



16th International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov, CCE 2015

Polymers based on norbornene derivatives

G.S. Bozhenkova^a, A.P. Samochnova^a, R.V. Ashirov^a, A.A. Lyapkov^{a*}

^a*Department of Technology of Organic Substances and Polymer Materials
National Research Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia*

Abstract

This study presents the influence of *exo,exo*-N,N'-hexylene-di(5-norbornene-2,3-dicarboximide) on the degree of cross-linking and glass transition temperature of the polymers obtained from a mixture of dimethyl esters of *exo,exo*- and *endo,endo*-5-norbornene-2,3-dicarboxylic acid. It was found that *exo,exo*-N,N'-hexylene-di(5-norbornene-2,3-dicarboximide) can be used as a cross-linking agent in ROMP. Addition of the cross-linking agent leads to an increase in the degree of cross-linking polymers. The glass transition temperature of polymers increases with concentration increasing of the crosslinking agent.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of Tomsk Polytechnic University

Keywords: norbornene derivatives; metathesis; ROMP; cross-linking; gel content

1. Introduction

One of the effective methods for preparation of new polymers with functional groups is metathesis ring-opening polymerization (ROMP). Recently, norbornene-based polymers with substituents at 2,3-positions of functional

Nomenclature

<i>T</i>	temperature, °C
<i>w</i>	mole fraction of comonomers, %
<i>T_g</i>	glass transition temperature, °C

* Corresponding author. Tel.: +7-906-954-3336.
E-mail address: alexdes@tpu.ru

groups is of great interest. Such polymers have excellent dielectric properties, mechanical strength and exhibit good adhesive properties and can be used to create a variety of composite materials¹⁻³.

The presence of modern type Hoveyda-Grubbs catalysts allows us to use a great variety of monomers. Dimethyl ester of norbornene-2,3-dicarboxylic acid is a versatile monomer, obtained as an isomer mixture of endo,endo- and exo,exo-forms at a 3:2 ratio. The polymerization of the monomer under the influence of the catalyst⁴ results in a polymer under a glass transition temperature of 86–90 °C. This low glass transition temperature limits the scope of application of the polymer, causing its low heat resistance.

The method for improving the physical and mechanical properties of polymers is to use cross-linking agents which lead to the formation of a cross-linked polymer structure⁵. Compounds with two or more functional groups capable of reacting with a ring-opening metathesis are used as cross-linking agents in ROMP.

The aim of this work was to study the effect of concentration of cross-linking agent and the cross-linking degree of polymers on the glass transition temperature of the mixture of the exo,exo- and endo,endo-dimethyl ester of 5-norbornene-2,3-dicarboxylic acid (DME).

Exo,exo-N,N'-hexylene-di(5-norbornene-2,3-dicarboximide) (exo-C6D) were used as cross-linking agents. Exo-C6D is a bi-functional comonomer as it has two norbornene moieties in its composition, it can form a cross-linked structure and change the properties as a result of ring opening and polymerization. Figure 1 shows the preparation of the cross-linked polymer.

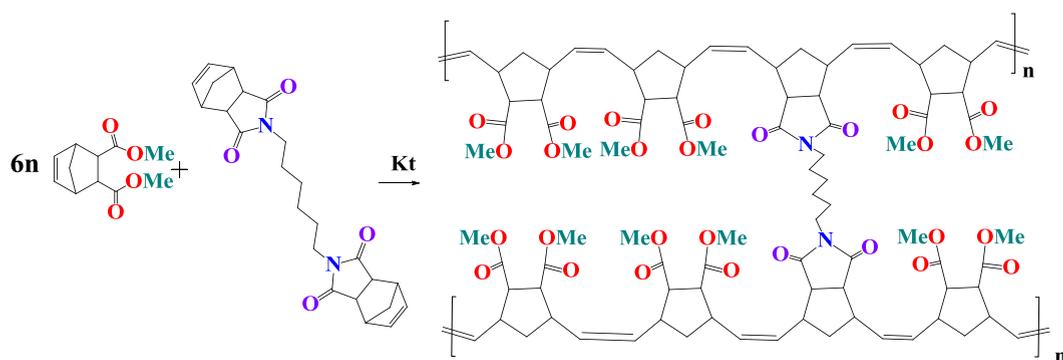


Fig. 1. Copolymerization scheme of DME and exo-C6D.

2. Experimental

2.1. Materials

Dimethyl maleate (95 %), exo-anhydride of 5-norbornene-2,3-dicarboxylic acid (95 %), hexamethylene diamine (98 %) are used in the production of Sigma Aldrich. Dicyclopentadiene (China) was previously purified from impurities.

2.2. Synthesis

The mixture of dimethyl ether of exo,exo- and endo,endo-5-norbornene-2,3-dicarboxylic acid, used as a monomer, was prepared by interaction of dimethyl maleate and dicyclopentadiene. 360 g (2.5 mol) of dimethyl maleate and 250 g of dicyclopentadiene (1,8 mol) were placed in a round bottom flask of 1 liter, and then 0.5 g of hydroquinone monomethyl ether was added as antioxidant. The reaction mass was heated on an oil bath at reflux under 150 °C for four hours under atmospheric pressure. Then the bath temperature was increased to 160 °C and the bath was heated for four hours. After cooling, the reaction mass was subjected to distillation at a pressure of 15 Torr. First, at temperature from 50 °C to 105 °C the excess of dicyclopentadiene was distilled, then the target product was collected at 105-110 °C. The yield was 470 g (corresponding to 89.5 % of the theoretical data). The ratio of the

endo,endo- and exo,exo-ester forms was found by gas chromatography with a mass selective detector and is 60 % and 40 %, respectively.

Synthesis of exo,exo-N,N'-hexylene-di(5-norbornene-2,3-dicarboximide) was performed according to the method described in the patent⁵ (Fig. 2).

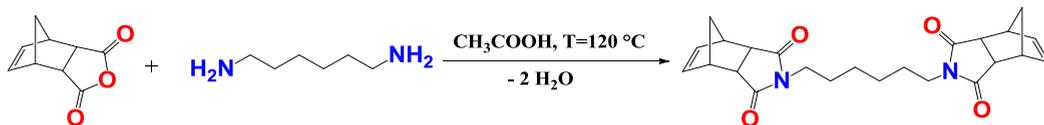


Fig. 2. Synthesis of exo,exo-N,N'-hexylene di(5norbornene-2,3-dicarboximide).

Exo-anhydride of 5-norbornene-2,3-dicarboxylic acid (50 g) was dissolved in glacial acetic acid (130 ml) at 118–120 °C in a flask equipped with a reflux condenser. 17.0 g of 1,6-hexamethylenediamine was added in the flask for 1 hour. The reaction mixture was heated for 3 hours to get a yellow solution. The obtained solution was poured into cold distilled water (5l ml), the precipitated white powder was washed with distilled water two times and dried. Purification of the product was carried out by recrystallization from acetone to give white crystalline powder with m.p. of 154 °C (55.0 g, 89.9 % yield). Elemental analysis: calculated for C₂₄H₂₈N₂O₄: C 70.57 %, H 6.84 %, N 6.84 %, found C 70.5 %, H 6.2 %, N 6.7 %. Elemental analysis was made using Vario MACRO CHNS. The method is based on the principle of catalytic combustion of samples at 1150 °C in the presence of pure oxygen. Determination of elements is based on the content of the combustion products of CO₂, N₂, H₂O, SO₂.

2.3. Polymerization

Exo-C6D was used in an amount of 0, 2, 3, 4, 6, 8 and 10 wt.%. The required weight of the cross-linking agent was dissolved in the monomer mixture at a temperature of 110–120 °C, then the mixture was cooled to 35–40 °C (comonomer crystallizing was not observed). The catalyst solution in toluene with concentration of 0.01 g/ml (the mass ratio of catalyst/monomer = 1/15000) was added to the mixture monomer and the cross-linking agent. The samples were placed in the oil bath for 30 min hold at 60 °C, then heated to 140 °C and kept for 30 min.

2.4. Characterization

Solvent extraction in boiling chloroform was used to determine the gel content of polymers. Chloroform being a suitable solvent for dissolving the monomer (DME), the cross-linking agent and the polymer of DME, it can be presumed that the obtained gel content corresponds to the insoluble part of the cross-linked polymer⁶ in the absence of any other extraneous reactions. For each polymer the samples of ~ 0.8–1.0 g were grounded (granulated), weighed and placed into a pouch of known weight. The samples were then directly immersed into a 250ml round bottom flask with 150ml of chloroform attached to the condenser and boiled for 7 days. The pouches were taken out and dried in a vacuum oven at 60 °C for 1 day and then they were weighed. Three values of gel content for each sample were converted to wt % fractions according to eq. (1).

$$C_{\text{GEL}} = \frac{G_{\text{R}}}{G_{\text{O}}} \cdot 100 \quad (1)$$

C_{GEL} – gel content, wt. %; G_{R} – weight of residue, g; G_{O} – original weight of sample, g.

Measurement of glass transition temperature of the polymers (T_g) was carried out using NETZSCH DSC 204 F1 Phoenix (ISO 11375). The heating rate was 10 K/min. The measurements were performed in a helium atmosphere (flow rate is 50 ml/min). The samples were heated from 20 °C to 200 °C, then cooled and reheated. The glass transition temperature and thermal effects of the glass transition were determined according to the second heating and cooling.

3. Results and discussions

The samples of the resulting modified copolymers, as well as the polymer synthesized from the initial monomer mixture are solid, odorless, transparent materials.

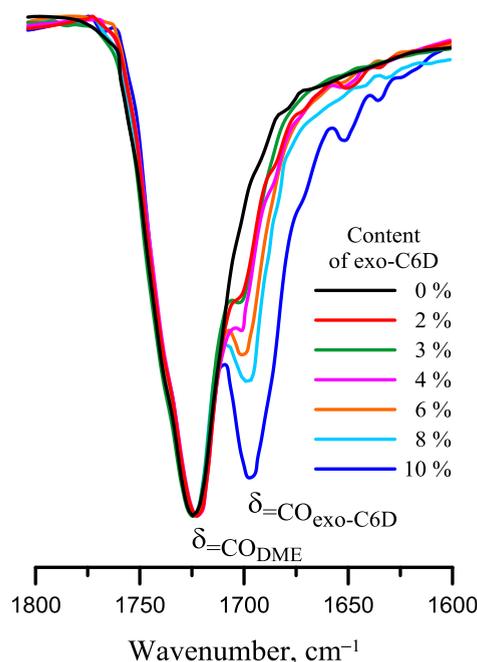


Fig. 3. IR-spectra of polymers.

Determining the gel content the experiment was performed to confirm the formation of a cross-linked polymer structure [7]. The polymer obtained without addition of the cross-linking agent is completely dissolved in chloroform. The samples of polymers with additives of the cross-linking agent contain more than 63 % of the insoluble portion. It was expected to find that the gel content increased to 86 % with increasing concentration of the cross-linking agent of 2 to 10 wt.%.

IR-spectra of polymers are also confirmation of the formation of the cross-linked polymers (Fig. 3). The characteristic line of 1680 cm⁻¹ shows that the cross-linking agent is in the cross-linked polymer. The intensity of the 1680 cm⁻¹ line increases with the initial concentration of the cross-linking agent.

The glass transition temperature of polymers increases with the concentration increasing of the cross-linking agent from 86 °C (PDME) and reaches its maximum when 10 wt. % of exo-C6D at 128 °C.

The Flory-Fox equation describes the empirical model for predicting the glass transition temperature change of the polymer composition and the glass transition temperature of the polymer of starting comonomers. The glass transition temperature of the copolymers can be calculated as a function of the mass ratio of two comonomers by equation⁷ (2):

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (2)$$

$T_{g1,2}$ – glass transition temperature of the comonomers, °C; $w_{1,2}$ – weight fraction of the comonomers.

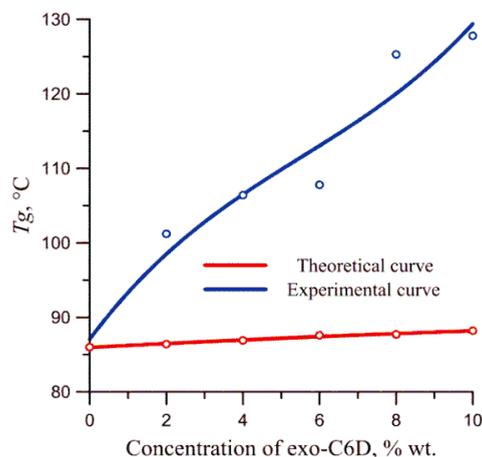


Fig. 4. Influence of concentration of exo-C6D on glass transition temperature of the polymer based PDME.

The experimental values of the glass transition temperature (T_g) is higher than the calculated values according to the formula of Flory-Fox (Fig. 4). The theoretical curve assumes a smooth change in the glass transition temperature with increasing of the bi-functional comonomer concentrations. However, the experimental curve with increasing of the comonomer concentration is up sharply and has no linear relationship. These data confirm that when using comonomers with two functional groups being active in ROMP, the glass transition temperature change of these polymers is not subjected to the Flory-Fox equation⁷, due to formation of cross-linked structures and influence of the nature of the cross-linker.

4. Conclusions

According to the results of this work it was found that *exo,exo-N,N'*-hexylene-di(5-norbornene-2,3-dicarboximide), can be used as a modifying agent in ROMP. The copolymerization of *exo-C6D* and the mixture of *exo,exo*- and *endo,endo*-dimethyl ether of 5-norbornene-2,3-dicarboxylic acid leads to the increase in the gel content of polymers and, consequently, to the glass transition temperature increase.

Exo,exo-N,N'-hexylene-di(5-norbornene-2,3-dicarboximide) comprises two norbornene rings into its structure, which are active in ROMP, and it, in fact, is a bi-functional comonomer. The mechanism of bi-functional comonomer action is the polymer formation of lattice pattern, whereby the resulting copolymer is not soluble in chloroform. IR spectra of the non dissolved polymers in chloroform confirm the presence of cross-linking agents in the structure of the polymer molecules.

It is shown that the experimental values of the glass transition temperature of the cross-linked polymer deviate from those calculated by the equation of Flory-Fox to a greater extent. These data confirm that the Flory-Fox equation is applicable for predicting the glass transition temperature of the copolymers produced in ROM-polymerization when using comonomers with two or more functional groups.

References

1. Kazunori T., Seiji O., Yasuo T., Zeon Corporation. Norbornene-based ring-opening polymerization polymer, product of hydrogenation of norbornene-based ring-opening polymerization polymer, and processes for producing these, *US Patent*, 7037993 B1 (2006).
2. Mulpuri S.V., Shin J., Shin B., Greiner A.. Synthesis and characterization of substituted polynorbornene derivatives. *Polymer* 2011; **52**:4377-4386.
3. Ashirov R.V., Zemlyakov D.I., Lyapkov A.A., Kiselev S.A.. Kinetics of the Metathesis Polymerization of 5,6-Di(methoxycarbonyl)bicyclo[2.2.1]hept-2-enes on an Original Hoveyda-Grubbs II Type Catalyst. *Kinetics and Catalysis* 2013; **54** (4):469-474.

4. Kolesnik V.D., Ashirov R.V., Scheglova N.M., Kiseleva N.V., Bogomolova M.N., Sibur. Ruthenium catalyst for the metathesis polymerization of dicyclopentadiene (embodiments) and method for producing polydicyclopentadiene (embodiments), *WO*, 2011149388 A1 (2011).
5. James F.W., Ezat K., Thanawadee L., Univ Durham. Process for polymerization of cycloolefins and polymerizable cycloolefins, *US Patent*, 6677418 B1 (2004).
6. Mascia L., Clarke J., Ng K.S., Chua K.S., Russo P. Cure Efficiency of Dodecyl Succinic Anhydride as a Cross-Linking Agent for Elastomer Blends Based on Epoxidized Natural Rubber. *J. Appl. Polym. Sci* 2015; **132** (23):1-8.
7. Shenghui H. *Synthesis and Characterisation of Degradable Thermosetting Materials*. Durham: Durham University; 2012. 74 p.