SYNTHESIS OF POLY(5-NORBORNENE-2,3-DICARBOXYLIC ANHYDRIDE) BY ROMP IN THE PRESENCE OF THE SECOND-GENERATION GRUBBS CATALYST AND 1-HEXENE IN DMF

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Abstract

The results of investigations on the ring-opening metathesis polymerization (ROMP) of 5-norbornene-2,3-dicarboxylic acid anhydride (NDA) under the action of the second-generation Grubbs catalyst in the presence of 1-hexene, acting as a chain transfer agent, in DMF in order to synthesize a soluble low-molecular-weight polymer containing reactive groups are presented. The effect of polymerization conditions on the molecular weight and thermal properties of the resulting metathesis polymers based on NDA was determined.

Key words: *cis*-5-norbornene-exo-2,3-dicarboxylic anhydride, ring-opening metathesis polymerization, chain transfer agent, DMF, second generation Grubbs catalyst.
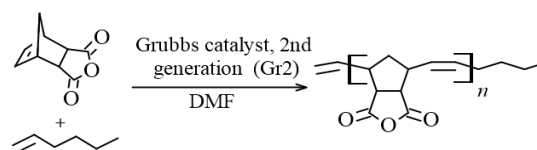
Introduction

The search for new polymeric materials with improved performance properties is one of the permanent tasks of modern polymer science. Its solution is based either on the search for new monomers allowing for obtaining polymers with unique properties or on various postpolymerization modifications of already known objects. Reactive homo- and copolymers themselves can act as modifiers of other polymeric materials, in particular, epoxy systems. For example, the addition of maleic anhydride and styrene [1] or maleic anhydride and α-olefin [2] copolymers to an epoxy system leads to the preservation of their optical transparency with a simultaneous increase in the glass transition temperature of the resulting product, as well as bending strength, impact strength, shear adhesion strength to metal of the cured samples compared to the unmodified system. We believe that the key structural fragment of these copolymers, which improves the performance properties of epoxy systems, is a maleic anhydride link, capable of opening during resin curing with the formation of additional transverse chemical bonds. The disadvantages of the above modifiers are the radical method of their polymerization, leading to a wide molecular weight distribution and difficulties in controlling the molecular weight of the final product, as well as strictly alternating nature of the resulting copolymers, preventing the regulation of a microstructure. The solution to these problems may be the use of a homopolymer of exo-anhydride of 5-norbornene-2,3-dicarboxylic acid (poly(NDA)), synthesized by the ROMP, as a modifier. The structure of this polymer is characterized by the presence of an anhydride unit in each monomeric link and its distance from the main chain, which may facilitate access to it by epoxy groups, as well as a strictly defined molecular weight and easily controlled chain architecture. Both classical three-component catalytic systems based on WCl$_6$/Et$_3$Al, Et$_2$AlCl, or EtAlCl$_2$/Et$_4$Sn [3] and the single-component Schrock [4], the first- (Gr1) [5], second- (Gr2) [6–8] and third-generation [7, 9–11] Grubbs carbene catalysts have been used as initiators for the metathesis polymerization of NDAs. The molecular weight of poly(NDA) was controlled by conducting the reaction either at a low NDA/catalyst ratio [4] or in the presence of chain transfer agents, such as 1-hexene [3] or 1-decene [6, 8]. It should be noted that the synthesis of poly(NDA) was accomplished in different organic solvents; however, only some authors took into account that this polymer is soluble only in DMF and DMSO and used a suitable solvent [7, 11]. Furthermore, the polymerization reaction of NDA was not studied in detail in Refs. [7, 11]. In particular, the effect of the synthesis conditions, including the presence of a chain transfer agent, on the molecular weight of the resulting product was not evaluated, nor was the molecular weight of poly(NDA) itself determined. In those cases where an attempt was made to determine the molecular weight of poly(NDA), a poor solvent was chosen as an eluent [6, 8–11]. Therefore, the goal of this work was to study the effect of the conditions of metathesis polymerization with the opening of the NDA ring under the action of the second-generation Grubbs catalyst in the presence of 1-hexene, acting as a chain transfer agent, in DMF on the molecular weight and thermal properties of the product.

Results and discussion

The synthesis of poly(NDA) was carried out according to Scheme 1 at different ratios of the reagents (Table 1). The final products were isolated by precipitation of the polymer with excess methanol and subsequent drying under vacuum. As a result, soluble fibrous or powdery polymers were obtained in

yields up to 92%. All the resulting polymers were characterized by GPC, DSC and TGA methods.
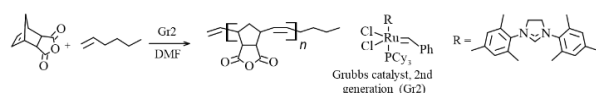
Scheme 1. Synthesis of poly(NDA) by the ROMP in the presence of the second-generation Grubbs catalyst and 1-hexene in DMF.

Table 1. Effect of the synthesis conditions on the molecular weight and glass transition temperature of poly(NDA)^a

Entry	NDA/hexene-1/Gr2 mol/mol/mol	Yield, %	M_n^{GPC}, kDa^b	Đ	M_n^{NMR}, kDa^c	T_g, °C
1	2000/20/1	92	46	1.3	18.4	230^d
2	2000/40/1	91	37	1.2	13.0	213
3	2000/120/1	60	22	1.6	3.7	185
4	2000/240/1	58	8	2.0	1.3	abs.

^{a} DMF, C_M (NDA) = 1.0 mol/L; DMF used as an eluent; according to the ^{1}H NMR data; T_d = 340 °C.

The structures of all poly(NDA) samples were confirmed by ^{1}H and ^{13}C NMR and IR spectroscopy (Figs. S1, S2, and S7 in the Electronic supplementary information (ESI), respectively). The spectra are consistent with those reported in the literature [6, 11]. According to the data of ^{1}H–^{13}C HSQC (DEPT-135) two-dimensional correlation spectroscopy (Figs. 1 and S3 in the ESI), the chemical shifts of the proton signals of the terminal double bond ($I_{5.6-5.1}$, (=CH$_2$) and the double bonds of the main chain ($I_{5.1-4.9}$) were determined, based on the integral intensity of which the molecular mass (M_n^{NMR}) of these polymers was calculated according to the following formula

$$M_n^{NMR} = \frac{I_{5.6-5.1}}{I_{5.1-4.9}} \cdot M(\text{NDA}) + M(1\text{-hexene})$$

where M(NDA) is the molecular mass of NDA equal to 164.16 g/mol and M(1-hexene) is the molecular mass of 1-hexene equal to 84.16 g/mol.

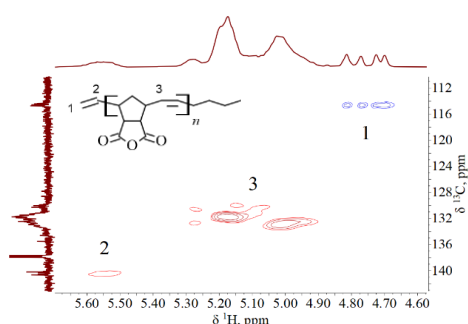**Figure 1.** Region of the double bond signals in the ^{1}H–^{13}C HSQC (DEPT-135) spectrum of poly(NDA) with M_n^{GPC} = 8 kDa and Đ = 2.0.

As can be seen from the presented data (Table 1), an increase in the amount of 1-hexene in the reaction mixture leads to a gradual decrease in the values of M_n^{GPC} and M_n^{NMR}, affording polymer samples with the desired molecular weights by adjusting the 1-hexene/NDA ratio at high monomer/catalyst ratios.

According to the DSC data, all the products obtained in this work are amorphous polymers. It is known that high-molecular-weight poly(NDA) is characterized by T_g, the value of which is higher than the decomposition temperature [9]. Due to a decrease of M_n^{GPC}, it was possible to obtain the products with detectable T_g, which decreases with a decrease of M_n^{GPC}.

Conclusions

Poly(NDA) was synthesized for the first time by the ROMP in the presence of Gr2 and 1-hexene in DMF. It was shown that 1-hexene can act as an effective chain transfer agent in this reaction. The resulting samples of poly(NDA) are soluble and feature low dispersity (≤ 2.0), while their M_n values varied in the range of 8–46 kDa. A decrease in M_n^{GPC} of poly(NDA) leads to a decrease in the value of T_g.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental section, NMR and IR spectra, DSC curves. For ESI, see DOI: 10.32931/ioXXXXx.

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