

Development of Norbornene-dicarboximide Based Organic Polymers for Optoelectronics

Alisa Bannaron,¹ Andrew M. Spring,² Shiyoshi Yokoyama³

¹Interdisciplinary Graduate School of Engineering Sciences (IGSES), Kyushu University

²Green Asia Education Center, Kyushu University

³Institute for Materials Chemistry and Engineering (IMCE), Kyushu University
Kasuga koen, Kasuga, Fukuoka 816-8580, Japan

Abstract

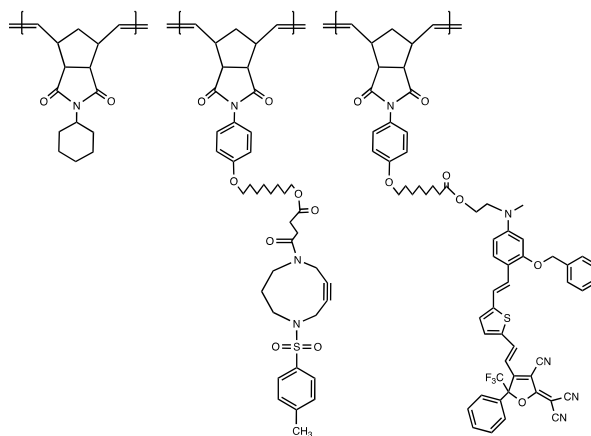
Side chain polymers containing three derivatives of norbornene-dicarboximide (NDI) based monomers were affectively synthesized in order to enhance thermal stability of organic polymer for optoelectronic applications. While the amount of cyclohexyl-substituted and *NSu*, *NTs-DACN*-substituted NDI monomers were constantly maintained, the content of phenyl vinylene thiophene chromophore monomer was precisely varied from 0 wt% to 40 wt% in order to achieve applicable optical activity. The polymerization was effectively performed via ring-opening metathesis polymerization (ROMP) technique utilizing Grubbs 1st generation catalyst as an initiator.

1. Introduction

Electro-optic (EO) polymers have been notably considered as the promising materials for applications of potential optoelectronic devices such as telecommunication, sensing, as well as, advanced computing. Recent progress leads to the development of polymers with several designs to meet all required properties. Poly(norbornene-dicarboximide)s (poly(NDI)s), which have been firstly prepared in 1992 by ROMP, the reaction has been confirmed the ability for both well-controlled polymerization, and functionalization.^[1] Since then, the functionalized polymers have been extensively developed with several active groups to extend their range of applications. This includes the utilization in organic electronic and optical applications because of their essential thermal properties, optical transparency, and film forming characteristics.

In previous work, cyclohexyl-substituted NDI monomer (**1**) was copolymerized with FTC chromophore-NDI monomer (**3**) via ROMP using Grubbs initiator, resulting in series of well-controlled copolymers with high *T_g*.^[2] However, in order to further enhance thermal stability of the copolymer, crosslinking is one of the potential approaches to perform.

In this work, *N*-succinoyl-*N'*-*p*-toluenesulfonyl-4,8-diazacyclononyne (*NSu*, *NTs-DACN*) has been introduced as a pendant to NDI monomer (**2**) in order to crosslink with diazide compound via Huisgen cycloaddition reaction of an alkyne.^[3]

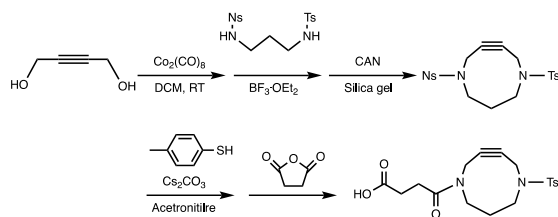
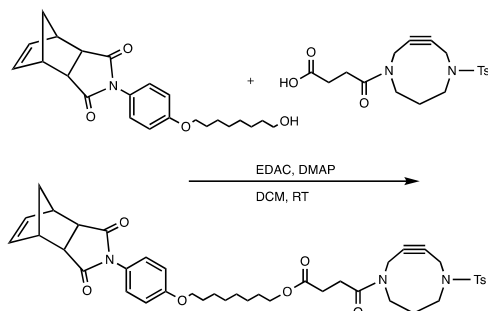


Scheme 1. NDI based copolymer containing three NDI monomers

2. Results and discussion

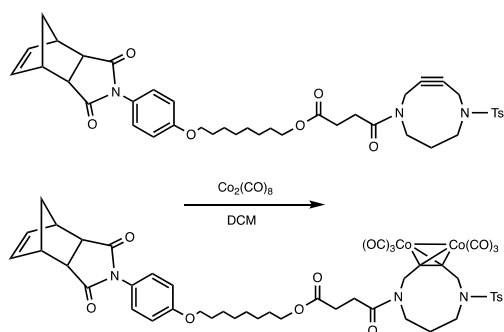
2.1 Preparation of NDI monomers

The synthesis of NDI monomers (**1**) and (**3**) were reported in [3]. *NSu*, *NTs-DACN* was originally investigated by Tomooka laboratory (Scheme 2). Then *NSu*, *NTs-DACN* was connected to NDI derivative monomer as in Scheme 3 with the yield of 80%.


Scheme 2. Synthesis of *NSu*, *NTs-DACN*

Scheme 3. Synthesis of NDI monomer (**2**)

2.2 Investigation and protection of alkyne on NDI monomer (**2**)

Homo-polymerization of NDI monomer (**2**) was conducted in order to investigate the competitive reactivity of alkene and alkyne sites on its monomer. However, it has been found that alkyne on *NSu*, *NTs-DACN* was incompatible with Grubbs initiator. Therefore, the particular alkyne was protected by using $\text{Co}_2(\text{CO})_8$ (**Scheme 4**).^[4] The polymerization ability of protected NDI monomer (**2**) was then confirmed by homo-polymerization.


Scheme 4. Protection of alkyne on NDI monomer (**2**) by addition of $\text{Co}_2(\text{CO})_8$

2.3 Polymer synthesis and characterization

All copolymers were synthesized in anhydrous chloroform via ROMP using Grubbs 1st generation initiator at room temperature for 12 hours. The amount of monomer (**1**) and (**2**) were maintained at 0.3 g and 20 wt%, respectively,

while the content of NDI monomer (**3**) was gradually increase from 0 to 40 wt%. After the precipitation, structures and molecular weights of copolymers were confirmed NMR and GPC as shown in **Table 1**.

Table 1. Molecular weight and PDI of copolymers

Copolymer	NDI monomer (3) (wt%)	Mn	PDI
P-01	0	6442	1.43
P-02	20	8847	1.90
P-03	30	9279	2.35
P-04	40	7304	2.19

2.4 Deprotection of Cobalt moiety by CAN

After the completion of polymerization, the copolymers containing cobalt complex were deprotected by Cerium Ammonium Nitrate (CAN). Unfortunately, decomposition of FTC chromophore on monomer (**3**) was observed according to color change from green to yellow. This is probably because of the interaction of electron deficient-cobalt complex and electron rich-chromophore.

3. Conclusion

NDI monomers were successfully synthesized and characterized. However, new approach for introducing *NSu*, *NTs-DACN* has to be conducted to avoid the use of protection reaction. This could be achieved by post-polymerization. By this procedure, *NSu*, *NTs-DACN* will be connected to NDI monomer after polymerization.

Acknowledgement

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References

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Email: alisa.bann@s.kyushu-u.ac.jp