

## Archives of Polymer Engineering and Science

# Physicomechanical Properties of 5-Norbornene-2,3-Dicarboxylic Acid Dimethyl Ether Polymers

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## Publication Dates

Received date: January 16, 2022

Accepted date: February 16, 2022

Published date: February 18, 2022

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## Citation

Lyapkov AA, Bozhenkova GS, Kiselev SA, Smirnova NA, Ashirov RV, et al. (2022) Physicomechanical Properties of 5-Norbornene-2,3-Dicarboxylic Acid Dimethyl Ether Polymers. Arch Polym Eng Sci 1: 1-14

## Abstract

The aim of this work is the preparation of polymers based on a mixture of *exo,exo*- and *endo,endo*-dimethyl esters of 5-norbornene-2,3-dicarboxylic acid and bi-functional comonomers of 5-norbornene-2,3-dicarboximides. The effect of the concentration and length of 5-norbornene-2,3-dicarboximides linker on the mechanical and physical properties of 5-norbornene-2,3-dicarboxylic acid polydimethyl ether was studied. The use of *exo,exo*-N,N'-butylene-di(5-norbornene-2,3-dicarboximide) in an amount of 1.0 to 2.5 mole% leads to the formation of a polymer with the highest degree of cross-linking and physicochemical properties, such as elastic moduli in bending and stretching, glass transition temperature. *Exo,exo*-N,N'-hexylene-di(5-norbornene-2,3-dicarboximide) is characterized by the longest linker, and therefore the polymer containing this comonomer does not lose plasticity and the Izod impact strength does not decrease with increasing comonomer concentration.

**Keywords:** Ring Opening Metathesis Polymerization; 2,3-Dicarbomethoxy-5-Norbornene; Bi-Functional Monomers; Cross-Linking Agent; Norbornene Derivatives; Hoveyda-Grubbs Ii Catalyst

## Introduction

Ring Opening Metathesis Polymerization (ROMP) is an effective polymerization process for the preparation of polymers with different functional groups, structure and properties [1]. The development and application of highly active metal-alkylidene catalysts opens up new opportunities in the metathesis reaction of olefins [2-5]. The use of POMP extends to interdisciplinary areas. So, ROMP is increasingly used in high-tech applications, such as obtaining self-healing materials [6,7]. One of the advantages of ROMP is the polymerization of strained cyclic monomers with different functional groups. In turn, ruthenium catalysts with N-chelating ligand was tolerant to most functional groups, such as alcohols, aldehydes, ketones, acids and amides [8-10].

Some of the most common functional substituents in the norbornene molecule are ester groups. There is a sufficient number of scientific papers dealing with the synthesis, kinetic studies and polymerization of mono- and dimethyl ethers of norbornene-2,3-dicarboxylic acid (DME) [11-16].

Like all norbornene derivatives, the norbornene dicarboxylic acid esters obtained by the Diels-Alder reaction exist in several isomeric configurations [17]. Depending on the conditions of synthesis and reacting substances, the ratio of isomeric forms in the product is different [18,19].

It is known from early studies that esters of norbornene dicarboxylic acid in *exo*-form are more reactive than *endo*-isomers [20-22]. In the literature on norbornene esters, the properties of the resulting polymers are rarely described, and no mention is made of the practical use of such materials.

The present work is devoted to the preparation of polymers in a monomer mass from norbornene-2,3-dicarboxylic acid dimethyl esters. Such polymers can be used as constructional plastics. However, polydimethylether of norbornene dicarboxylic acid (PDME) is a linear polymer that dissolves in polar solvents and has a low glass transition temperature (100 °C). To increase the performance of the polymer based on norbornene derivatives, bi-functional monomers leading to the formation of cross-linked polymers are introduced into the monomer [22-25]. In this work, norbornene-dicarboximides were used as bi-functional monomers.

To polynorbornene dicarboximides, scientific and practical interest has recently increased significantly. Their application covers the fields of chemistry [26], physics [27] and biology [28,29]. Most often these polymers are used for the production of biodegradable thermoplastics [30,31], adhesives [32], in microelectronics [33]. The wide use of norbornene-based polymers is due to attractive properties, such as high transparency, chemical resistance, electrical properties, high glass transition temperature [34,35].

This article is devoted to obtaining and studying the mechanical and physical properties of copolymers based on a mixture of *exo,exo*- and *endo,endo*-dimethyl ethers of norbornene-2,3-dicarboxylic acid and norbornene dicarboximides obtained by ROMP in the presence of a catalyst of the type Hoveyda-Grubbs II generation with an N-chelating ligand.

## Experimental

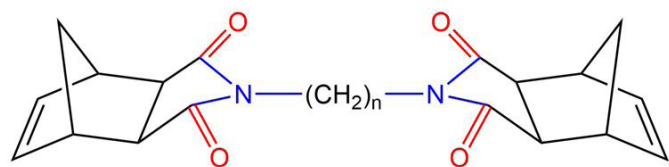
### Synthesis and characterization of monomer

A mixture of *exo,exo*- and *endo,endo*-dimethyl esters of 5-norbornene-2,3-dicarboxylic acid was obtained from dimethyl maleate and dicyclopentadiene (it is so called "green synthesis") [36]. It was synthesized in a 1-L round-bottom flask with a backflow condenser. 360 g (2.5 mole) of dimethyl maleate (Aldrich, 96%) and 250 g (1.8 mole) of dicyclopentadiene (Hangzhou Uniwise International Co. Ltd., 99%) were transferred into the flask together with 0.5 g of hydroquinone monomethyl ether as an antioxidant. The reaction mixture was heated to 150 °C using an oil bath for 8 hours under atmospheric pressure. After cooling down, the reaction feed was removed under a pressure of ~ 2 kPa. The desired product was obtained using vacuum distillation (~ 2 kPa) at 105-110 °C. In this way, 470 g of product was obtained corresponding to a yield of 89.5%. The composition was analyzed by gas chromatography-mass spectrometry (GCMS) confirming that the monomer is a mixture of *exo,exo*- and *endo,endo*-dimethyl esters of 5-norbornene-2,3-dicarboxylic acid in a mass ratio of 40% and 60%, respectively.

### Synthesis and characterization of bi-functional monomers

*Exo,exo*-N,N'-alkylene-di(5-norbornene-2,3-dicarboximides) were used as bi-functional monomers with the general formula:

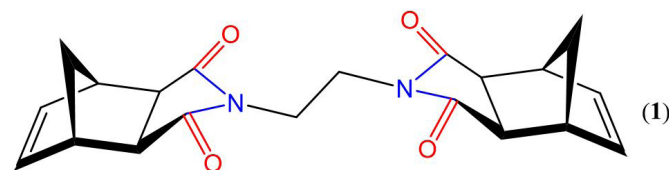
where alkylene was  $-(\text{CH}_2)_2-$  (*exo*-C2D),  $-(\text{CH}_2)_4-$  (*exo*-C4D),



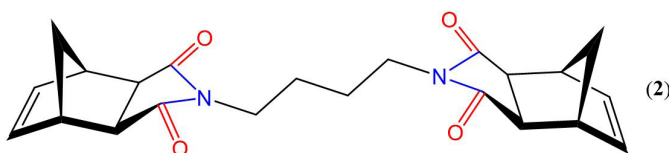
*exo-C<sub>n</sub>D*,  $n = 2, 4, 6$

$-(CH_2)_6-$  (*exo-C6D*). Bi-functional monomers were prepared according to the procedure described in [37]. A detailed description of the substances is given in [38].

*exo-C2D* (1)



*exo-C4D* (2)



*exo-C6D* (3)

## Polymerization

Polymerization of the DME monomer and its copolymerization with bi-functional monomers was carried out in bulk by a ruthenium carbene complex with an N-chelating ligand [39]. The catalyst solution in the monomer ratio of 1: 15,000 was placed in a polymerization mold. The polymerization was carried out with stepwise heating from 60 to 120 °C for 90 minutes.

To prepare copolymers, bi-functional monomers were added in an amount of 1 to 3.5 mole %. Prior to copolymerization, the bi-functional monomers were dissolved in the monomer (DME) at 110-120 °C, then the solution was cooled to 35-40 °C and a catalyst was added. Copolymerization parameters are the same as for polymerization. All operations were carried out in an inert atmosphere in the glove box MBraun Labstar.

## Characterization

### GCMS

Monomers were analyzed using an Agilent 7890A gas chromatograph with an MSD 5975C mass spectrometric detector (the HP-5MS column is 30 m long and 0.25 mm in internal diameter; the coated phase width is 0.25 μm; the column heating rate is 20 °C·min<sup>-1</sup> up to 290 °C; the evaporator temperature is 290 °C; the carrier gas is helium with a flow rate of 1 ml/min).

### DSC

Glass transition temperature measurements were conducted with DSC 204 F1 Phoenix (NETZSCH) in accordance with ISO 11375 at heating rate 10 °C·min<sup>-1</sup>. Measurements were carried out under inert helium atmosphere at a flow rate of 50 ml/min. Samples were heated from 20 °C up to 200 °C, then cooled and heated again. Glass transition temperature and heat effects of glass transition were estimated with help of the second heating and cooling data.

### Gel content

The gel content of polymers was determined using boiling chloroform. In the absence of side reactions, the obtained gel content corresponds to the non-soluble part of the cross-linked polymer [40]. Chloroform is a suitable solvent for monomer (DME), bi- and tri-functional comonomers and PDME. Each polymer sample (~0.8-1.0 g) was dispersed, weighted and placed into ashless sack with known mass. Then the samples were directly immersed into 250 ml round bottomed flask with 150 ml of chloroform with back flow condenser and refluxed for 7 days. Thereafter, the sacks were examined, dried at 60 °C for 24 hours and weighted.

The gel content was calculated on the base of three gel content measurements in accordance with the equation (1).

$$\text{Gel content (wt.\%)} = \frac{\text{Weight of residue}}{\text{Original weight of sample}} \times 100 \quad (1)$$

## Mechanical properties

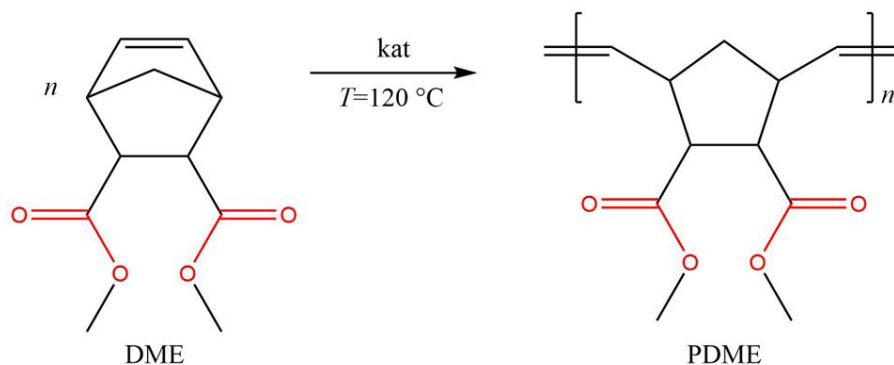
Mechanical and physical properties of polymers were investigated using a GOTECH AI 7000M universal testing machine under ambient conditions (23±2 °C). The tensile modulus, flexural modulus, tensile elongation and tensile strength were measured for all the polymer samples. The flexural strength was tested at a

rate of 2 mm/min and the tensile test rate was 5 mm/min. The samples were treated and flexural strength tests were conducted in accordance with ISO178. The tensile strength tests were conducted according to ISO527.

Izod impact strength was estimated with GOTECH GT-7045-HMH in accordance with ISO 180/1A. The samples were conditioned at  $23 \pm 2$  °C and rH was  $50 \pm 5\%$ .

## Result and Discussion

Dimethyl esters of norbornene-2,3-dicarboxylic acid are attractive raw materials for the preparation of polymers for various purposes. Synthesis of DME does not require expensive raw materials and is simple in hardware design. DME are obtained by the Diels-Alder reaction from dimethyl maleate and dicyclopentadiene [36]. As a result of the reaction, a mixture of *exo,exo*- and *endo,endo*-isomers with a content of 40 and 60% by weight, respectively, is formed.



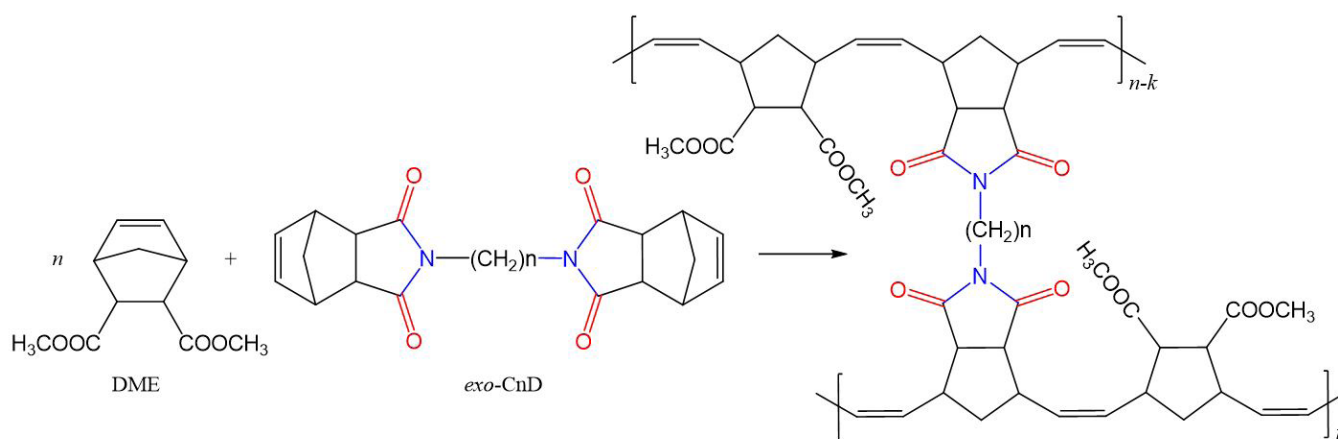
Scheme 1

The polymer from this monomer mixture (PDME) is linear, having a statistical structure (Scheme 1).

Conversion of the monomer to the polymer is quite high and is not less than 98%. In addition, PDME has a high molecular weight (greater than  $4.5 \cdot 10^6$  g·mol<sup>-1</sup>) and unimodal molecular weight distribution (PDI = 1.1), but is completely soluble in polar solvents, which may limit its practical application.

*endo*-Isomers of norbornene functional derivatives have lower reactivity than *exo*-isomers in ROMP reactions under the action of ruthenium catalysts due to steric hindrance between growing polymeric chains and monomer molecules [20-22, 41]. In this connection, norbornene dicarboximides used as bifunctional monomers were used in *exo*-form.

The preparation of copolymers from DME and norbornene dicarboximides is shown in Scheme 2.



Scheme 2

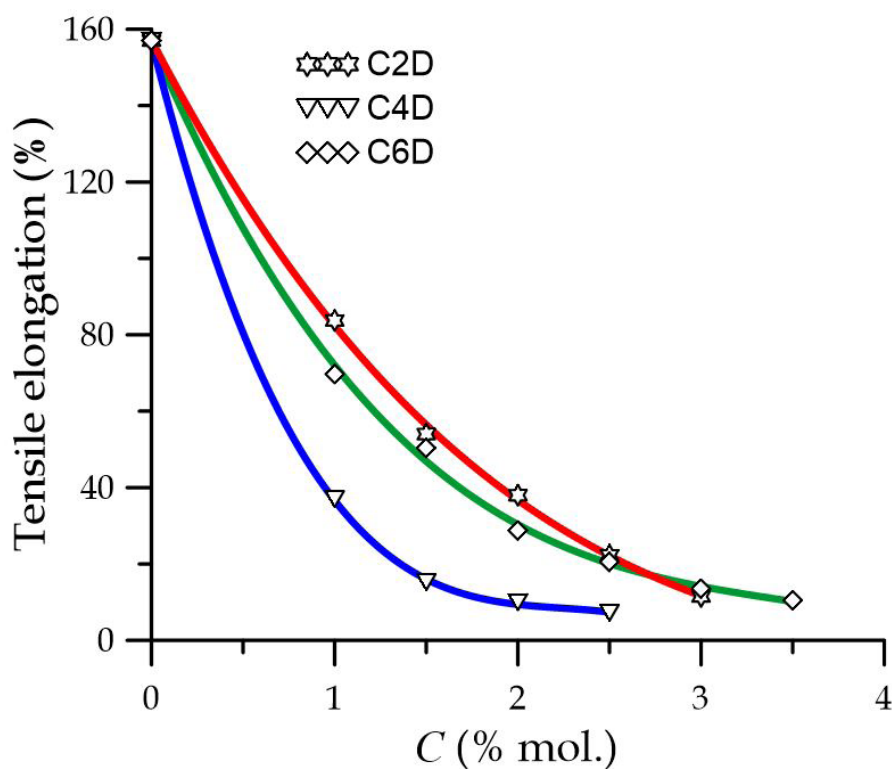
As a result of copolymerization of mono- and bi-functional monomers, branched polymers are formed which do not dissolve and do not swell in solvents. In addition, the mechanical and physical properties of such polymers are increased compared to linear PDME.

In this paper, we studied the effect of the concentration of bi-functional monomers on the mechanical and physical properties of polymers based on dimethyl ethers of norbornene-2,3-dicarboxylic acid, and the relationship between the properties of the resulting polymers and the linker length of bi-functional monomers was studied.

When bi-functional comonomers are introduced into the mixture of *exo,exo*- and *endo,endo*-dimethyl esters of

norbornene dicarboxylic acid, the obtained copolymers exhibit a strong decrease in the relative elongation at break (Figure 1). For copolymers obtained using *exo*-C2D and *exo*-C6D, the values of the elongation at break with increasing concentration of bi-functional monomers decrease smoothly.

In the case of the *exo*-C4D monomer, when it is already 1.5 mole %, the elongation at break of the resulting copolymer decreases by more than 10 times as compared to PDME. Such a significant decrease in the relative elongation at break with the introduction of bi-functional monomers indicates that the comonomer forms branches in the polymeric chain of PDME and the resulting copolymers acquire a crosslinked structure.

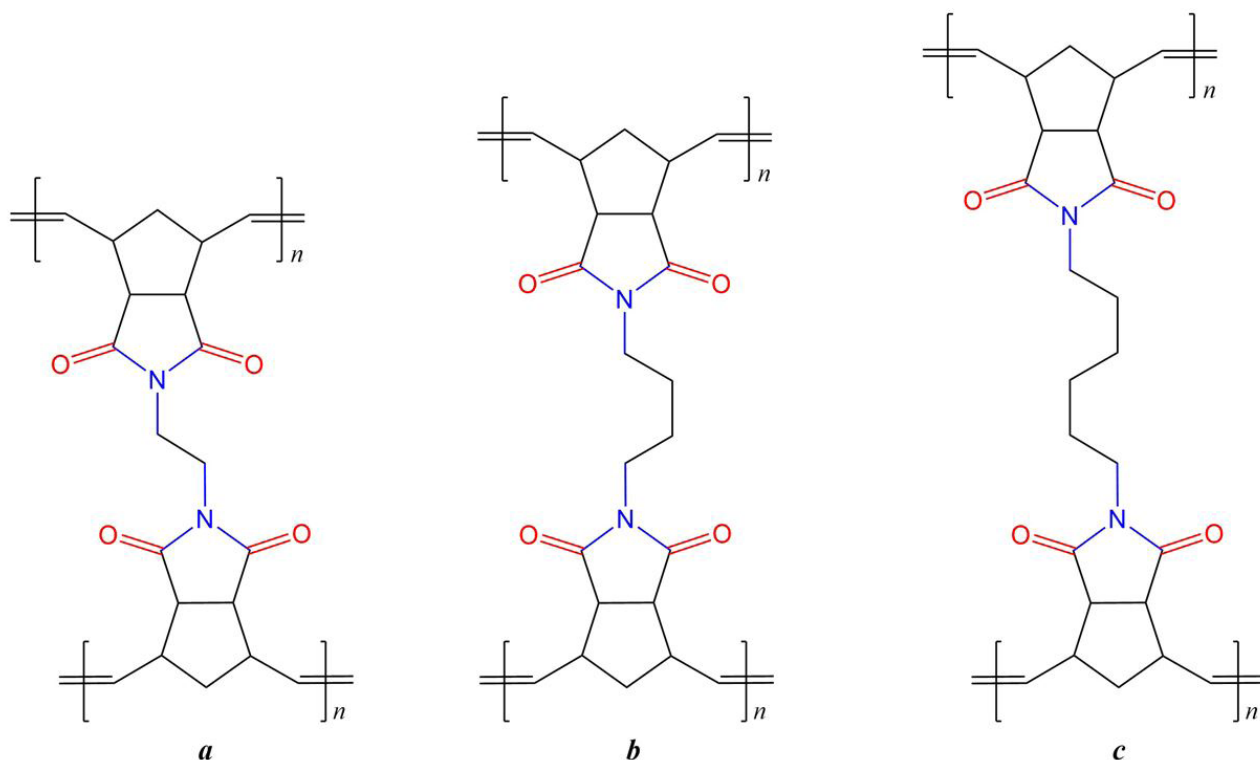


**Figure 1:** Dependence of the tensile elongation ( $\epsilon_{pp}$ ) of copolymers on the concentration of bi-functional comonomers

The relative elongation at break is ambiguously dependent on the length of the linker of the bi-functional monomer. The length of the linker affects the mobility of the polymer macromolecules, and also most likely determines the nature of the interaction of the molecules of the bi-functional monomer with the catalyst during copolymerization. The effect of *exo*-C4D monomer on the elongation at break is significantly different from the dependencies determined for *exo*-C2D and *exo*-C6D.

Such an effect of the bi-functional monomer can be related to the length of its linker and, correspondingly, the distance between the branching nodes in the polymer chain. When DME *exo*-C2D is introduced into the DME, the length of the bridge between the rigid fragments of the branches of the polymer chain is only 2 methylene groups (Scheme 3, a), for *exo*-C4D four (Scheme 3, b), and for *exo*-C6D – six (Scheme 3, c).

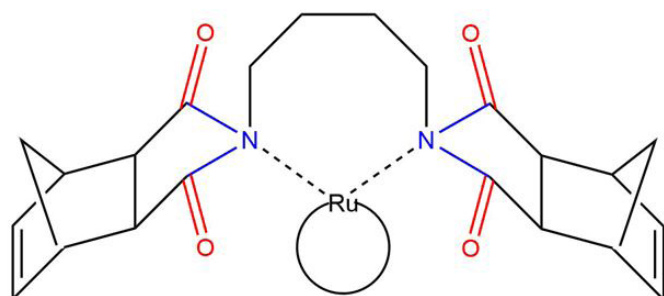




Scheme 3

The less effective effect of the *exo*-C2D monomer on the formation of the crosslinked polymer structure is associated with a short linker. The bulky imide groups are too close to each other, thereby hampering the approach of the catalyst to the second double bond of the bi-functional monomer during copolymerization.

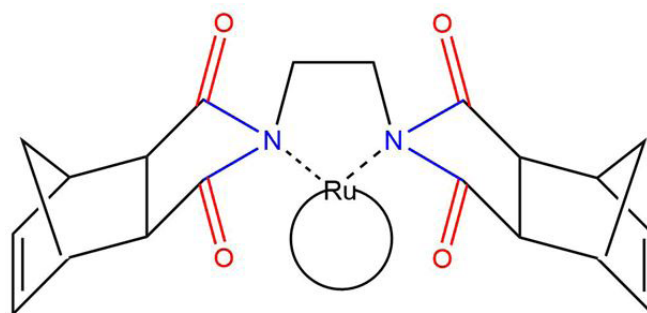
This fact can also be explained by the specific interaction of *exo*-C4D with the catalyst in the polymerization process, in which a seven-member intermediate is formed (Figure 2), which facilitates more efficient and uniform *exo*-C4D involvement in the ROMP process. Most likely, the catalyst leaves the fragment of the *exo*-C4D molecule only after both norbornene rings have entered the ROMP, therefore, they have formed a cross-linking or branching of the polymer chain.



**Figure 2:** Catalyst intermediate complex with comonomer molecule *exo*-C4D

The *exo*-C2D comonomer could theoretically form a five-membered complex  $-N-CH_2-CH_2-N-Ru-$  (Figure 3), but the bulky imide substituents exert a steric effect and hamper such *exo*-C2D interaction with the catalyst.

In this regard, copolymers containing *exo*-C2D are characterized by lower values of the degree of cross-linking and elongation at break as compared to *exo*-C4D (Figure 3).



**Figure 3:** Catalyst intermediate complex with comonomer molecule *exo*-C2D

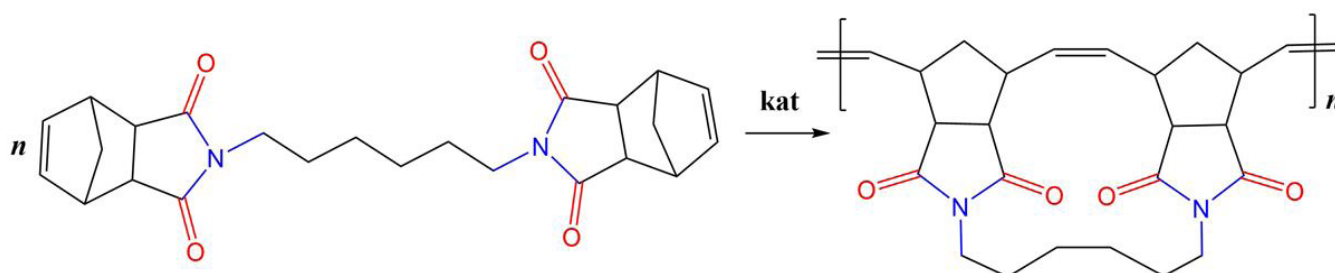
The hypothetical nine-membered intermediate, which with the catalyst could form *exo*-C6D, is likely to be thermodynamically unstable. The monomer *exo*-C6D has a rather long linker. On the one hand, easily formed cross-linked polymers with the participation of *exo*-C6D have a fairly flexible and mobile structure. On the other hand, it is possible that the *exo*-C6D comonomer under the action of a catalyst is able to enter ROMP not only by crosslinking polymer chains, but also interacting with itself, to form a linear polymer with cyclic fragments (Scheme 4).

In this regard, the degree of crosslinking of copolymers with *exo*-C2D and *exo*-C6D is lower than for copolymers containing *exo*-

C4D (Fig. 4). Thus, the comonomer *exo*-C4D most effectively enters the copolymerization process and forms a copolymer with the highest content of gel fraction and, therefore, with the least elongation at break.

With an increase in the concentration of comonomers introduced, the content of the gel fraction in the copolymers increases rapidly (Figure 4).

With an increase in the concentration of bi-functional comonomers, the elastic moduli in bending and stretching gradually increase (Figures 5 and 6).



Scheme 4

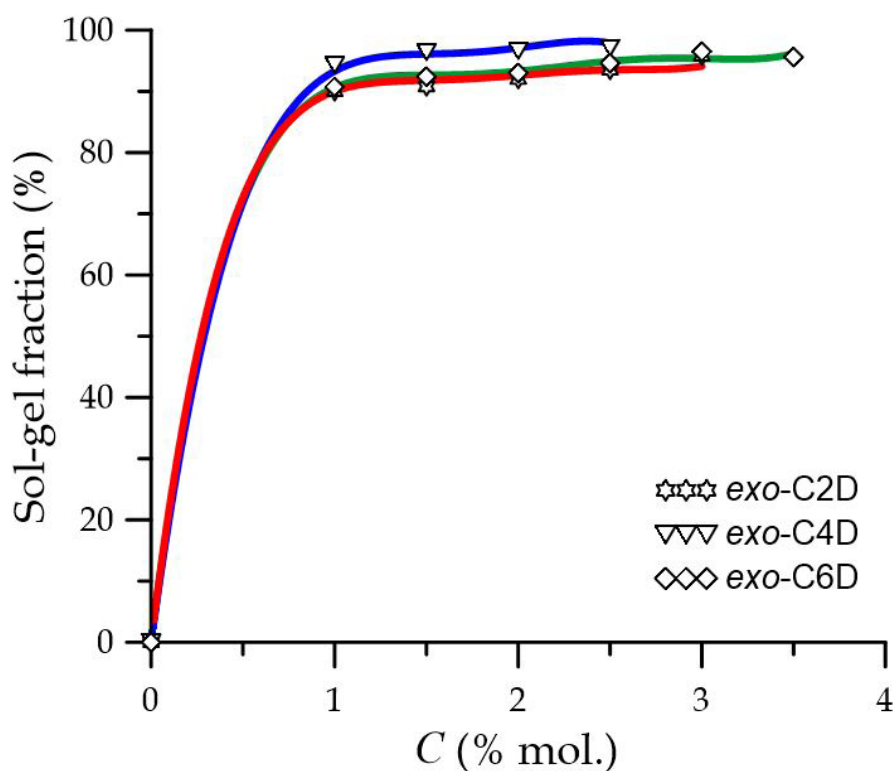
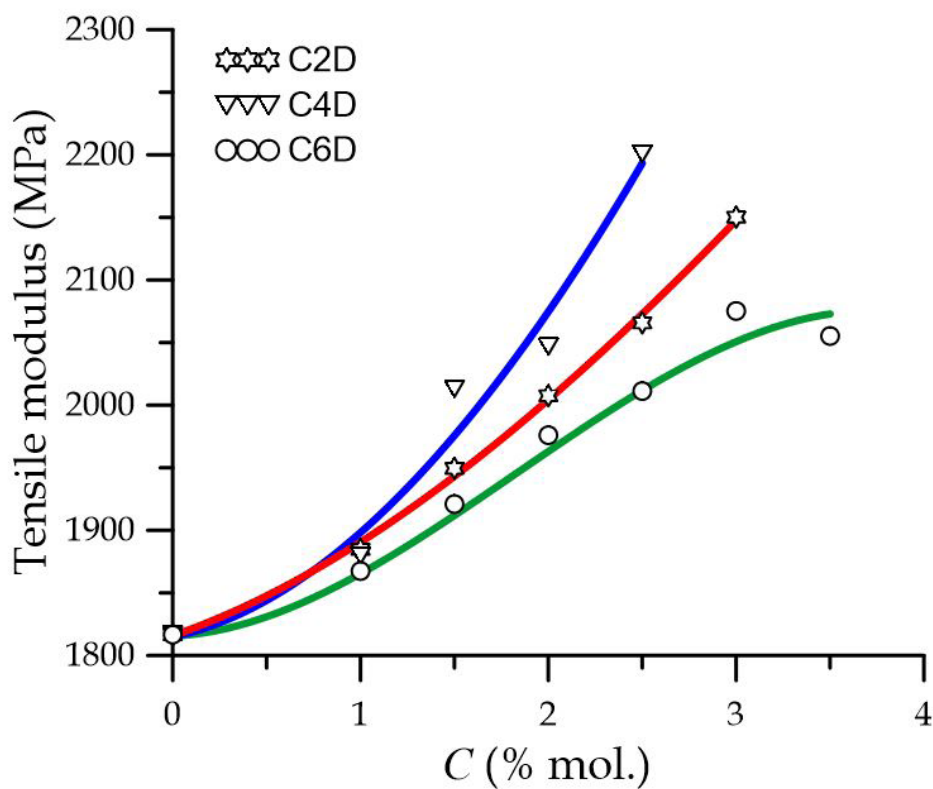
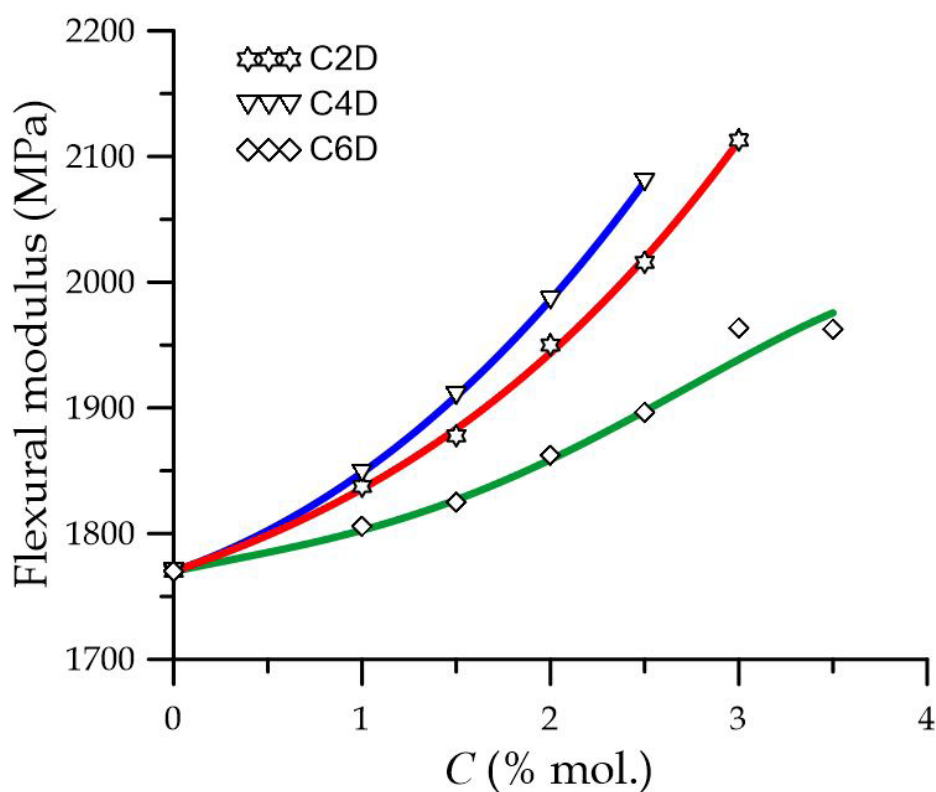


Figure 4: Dependence of the content of sol-gel fraction in copolymers on the concentration of bi-functional comonomers



**Figure 5:** Influence of the amount of bi-functional monomer monomers on the tensile modulus ( $E_{ten}$ ) of copolymers



**Figure 6:** Influence of the amount of bi-functional monomers on the flexural modulus ( $E_{flex}$ ) of its copolymers with DME



Studies have shown that the tensile yield strength and the breaking strength are practically independent of the concentration and the length of the linker of bi-functional monomers (Table 1).

With an increase in the content of the gel-fraction in the samples, the strength and brittleness of the polymers increases, and the

Izod impact strength, on the contrary, decreases (Figure 7). It is seen from Figure 7 that with increasing length of the linker of bi-functional monomers from 2 to 4 methylene groups, Izod impact strength decreases throughout the concentration line. However, it was unexpectedly found that the Izod impact strength did not change for copolymers obtained using *exo*-C6D.

Concentration of comonomer CnD, mole %	<i>exo</i> -C2D		<i>exo</i> -C4D		<i>exo</i> -C6D	
	$\sigma_r$ , MPa	$\sigma_{pp}$ , MPa	$\sigma_r$ , MPa	$\sigma_{pp}$ , MPa	$\sigma_r$ , MPa	$\sigma_{pp}$ , MPa
PDME	44,0±0,4	28,2±1,2	44,0±0,4	28,2±1,2	44,0±0,4	28,2±1,2
1	44,6±0,9	30,9±0,3	44,0±0,1	29,1±0,1	44,1±0,3	29,9±0,3
1,5	45,0±0,1	32,1±0,2	43,9±0,2	31,9±2,6	44,3±0,4	31,0±0,5
2	45,3±0,1	30,2±0,3	43,9±0,1	31,2±0,5	44,5±0,2	31,8±0,1
2,5	45,4±0,5	31,4±2,6	44,0±0,5	32,1±0,3	44,3±0,1	31,7±1,0
3	45,6±1,4	30,2±1,1			44,7±0,6	31,9±1,0
3,5					44,6±0,3	32,0±2,2

Table 1: Yield strength  $\sigma_r$  at tension and strength at break  $\sigma_{pp}$  of copolymers

This is obviously due to the longer linker length and, consequently, the greater mobility of the crosslinked macromolecules of these copolymers. Thus, the values obtained once again confirm that the length of the linker is also influenced by the properties of the copolymers in addition to the concentration of the bi-functional monomer.

Among the various operational parameters, the glass transition temperature ( $T_g$ ) is the most important characteristic of

polymers, which affects their thermal stability [42]. The glass transition temperature of polymers obtained by the ROMP method can be increased by adding sterically hindered cycloolefins or bi-functional monomers leading to the formation of crosslinked polymers.

Figure 8 shows the dependence of the change in the glass transition temperature of copolymers on the length of the linker of bi-functional monomers.

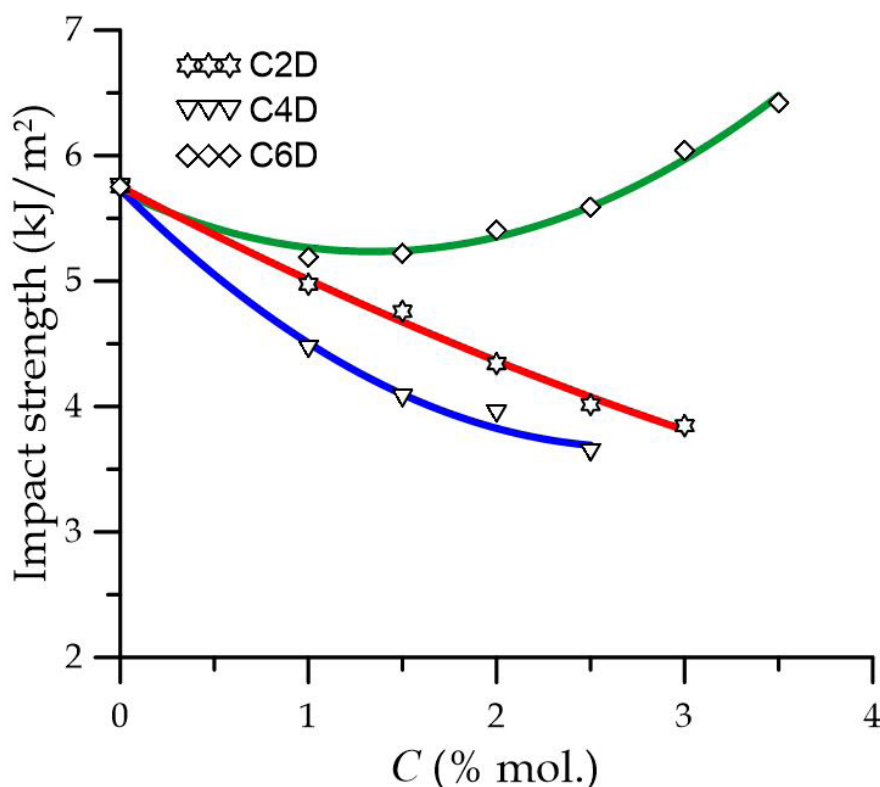
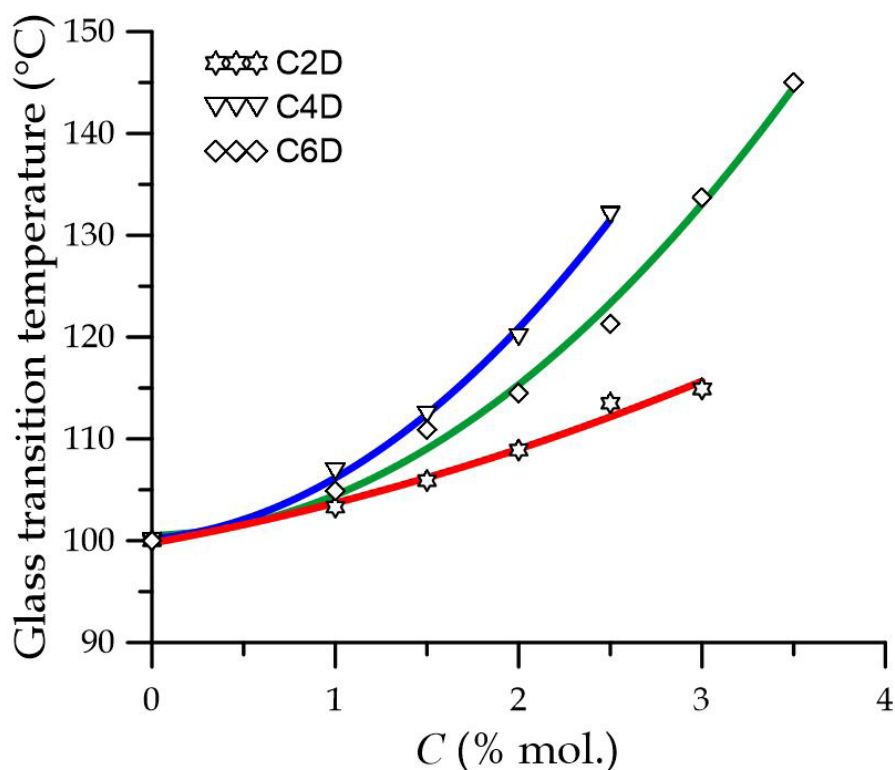


Figure 7: Dependence of the Izod impact strength of copolymers on the concentration of bi-functional monomers



**Figure 8:** Dependence of the glass transition temperature ( $T_g$ ) of copolymers on the amount of bi-functional monomers

It can be seen from the presented curves (Figure 8) that the introduction of up to 1 mole % of bi-functional monomers, the length of the molar linker, affects the change in the glass transition temperature. With the addition of 2.5 mole %, the highest glass transition temperature is characterized by a copolymer containing *exo*-C4D, and the least – *exo*-C2D. When 3 and 3.5 mole % of comonomers *exo*-C2D and *exo*-C6D are introduced, the copolymers containing *exo*-C6D have the highest glass transition temperature.

## Conclusions

Thus, copolymers with bi-functional monomers based on norbornene-dicarboxyimide with different linker lengths were obtained in this study.

As a result, *exo,exo*-N,N'-alkylene-di(5-norbornene-2,3-dicarboximides) were found to enter the ROMP with DME to form crosslinked copolymers.

It was determined that the content of the gel fraction in the copolymers increases with increasing concentration of bi-functional monomers. The higher the values of the gel of the copolymer fraction, the lower the values of the elongation at break and the higher the modular characteristics of the copolymers.

It has been established that as the concentration of comonomers increases for all samples, elastic moduli increase during bending

and stretching, the glass transition temperature, Izod impact strength for copolymers containing *exo*-C2D and *exo*-C4D decreases.

It was found that the length of the linker of the bi-functional monomer greatly influences the structure of the macromolecules of the resulting copolymers, which, in turn, determines their physical and mechanical properties.

It has been established that the monomer *exo*-C4D possesses the optimum length of the linker for obtaining copolymers with the highest physical and mechanical indexes.

## Acknowledgements

The authors acknowledge the support from the Tomsk Polytechnic University development program "Priority 2030". This work was supported by "SIBUR HOLDING" within the framework of a single charitable program "Formula of Good Deeds".

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