

Ring Opening Metathesis Polymerization of 7-Oxabicyclo[2.2.1]Hept-5-Ene-2,3-Dicarboxylic Acid Dimethyl Ester

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Abstract

All the monomers used in ring opening metathesis polymerization (ROMP) were synthesized by two step reactions. The first step of the synthesis was the Diels-Alder reaction between furan and maleic anhydride to produce *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride. The second step was to prepare 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, dimethyl ester by Fischer esterification of *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride in refluxing methanol. 7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, dimethyl ester was polymerized by ROMP catalyzed by commercially available ruthenium catalyst $\text{Ru}(\text{PPh}_3)_2(\text{Cl})_2(\text{CHPh})$ at defined concentrations relative to the monomer. Depending on the molar ratio of the monomer to the catalyst polymers with different large molecular weight were obtained. Molecular weights and polydispersities were confirmed by gel permeation chromatography. Monomers and polymers were also analyzed by FT-IR. Polyanions of poly(7-oxanorbornene-2,3-dicarboxylate) were prepared by hydrolysis of poly(dimethyl-7-oxabicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid). It is worth noting that the polyanions in aqueous solution form hydrogels. The properties of the prepared polymers will be discussed in full paper.

Key words: Ring Opening Metathesis Polymerization, 7-oxanorbornene, polyanions

Introduction

Ring-opening metathesis polymerization (ROMP) is a type of cycloolefin polymerization that produces industrially important products. ROMP of 7-oxanorbornene derivatives is a method to synthesize high molecular weight polymers using commercially available ruthenium catalyst (e.g. Grubbs catalyst generation II). Grubbs' Catalysts are a series of transition metal carbene complexes used as catalysts for olefin metathesis [1-4].

Poly(dimethyl-7-oxabicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid) was synthesized by polymerization of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, dimethyl ester, which was prepared by Fischer esterification of *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride. To synthesize this monomer, Diels Alder reaction of furan and maleic anhydride was carried out [5-9].

Experimental

Chemicals

THF, methanol, reagents and ruthenium catalyst $\text{Ru}(\text{PPh}_3)_2(\text{Cl})_2(\text{CHPh})$ were purchased from Aldrich and Avantor as high purity grade. All the reaction were carried out under nitrogen atmosphere.

General procedures and characterization

The molecular weights of the polymers were estimated in THF (stabilized with BHT) by gel permeation chromatograph (GPC) using a Shimadzu UFLC chromatograph equipment with CTO-10AS vp column oven and refractive index detector RID-10 A. A calibration curve was obtained by using polystyrene standards.

The IR spectra were recorded on KBr discs in the wavenumber of $4000\text{-}400\text{ cm}^{-1}$ on FT-IR BIORAD FTS-165 spectrophotometer.

The melting point was determined by Labo Plus 9200 camera.

Synthesis of the monomers

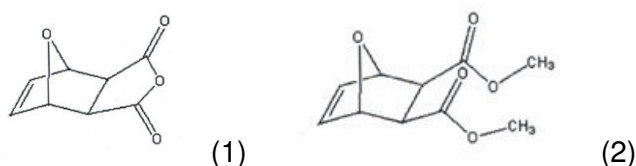


Fig.1. The chemical structure of exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (1), 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, dimethyl ester (2)

Exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, **1**, was prepared by Diels - Alder reaction between maleic anhydride and furan. Maleic anhydride (50 g, 509 mmol) was dissolved in THF in a 500 ml flask. Then furan (33ml, 453 mmol) was added and the flask was swirled for several minutes. The flask was allowed to stand for several days to form large crystals. The crystals were isolated on the Hirsch funnel and wash with small amount of tetrahydrofuran than were dried in vacuo for 24 hours. M.p. $114\text{ }^{\circ}\text{C}$.

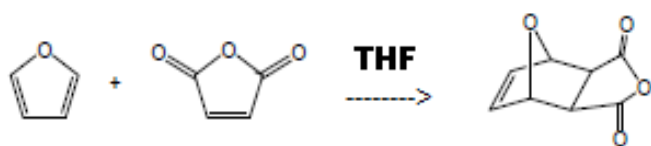


Fig. 2. Diels-Alder reaction of furan and maleic anhydride

The second step was to prepared 7-oxabicyclo[2.2.1]hept-5-ene-2,3- dicarboxylic acid methyl ester, **2**, by Fischer esterification of exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride in refluxing methanol. The crystals were formed after 1-2 days and were dried under vacuum for 24 hours, 30°C. M.p. 118°C.

Synthesis of the polymers:

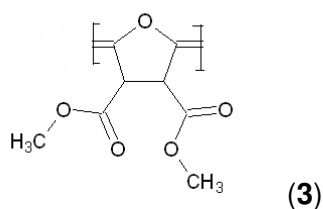


Fig. 3. The chemical structure of poly(dimethyl-7-oxabicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid)



Fig.4. The white polymer of poly (dimethyl-7-oxabicyclo (2.2.1)hept-5-ene-2,3-dicarboxylic acid)

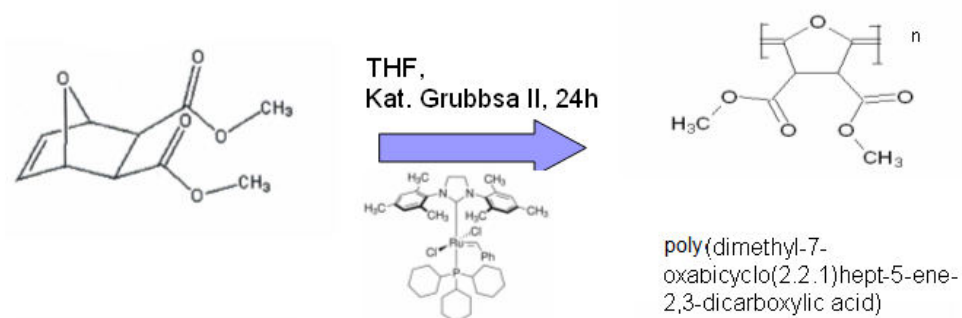
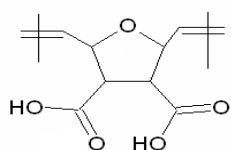


Fig. 5. Ring opening metathesis polymerization of dimethyl-7-oxabicyclo[2.2.1]hept-5-ene exo 2,3-dicarboxylate

Poly(dimethyl-7-oxabicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid), **3**, was prepared by dissolving 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, dimethyl ester, **2**, (2g, 9,43 mmol) in 30 ml THF. The ruthenium catalyst $\text{Ru}(\text{PPh}_3)_2(\text{Cl})_2(\text{CHPh})$ was added and the solution was stirred under nitrogen for 0.5 h. The polymerization reaction was terminate by adding ethyl vinyl ether and the solution was stirred for 30 min. The polymer was precipitated by addition of methanol to yield 80-85 % of white polymer.

Synthesis of the polyanions:



(4)



Fig. 6. The chemical structure of poly(7-oxabicyclo [2.2.1]hept-5-ene-2,3-dicarboxylic acid) (4)

Fig.7. The gel of polyanion poly(7-oxanorborene-2,3-dicarboxylate)

Poly(7-oxanorborene-2,3-dicarboxylic acid) was prepared by dissolving poly(dimethyl-7-oxabicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid) – 0,5 g, **4**, in THF (125 ml) and 1 M NaOH (125 ml). The solution was stirred under nitrogen for 24 hours. The polyanions were precipitated by adding 1M HCl (yield: 95%).

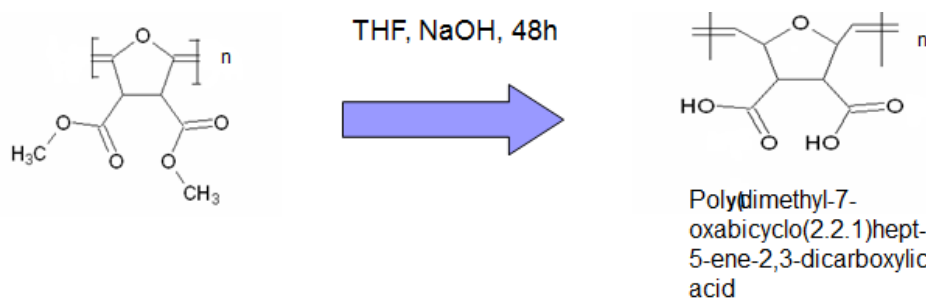
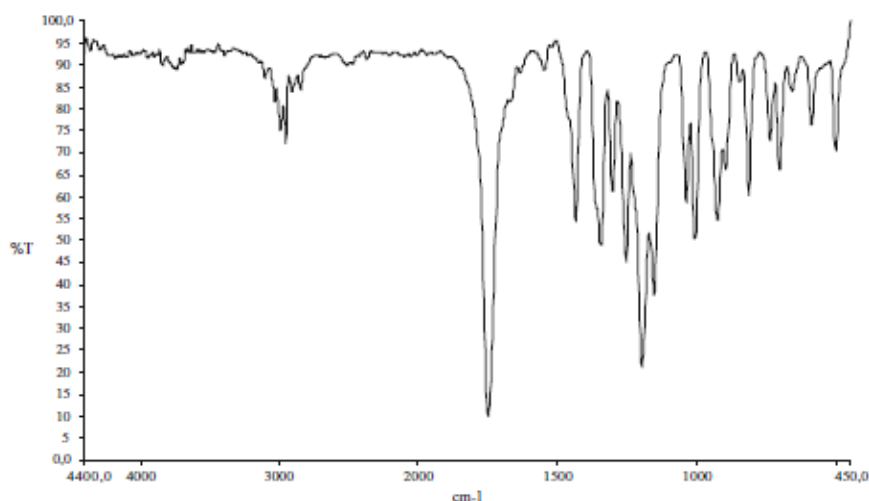


Fig. 8. The hydrolysis reaction of poly(dimethyl-7-oxabicyclo (2.2.1) hept-5-ene-2,3-dicarboxylic acid)

Results and discussion

During each step of the synthesis in order confirm the structure of the monomer, the compound **2** and polymers **3** were characterized by FT-IR and GPC. The FT-IR spectrum are presented in Figure 9 and showed the typical absorptions of these compounds.

a)



b)

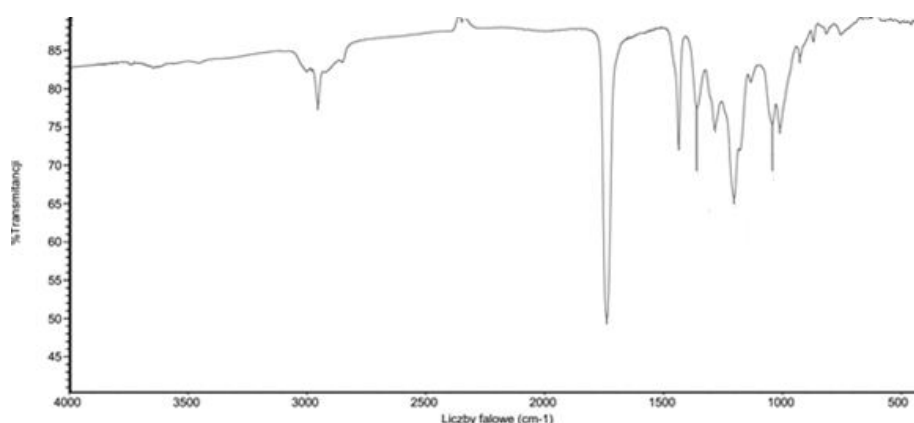


Fig. 9. FT-IR spectra of a) 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester, **2**, c) poly(dimethyl-7-oxa-bicyclo(2.2.1)hept-5-ene-2,3-dicarboxylic acid), **3**.

For instance FT-IR spectra of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester, **2**, was characterized by IR (cm^{-1}): 3098 λ (C-H sp^2 symmetric), 3032 λ (C-H sp^2 asymmetric), 2990 λ (C-H bridge head), 2948 λ (C-H sp ring), 1748, 1732 λ (C=O), 1634 λ (C=C tension), 1254 λ (C-O ester vibration).

Finally, the results of the polymerization reaction of prepared 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid methyl ester, **2**, are presented in Table 1. It was proved that Grubbs catalyst II are efficient catalyst for ROMP of **2**. Depending of the ratio of the monomer to catalyst, polymers with high weight average molecular weights were obtained starting from 1100000 to 4500000 g/mol for 16200:1 to 24000:1 monomer : catalyst ratio, respectively.

Table 1. The polymerization reaction of prepared 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, dimethyl ester, **2**, (30 min., 25°C)

Solvent	Catalyst	Ratio	Mw (g/mol)	PDI	Yield (%)
THF	Ru(PPh ₃) ₂ (Cl) ₂ (CHPh)	16200:1	1100000	2,8	85
THF	Ru(PPh ₃) ₂ (Cl) ₂ (CHPh)	20 800:1	2900000	2,1	80
THF	Ru(PPh ₃) ₂ (Cl) ₂ (CHPh)	24 000:1	4500000	1,21	85

Conclusions

Polyanions of poly(7-oxanorbornene-2,3-dicarboxylate), **4**, were prepared by hydrolysis of poly(dimethyl-7-oxabicyclo (2.2.1) hept-5-ene-2,3-dicarboxylic acid), **3**. It is worth noting that the polyanions in aqueous solution form hydrogels even in a low concentration (Fig. 7).

References

- Piotti, Marcelo E. 2000. "Ring Opening Metathesis Polymerization." 4(1999): 539–47.
- Grubbs, Robert H. 2004. "Olefin Metathesis." *Tetrahedron* 60(34): 7117–40. <http://linkinghub.elsevier.com/retrieve/pii/S004040200400941X> (October 13, 2014).
- Binder, J. B., & Raines, R. T. (2008). Olefin metathesis for chemical biology. *Current Opinion in Chemical Biology*, 12(6), 767–73. doi:10.1016/j.cbpa.2008.09.022
- France, M. B., Alty, L. T., & Earl, T. M. (1999). Synthesis of 7-Oxanorbornene Derivatives: A Two-Step Sequence Preparation for the Organic Laboratory, 76(5), 659–660.
- Miró Vera, A., Velásquez, W., Briceño, A., Bahsas Bahsas, A., Ramírez Valero, B., & Diaz de Delgado, G. (2007). Synthesis and Crystal Structure of Dimethyl-7-oxabicyclo[2.2.1]hept-5-ene exo,exo-2,3-dicarboxylate. *Journal of Chemical Crystallography*, 37(8), 543–548. doi:10.1007/s10870-007-9206-9
- Wathier, M., Lakin, B. a, Bansal, P. N., Stoddart, S. S., Snyder, B. D., & Grinstaff, M. W. (2013). A Large-Molecular-Weight Polyanion, Synthesized via Ring-Opening Metathesis Polymerization, as a Lubricant for Human Articular Cartilage. *Journal of the American Chemical Society*, 36–39. doi:10.1021/ja400695h
- Wathier, M., Lakin, B. A., Bansal, P. N., Stoddart, S. S., Snyder, B. D., Mark, W., Medical, D. (n.d.). SUPPORTING INFORMATION A Large Molecular Weight Polyanion, Synthesized via ROMP, as a Lubricant for Human Articular Cartilage, 2–8.
- Wathier, M., Stoddart, S. S., Sheehy, M. J., & Grinstaff, M. W. (2010). Acidic polysaccharide mimics via ring-opening metathesis polymerization. *Journal of the American Chemical Society*, 132(45), 15887–9. doi:10.1021/ja106488h
- Wathier, M., Stoddart, S. S., Sheehy, M. J., & Grinstaff, M. W. (n.d.). SUPPORTING INFORMATION Acidic Polysaccharide Mimics via Ring-opening Metathesis Polymerization Michel Wathier, Stephanie S. Stoddart, Matthew J. Sheehy, and Mark W. Grinstaff*, 1–10.