Original Article

SYNTHESIS AND MICROSTRUCTURE OF PROPENE-NORBORNENE COPOLYMERS NORBORNENE COPOLYMERS

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Abstract

The overall series of "P-N copolymers are also synthesized within the overall presence of two of the C2 symmetric "rac-Et (Indenyl) 2ZrCl2" and "rac-Me2Si (Indenyl) 2ZrCl2" with other co-catalysts. Alternatively, the overall P-N copolymers are characterized by the C-13 NMR spectroscopy". The overall study also includes the copolymer synthesis of propene-norbornene. Apart from that, the study also illustrates the NMR spectra of P-N copolymer and states the microstructure of the copolymer (propene-norbornene). The project also suggests the mechanism and reactivity ratio of the copolymer and its monomer. On the other hand, it also illustrates assigning the "spectra of C-NMR of the cyclic olefin based on the overall co-polymers by choosing the appropriate tools. Apart from that, it also includes the synthesis of copolymers with various co-monomer contents and with catalysts with various symmetries. The chemical shifts of the C-13 NMR include the combination of the statistics regarding the P-N chain and it also gives significant and appropriate information regarding the overall assessment of the C-13 NMR spectra of all the copolymers". Therefore, these overall assignments are used for calculating the overall copolymer and also comparing the N values that are obtained from various areas of the spectra. As a result, the primary goal of finding the overall triads is not met, and this also applies to the overall estimation of the molar fractions within the standard deviation, which is only acquired to a level of 2-4%.

Keywords: P-N copolymer, Monomer, Reactivity ratio, 13C NMR spectroscopy.

INTRODUCTION

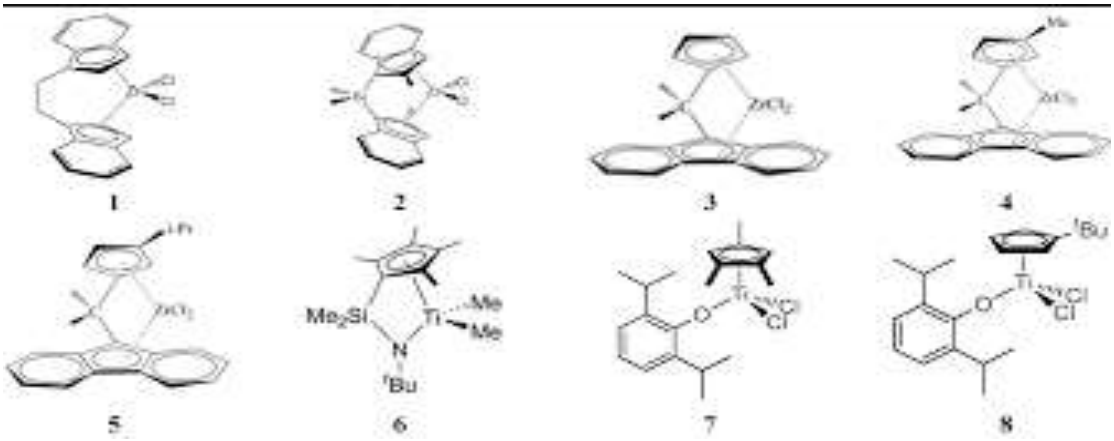
The series of the propene−norbornene "(P−N) copolymers are synthesized within the overall presence of the "rac-Et(indeny) 2ZrCl2/MAO" in toluene at around 30 degrees centigrade. The overall P-N copolymers are also characterized by C-13 NMR spectroscopy", DSC and SEC. In contrast, under the overall experimental conditions, the overall P-N copolymers are likewise synthesized when "rac-Me2Si (Indenyl)2ZrCl2/MAO" is present. The copolymer synthesis for propene norbornene (PN) is part of the overall endeavor. Additionally, it contains the mechanism and reactivity ratio of the copolymer (propene-norbornene), as well as the copolymer's overall microstructure. On the other hand, it also includes the methodology regarding the overall study with its findings and discussions. Therefore, it is to illustrate that the overall relative activity of low polymerization includes a ratio of "lower norbornene than the prepared E-N copolymers within similar conditions". Hence, it states that the copolymer is a polymer that is made of more than one monomer species and these copolymers are the important polymers that are commercially used.

COPOLYMER SYNTHESIS OF PROPENE-NORBORNENE

The overall copolymerization of the norbornene and propene by the overall catalytic systems are fully composed of the "C^2

symmetric rac-Et (Ind)2ZrCl^2", "triisobutylaluminum" and "methyl aluminoxane" is investigated. On the other hand, the "propene−norbornene (P−N) copolymers are having 50 mol% f norbornene and it is highly alternating within the lower pressure and temperature". Apart from that, the overall influence regarding the propene pressure and the temperature within the activity includes the molar masses, the temperature of glass transition, and the overall norbornene content of the P-N copolymers (Boggioni *et al.* 2018). On the other hand, there is a deeper analysis regarding the complex spectra of C-13NMR regarding the overall copolymer which is allowed for calculating the overall composition. Furthermore, it also includes the overall placement of propene within the chain.

Figure 1: NMR spectra of P-N copolymer



(Source: Boggioni *et al.* 2018)

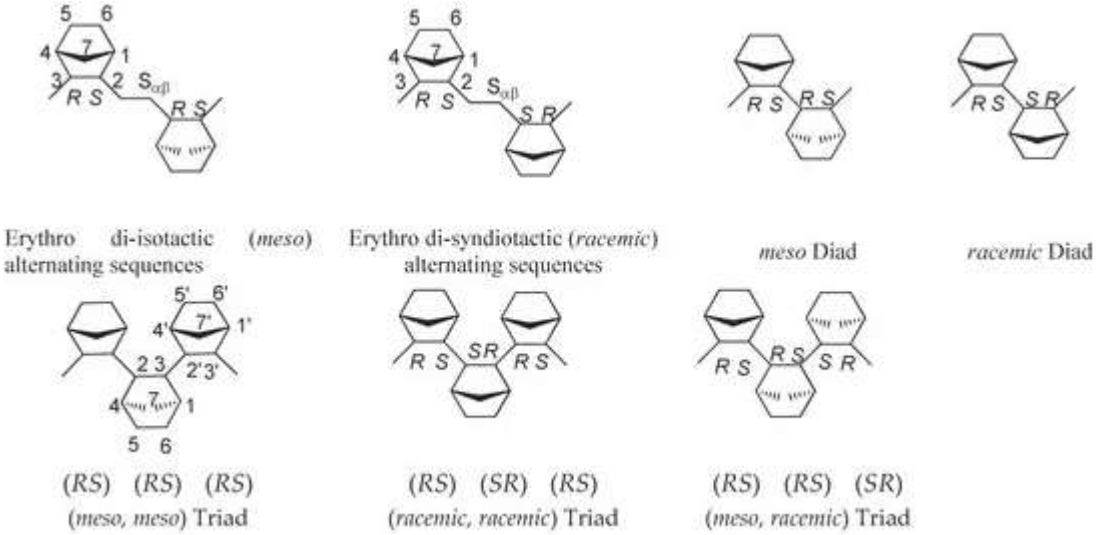
In contrast, a greater number of intersections regarding "1,3 propene are also found and all are occurring after inserted norbornene units that are especially at the higher pressure and temperature". Apart from that, this also indicates the overall limiting step regarding the P-N copolymerization parameters that are estimated within the study. On the other hand, it is also found that the P-N copolymerization is also alternating at the overall temperature as it is lower at 30-40 degree Celsius (Losio *et al.* 2020). And it also tends to become the random copolymer as the overall temperature increases. Apart from that, the overall chain terminations are generally occurring when the last inserted unity is propane. Furthermore, this will be increasing the (kp) which generally explains the decrease regarding the norbornene content, the temperature of glass transition, and the overall molar mass which is observed at high P and T.

The overall "spectra of the P-N copolymer with various N contents and the microstructures include all the series of copolymers. On the other hand, the overall polymerization activity generally appears to be much lower in comparison with E-N copolymerization. Apart from that, the overall assignment with the C-13 NMR signals regarding the P-N copolymers generally contains the isolated N units which were obtained as per the basis of overall distortion less enhancement". Furthermore, it is regarding the polymerization transfer of the (DEPT) C-13 spectra and it is compared with the isotactic polypropylene and the spectra of E-N copolymer spectra.

MICROSTRUCTURE OF THE COPOLYMER (PROPENE-NORBORNENE)

The main microstructure of the P-N copolymers includes the procedure regarding "the quantitative determination regarding the molar fractions of the stereo sequences. On the other hand, it also defines the microstructure regarding the P- N copolymer that is from the spectra of C-13 NMR for the overall setup (Xi *et al.* 2019). On the other hand, this overall method generally utilizes the overall peak regarding the areas of the 13C signals. Furthermore, it also takes into account the overall consistency regarding the overall peal areas and the stoichiometry regarding the overall chain of copolymer". On the other hand, the overall support of the homonuclear and the heteronuclear NMR techniques is identified by guessing the overall assignments regarding the unknown signals. Furthermore, it is also done by discarding the inconsistent hypothesis and also the extension of the overall signal assignment.

Figure 2: Microstructure of P-N copolymer



(Source: Huang *et al.* 2021)

On the other hand, the overall procedure generally allows the quantitative analysis regarding the copolymer sequences perfectly and accurately while it was applied for the overall analysis regarding the spectra of "13C NMR (Huang *et al.* 2021). On the other hand, it also includes the number of P-N polymers that are fully prepared with the catalyst precursors" "rac-Me2Si(2-Me-Indenyl)2ZrCl2 and rac-Et (Indenyl)2ZrCl2". The overall description regarding the overall microstructure at the triad level generally includes the "2,1-propene insertions and 1,3-propene insertions". On the other hand, the overall new signals are assigned regarding the carbons of the propene within the alternating triad of "NP^12N" and also the norbornene within the tetrad of NP^12 NP^12. Apart from that, it also includes overall signals of Pβ methyl groups within the overall triads of NP^12 NP^12 (Wei *et al.* 2018). "Furthermore, it is adjacent to the variable number of P^12 units that are all in the isotactic relationship and also the Sαγ methylene of a 1,3 propene". On the other hand, it is the inserted unit within the methyl carbon atom and NP13P12 within the central monomer in the NP21P12 and P21P12N.

MECHANISM AND REACTIVITY RATIO OF THE COPOLYMER AND MONOMER

The overall copolymer generally constitutes the largest portion of the overall commercial polymers and they generally vary in distribution and composition regarding the other various monomers along the overall backbone. On the other hand, the overall monomers can also have similarities in various physical properties and overall end uses (Toms *et al.* 2022). Apart from that, "the smaller amounts of the dienes or the trifunctional monomers which can be also introduced within the aliphatic polymer that allows in cross-linking of the overall polymer that helps in achieving the overall mechanical properties". The overall blending of the two monomers general result in four propagation reaction that is simultaneously occurring with various rate equations and they are

Table 1: Rate equations of the polymers

Chain Radicals	**Radical Bearing Unit**
"M1· + M1 → M1"	"R11 = k11 [M1·] [M1]"

“M1· + M2 → M2”	“R12 = k12 [M1·] [M2]”
“M2· + M2 → M2”	“R22 = k22 [M2·] [M2]”
“M2· + M1 → M1”	“R21 = k21 [M2·] [M1]”

(Source: Kamet ani *et al.* 2018)

Here, “M1 and M2 generally represent the chain radicals regarding the type 1 and type 2 while it is the unit of free radical bearing and chain terminal of the monomer of type 1 and type 2. On the other hand, if the overall polymer chains are longer and it also includes both termination and initiation that are exceedingly rare events (Kametani *et al.* 2018). Apart from that, within the overall steady state, the elimination and generation of the overall radicals are also equal. On the other hand, it also includes the formula that is “k21 [M2·] M1] = k12 [M1·] [M2]”. Apart from that the overall rates of monomer consumption” are also given by

“d[M1]/dt = k11 [M1·] [M1] + k21 [M2·] [M1]”

“d[M2]/dt = k22 [M2·] [M2] + k12 [M1·] [M2]”

For eliminating “the concentration of overall radical, the first equation is divided by the second equation while after that the equation of Mayo-Lewis is obtained which states that

“d[M1]/d[M2] = (|M1|/|M2|) · (r1[M1]/[M2] + 1) / ([M1]/[M2] + r2)”, where r1 and r2 are overall monomer reactivity ratios which is defined by “r1 = k11 / k12, r2 = k22 / k21”

Therefore, predicting the overall composition of the copolymer is based on the overall reactivity ratios (Scott and Penlidis, 2018). On the other hand, two of the variables are also introduced the mobile fraction regarding the increment of the polymer F1 and the mole fraction regarding the unreacted monomer f1. Therefore, these are formed at the given stage regarding the overall polymerisation process which is also known as the instantaneous composition which includes, “f1 = [M1] / ([M1] + [M2]) = 1 - f2” and “F1 = (r1f12 + f1f2) / (r1f12 + 2f1f2 + r2f22)”. The r1 and r2 generally describe the overall relative preferences regarding the certain radical for adding its monomer and help in growing the overall polymer chain”.

METHODOLOGY

The overall methodology includes the methods of evaluating “the overall impact of the substitutional changes regarding the overall catalytic systems on the overall copolymer microstructures and the overall molar masses”. On the other hand, it also includes the overall copolymer that is investigated by the 13 C-NMR analysis. Apart from that, the high-resolution 13 C-NMR is also a valuable method that studies the copolymer composition and the overall microstructure (Braband *et al.* 2021). On the other hand, it also includes the methods that contribute the significant efforts for elucidating the overall 13 C-NMR spectra regarding the copolymer and the homeo polymer such as “poly(ethylene-co-4-methyl-1-pentene)”, “poly(E-co-P) s”, “poly-

(Propene-co-4-methyl-1-pentene)”, “poly(propene-co-norbornene)” and the overall ethylene polymers. Therefore, it states that the 13 C-NMR spectra regarding the “poly(ethylene-co-propylene)” are having various comonomers in which the overall contents are prepared with the three of the catalysts.

FINDINGS AND DISCUSSION

The overall values regarding the 13 C-NMR chemical shifts are generally computed for the overall conformers regarding the overall simple compound model. On the other hand, it also uses the RIS conformer populations that are also estimated for the overall isotactic chain "(P4−N) x". Apart from that, "it also gives the important and detailed indications regarding the overall assignment of the complex 13C spectra regarding the P-n copolymers with the n content which is up to 35 mol% (Correa *et al.* 2019). On the other hand, the overall assignment is also used in estimating the content of N copolymer. Apart from that, the overall discrepancy regarding the overall values is generally obtained from the overall areas regarding the signals that are assigned to the norbornene carbons that were also found to be partial values. Furthermore, it is due to the overall presentation of the disinsertion of 1,3-propene and it is also formed within the significant amount by increasing the [N]/[P] ratio of the overall feed".

Table 2: Copolymerisation with norbornene with different ratios

Sample	**Norbornene in the feed (mol%)**	**Copolymerization activity**	**Norbornene Content in the copolymer (mol%)**
C10	10	261	6.8
C15	15	980	10.7
C20	20	4052	14
C25	25	3921	16.3

(Source:)

The above table states the copolymerization with norbornene with different ratios. The overall results confirm that the overall activity of the polymerization at the lower norbornene ratio is having the possibility of obtaining the P-N copolymer. "On the other hand, these are much richer within the norbornene than the overall E-N copolymers which are prepared within similar conditions (You *et al.* 2020). Apart from that, the higher ratio of norbornene is having a greater amount of mis insertions of 1,3-propene that reveals the overall steric hindrance regarding the Mt Tertiary carbon bond". Furthermore, it is done when N is the overall unit that is inserted last and also makes it difficult for the next insertion of propene. Therefore, it also causes the overall activities regarding low polymerization while it also includes the Tg and overall molecular masses.

The overall methodologies generally elucidate the overall microstructure of the copolymers of P-N and it also includes the C NMR spectra for the overall analysis. The C-NMR spectra of all the copolymers are much more complex as it includes the overall presence of the stereo-genic carbons within the overall monomer units. Apart from that, it also includes the facts that "the chemical shifts regarding the overall copolymers which do not obey the straightforward additive rules (Chowdhury *et al.* 2019). Furthermore, it also includes the use of one-dimensional and two-dimensional NMR techniques. Therefore, the overall consideration includes the characteristics of the copolymer chain and also includes the exploitation of the overall peak areas regarding the spectra by accounting for the overall stoichiometric requirements of the copolymer chain".

CONCLUSION

Based on the findings of the aforementioned study, an overall copolymer is a polymer made up of more than two monomer species. On the other hand, the focus of this entire work is the microstructure and general synthesis of the copolymer of propene and norbornene. However, these overall copolymers often operate at lower temperatures and pressures, which may not be feasible under industrial circumstances. In addition to that, it also characterizes P-N copolymers and largely concentrates on

the total NMR study. A lower concentration of inverted propylene sequences is therefore often implied by the overall existence of the smaller resonance.

REFERENCES

1. Boggioni, L., Losio, S. and Tritto, I., 2018. Microstructure of copolymers of norbornene based on assignments of 13C NMR spectra: Evolution of a methodology. Polymers, 10(6), p.647.
2. Braband, H., Benz, M., Spingler, B., Conradie, J., Alberto, R. and Ghosh, A., 2021. Relativity as a Synthesis Design Principle: A Comparative Study of [3+ 2] Cycloaddition of Technetium (VII) and Rhenium (VII) Trioxo Complexes with Olefins. Inorganic chemistry, 60(15), pp.11090-11097.
3. Chowdhury, S.I., Tanaka, R., Nakayama, Y. and Shiono, T., 2019. Copolymerization of norbornene and styrene with anilinonaphthoquinone-ligated nickel complexes. Polymers, 11(7), p.1100.
4. Correa, S.A., Diaz-Droguett, D.E., Galland, G.B., Maraschin, T.G., Basso, N.D.S., Dogan, F. and Rojas, R.S., 2019. Modification of rGO by B (C6F5) 3 to generated single-site Lewis Acid rGO-OB (C6F5) 2 as co activator of nickel complex, to produce highly disperse rGO-PE nanocomposite. Applied Catalysis A: General, 580, pp.149-157.
5. Huang, C., Zhu, Y. and Man, X., 2021. Block copolymer thin films. Physics Reports, 932, pp.1-36.
6. Kametani, Y., Sawamoto, M. and Ouchi, M., 2018. Control of the Alternating Sequence for N-Isopropylacrylamide (NIPAM) and Methacrylic Acid Units in a Copolymer by Cyclopolymerization and Transformation of the Cyclopendant Group. Angewandte Chemie, 130(34), pp.11071-11075.
7. Losio, S., Boggioni, L., Cornelio, M., Razavi, A. and Tritto, I., 2020. Ethylene-propene copolymerization with C1-symmetric ansa-fluorenyl-zirconocene catalysts: effects of catalyst
8. organocatalysts on copolymerization kinetics and copolymer microstructures. Biomacromolecules, 19(6), pp.2294-2301.
9. Scott, A.J. and Penlidis, A., 2018. Binary vs. ternary reactivity ratios: Appropriate estimation procedures with terpolymerization data. European Polymer Journal, 105, pp.442-450.
10. structure and comonomer on molar mass. Chinese Journal of Polymer Science, 38(3), pp.220-230.
11. Toms, R.V., Prokopov, N.I., Mineev, K.O., Plutalova, A.V. and Chernikova, E.V., 2022. Controlling monomer sequence distribution in RAFT polymerization of styrene and acrylic acid. Mendeleev Communications, 32(2), pp.238-240.
12. Wei, J., Meng, H., Guo, B., Zhong, Z. and Meng, F., 2018. Organocatalytic ring-opening copolymerization of trimethylene carbonate and dithiolane trimethylene carbonate: Impact of
13. Xi, S., Wang, L., Liu, J. and Chapman, W., 2019. Thermodynamics, Microstructures, and Solubilization of Block copolymer Micelles by density functional theory. Langmuir, 35(14), pp.5081-5092.
14. You, W., Noonan, K.J. and Coates, G.W., 2020. Alkaline-stable anion exchange membranes: A review of synthetic approaches. Progress in Polymer Science, 100, p.101177.