduced slightly with the introduction of CPE. The weight loss rate of the copolymer is a little lower than that of the DCPD homopolymer.

In the tension test, both PDCPD and poly(DCPD-co-CPE) materials show similar behaviors as well as the good properties of rigidity and toughness. The necking gradually develops and becomes white until the material is broken. Because the PDCPD and poly(DCPD-co-CPE) have the crosslinking structure, the polymer chains are become straight with the orientation of chains that show the elastic deformation when the material is stressed. Subsequently, as the molecular chains are orientated, the material strength is further increased and stress gradually increases. After the orientation, the molecular chains show different refractive index, which leads to the stress whitening phenomenon.[21]

Table III compares the properties of RIM-poly(DCPD-co-CPE) with different fraction of CPE. It can be seen that the curve of mechanical properties versus the content of CPE show a typical mountain shape. The best properties can be achieved at the monomer ratio DCPD/CPE = 49/1. As DCPD is a high stain cycloolefin, which can be reacted quickly

TABLE IV
The Properties of Resulting Poly(DCPD-co-CPE) with Various Postcuring Temperature by RIM Process

Properties	Units	[M]/CAT = 30,000; DCPD/CPE = 9 Postcuring temperature/°C 160	180	200	[M]/CAT = 60,000; DCPD/CPE = 9 Post-curing temperature/°C 160	180	200
T_g	°C	145.3	144.0	144.4	145.1	145.1	145.6
Tensile modulus	Mpa	1560 ± 40	1660 ± 30	1530 ± 20	1430 ± 40	1390 ± 20	1490 ± 20
Tensile yield strength	Mpa	53.1 ± 2	52.4 ± 0.5	51.7 ± 1	51.9 ± 2	50.8 ± 2	52.4 ± 1
Yield elongation	%	8.7 ± 0.1	7.0 ± 0.2	6.8 ± 0.1	8.0 ± 0.1	7.5 ± 0.1	7.5 ± 0.1
Elongation at break	%	55.4 ± 2	11.6 ± 0.5	14.9 ± 0.5	32.7 ± 2	37.0 ± 2	16.3 ± 2
Flexural modulus	Mpa	1630 ± 40	1560 ± 40	1440 ± 30	1660 ± 40	1540 ± 20	1710 ± 30
Flexural strength	Mpa	67.0 ± 2	65.4 ± 2	63.6 ± 1	70.4 ± 1	65.9 ± 1	72.4 ± 1
Breaking displacements	mm	23.4 ± 0.5	21.7 ± 1	23.0 ± 0.5	23.0 ± 0.5	23.4 ± 0.5	23.0 ± 1
Notched impact strength	KJ/m^2	5.0 ± 0.2	4.62 ± 0.2	4.44 ± 0.2	4.30 ± 0.2	4.89 ± 0.2	5.0 ± 0.2

after initiation, the crosslinking structure of product maybe nonuniform. When a small amount of CPE is introduced, the homogeneity is improved, which results in better mechanical properties. With the increase in the CPE fraction, the crosslinking degree of the copolymer is reduced, which leads to decrease in tensile and flexural strength and modulus. On the other hand, the notched impact strength does not change significantly with the variation in monomer ratio.

The effects of catalyst concentration and the postcuring temperature on T_g and mechanical properties are presented in Table IV. It can be seen that the increasing catalyst concentration will improve the crosslinking degree, which results in higher tension module and low elongation at break. The influence of postcuring temperature on mechanical properties except elongation at break is insignificant. To obtain the suitable crosslinking degree, the desired postcuring temperature is different at various catalyst concentrations. When [M]/CAT is 30,000, 160°C is enough for the postcuring process. Higher temperature will lead to excessive crosslinking, which decreases the elongation at break. With [M]/CAT at 60,000, reaction rate is slower and the suitable temperature for postcuring is 180°C. With different catalyst concentration, the T_g of poly(DCPD-co-CPE) only change about 1°C when the postcuring temperature is raised from 160 to 200°C. Therefore, we can conclude that the postcuring temperature nearly has no effect on the T_g. Similarly, the effect of catalyst concentration on the T_g is insignificant.

CONCLUSION

Copolymers of DCPD-CPE have been synthesized by ROMP using the second-generation Grubbs catalyst both in a reactor and through RIM process. The gelification time can be changed significantly by polymerization temperature and catalyst concentration. Postcuring process is needed to reach 100% monomer conversion in RIM process. The incorporation of CPE into the polymers has a negative effect on T_g. On the other hand, the copolymer has lowered the weight loss rate in the TGA process. Copolymer with small amount of CPE has better mechanical properties than the DCPD homopolymer. However, too much CPE will reduce the crosslinking and leads to the decrease of properties.

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