Cycloolefin copolymers: Processing, Properties Application

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The aim of this Bachelor thesis is to compile a compact view on the processing, properties and application of cyclic olefin copolymers (COC). These new materials, which consist of amorphous, transparent copolymers based on cyclic olefins and linear olefins, exhibit a unique combination of properties customized by varying the chemical structure of the copolymer. Therefore, the study of COC is of great interest.

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G.M. Benedikt, B.L. Goodall, Metallocene-Catalyzed Polymers -- Materials, Properties, Processing and Markets, 1998, William Andrew Publishing/Plastics Design Library, ISBN 1-884207-59-6 and scientific articles

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ABSTRACT

The main object of this bachelor thesis is to compile the complex review of preparation, chemical structure, morphology, properties, processing and application of cyclic olefin copolymers. Recently, these modern materials have attracted the attention of the researchers as well as plastic processors. Cyclic olefin copolymers are prepared by copolymerization of cyclic and linear olefins. By varying the structure, they can be tailored for specific applications. Generally, they are characterized by almost amorphous structure, high glass transition temperature, high transparency and low density. Presently, they are successfully applied in packaging and pharmaceutics

ANOTACE

Hlavním účelem této bakalářské práce je sestavit přehlednou literární rešerši týkající se výroby, chemické struktury, morfologie, vlastností, zpracování a aplikací cyklických olefinických kopolymerů. V poslední době jsou tyto moderní materiály předmětem zájmu jak výzkumných týmů, tak především zpracovatelů plastů. Cyklické olefinické kopolymery se vyrábějí kopolymerací cyklických a lineárních olefinů. Změnou struktury lze vyrábět tzv. materiály na míru pro specifické aplikace. Obecně jsou charakterizovány téměř zcela amorfní strukturou, vysokou teplotou skelného přechodu, vysokou průhledností a nízkou hustotou. V současné době se s úspěchem využívají pro výrobu obalů a farmaceutických pomůcek.

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I declare I worked on this Bachelor Thesis by myself and I mentioned all the used literature.

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jméno

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INTRODUCTION

Cyclic polyolefin copolymers

Cyclic olefin copolymers (COC) are materials which attained economic relevance only in the last few years, although first developments range back to over 40 years. The beginnings were in Dupont in the USA followed by Montecatini in Italy (with support of Nobel prize winner Guilio Natta), by the ‘Leuna Werke’ in Eastern Germany and by Mitsui in Japan. Recent progress in metallocene catalysts enabled the industrial production of cyclic olefin copolymers of large structural and performance variety.

Cyclic olefin copolymers form a new class of copolymers with excellent optical, thermal and permeation properties. The copolymerization of olefins with a cyclic monomer leads to predominantly amorphous materials with relatively high glass transition temperatures, exhibiting numerous useful physical qualities, such as high optical transparency, low birefringence, low moisture absorption etc. These properties are very interesting for application in medicine and optics, especially for laser-optical devices like CDs, DVDs and optical lenses. Their high temperature resistance (compared with polycarbonate for example) combined with low dissipating and dielectric loss factors makes COC’s suitable also for microelectronic applications.

The properties of the COC depend strongly on the comonomer combination. At least one comonomer is a cycloolefin of norbornene type, the other belongs to the group of the 1-olefines. Beside traditional norbornene, also substituted norbornens or its higher homologes and their substituted variations can be used [1].

The purpose of this thesis is to review the knowledge of these promissing new class of polymer materials. The work presents the preparation methods, structure, properties and application of cyclic olefin copolymers.

1 PREPARATION

1.1 Monomers

Like any other copolymers, the COC are consisted of low molecular substances (monomers). Monomers exploited for production of COC and can be divided into two main categories in accordance with structure and that are cyclic monomers and linear monomers.

1.1.1 Cyclic monomers

A lot of cyclic monomers can be used to prepare COC; however, all of them are just derivates of norbornene or dicyclopentadiene with very similar properties. The most common ones are norbornene, 1,3-dicyclopentadiene and 5-vinyl-2-norbornene. These cyclic monomers are described thereinafter.

Norbornene

Norbornene is a bicyclic olefin. Which means, it is a bridged six-membered ring with a double bond on one side. The bridged ring puts extra strain on the double bond, making it highly reactive, giving many opportunities to modify the basic norbornene molecule or to incorporate it into bigger molecules, such as COC or other polymers. The methods used may include ring-opening metathesis polymerization (ROMP), copolymerization, radical or cationic polymerization, and vinyl or addition polymerization [3] The chemical structure of Norbornene is shown in Figure 1.

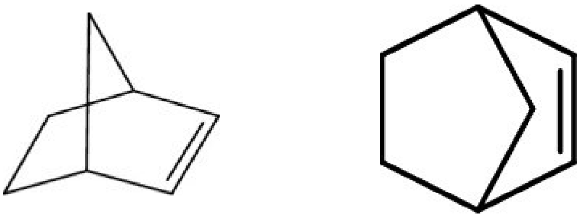


***Figure 1**.: Norbornene [3]*

Norbornene is a colourless or white solid with characteristic odour. Above 46℃ norbornene is a liquid with low viscosity. Solid norbornene has a high solubility in common organic solvents as for example in acetone and in aliphatic, cycloaliphatic or aromatic solvents. Some physical properties are presented in the Table 1 [3].

Table 1: *Physical properties of norbornene.*

Molecular weight	94.2 g/mol
Melting point	46 ℃
Boiling point	96 ℃
Density (50 ℃)	0.845 g/mL
Viskosity (50 ℃)	0.75 mPa s
Flash point	- 15 ℃
Ignition Temperature (DIN 51794)	445 ℃
Water solubility	70 mg/L
Odour threshold	0.25 mg/m3

1,3-Dicyclopentadiene

1,3-Dicyclopentadiene (DCPD) is co-produced with ethylene from the C5 fraction in the steam cracking of naphtha and gas oils. The largest consumption of dicyclopentadiene is linked to the production of resins including unsaturated polyester resins, petroleum resins, terpolymers, polynorbornenes, and other cyclic olefin polymers [4]. You can see the DCPD on Figure 2.

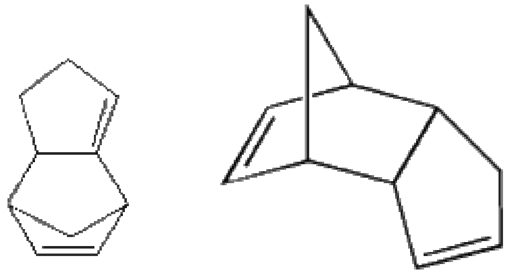


Figure 2: *Dicyclopentadiene [4]*

1,3-Dicyclopentadiene is colorless and crystalline at room temperature and is a liquid above 32.2 ℃. It possesses an odor that is described as sweet, sharp, disagreeable, and camphor-like. It is highly volatile at relevant ambient temperatures and is expected to volatilize when released into the environment. It has very low solubility in water. It may adsorb onto soil and suspended particulates that may slow its rate of volatilization [4]. Table 2 summarizes some physical properties of dicyclopentadiene.

Table 2: *Physical properties of 1,3-dicyclopentadiene*

Chemical formula	$C_{10}H_{12}$
Molecular weight	132.20 g/mol
Density	0.98 g/cm^3 at 25℃
Melting point	32.5 ℃
Boiling point	170 ℃
Flash Point	114 ℃

5-vinyl-2-norbornene

5-vinyl-2-norbornene is a vinyl derivate of norbornene and you can see some physical properties in the Table 3.

Table 3: *Physical properties of 5-vinyl-2-norbornene*

Molecular weight	120.2 g/mol
Boiling point	141℃
Melting point	- 80 ℃
Vapor pressure	6 mmHg
Vapor density	1 g/l
Density [20℃]	0.841 g/cm^3
Flash point	28℃
Refractive Index	1.481

1.1.2 Linear Monomers

Among linear monomers, the most exploited is ethene. Beyond it several others alphaolefines can be used, for example propene and 1-butene.

Ethene

Ethene is colourless and flammable gas which is the first member of the alkene series of hydrocarbons. It is the most widely used synthetic organic chemical and is used to produce the plastics polyethene (polyethylene), polychloroethene, polyvinyl chloride (PVC) and of course cyclic olefin copolymers. It is obtained from natural gas or coal gas, or by the dehydration of ethanol.

1.2 Copolymerization

Cycloolefin copolymers can be prepared by two ways, first way is vinyl copolymerization and the second way is a ring opening metathesis polymerization (ROMP). Figure 3 shows basic differences between vinyl copolymerization and ROMP.

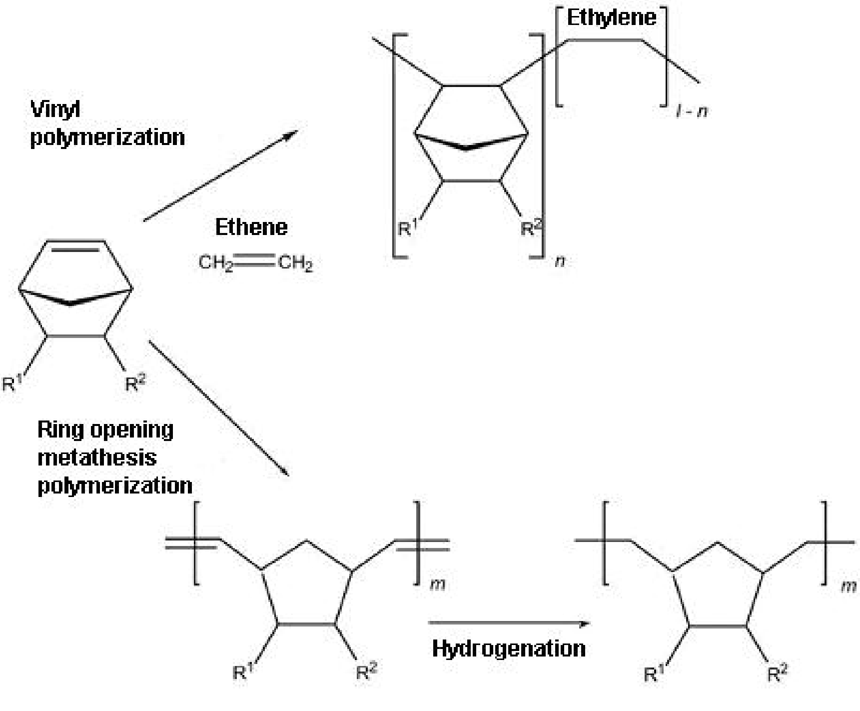


***Figure 3**: Main differences between vinyl polymerization and ROMP [12]*

1.2.1 Vinyl copolymerization

Vinyl copolymerization is a copolymerization of cyclic and acyclic olefins. A copolymerization can be carried out with metallocene and half-sandwich/MAO-catalysts [6]. Catalysts use for copolymerization contains the metals: titanium, zirconium, cobalt, chromium, nickel and palladium. Example of catalysis vinyl polymerization shows Figure 4.

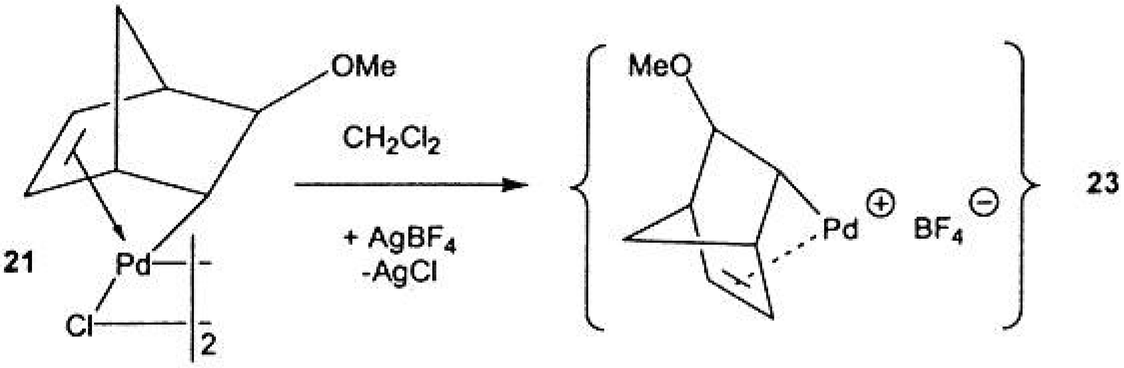


***Figure 4**: Example of catalysis vinyl polymerization by palladium catalyst [34]*

1.2.2 Ring opening metathesis polymerization

In the case of this preparation method the cycle of cycloolefin unit is implemented by this way: the cycle is opened by breaking of both bonds in the double bond, then is created quinary cyclic unit alternating with ethene group which make up the polymer chain. Next step is a hydrogenation by hydrogen which removes double bonds in main chain of the polymer. Ring opening metathesis polymerization processes generally employ tungsten, molybdenum, rhenium or ruthenium catalysts as metal halides, metal oxides or metal oxo-chlorides in combination with alkylating agents (e.g. R4Sn, Et2AlCl) and promoting agents (e.g. O2, EtOH, PhOH) [6]

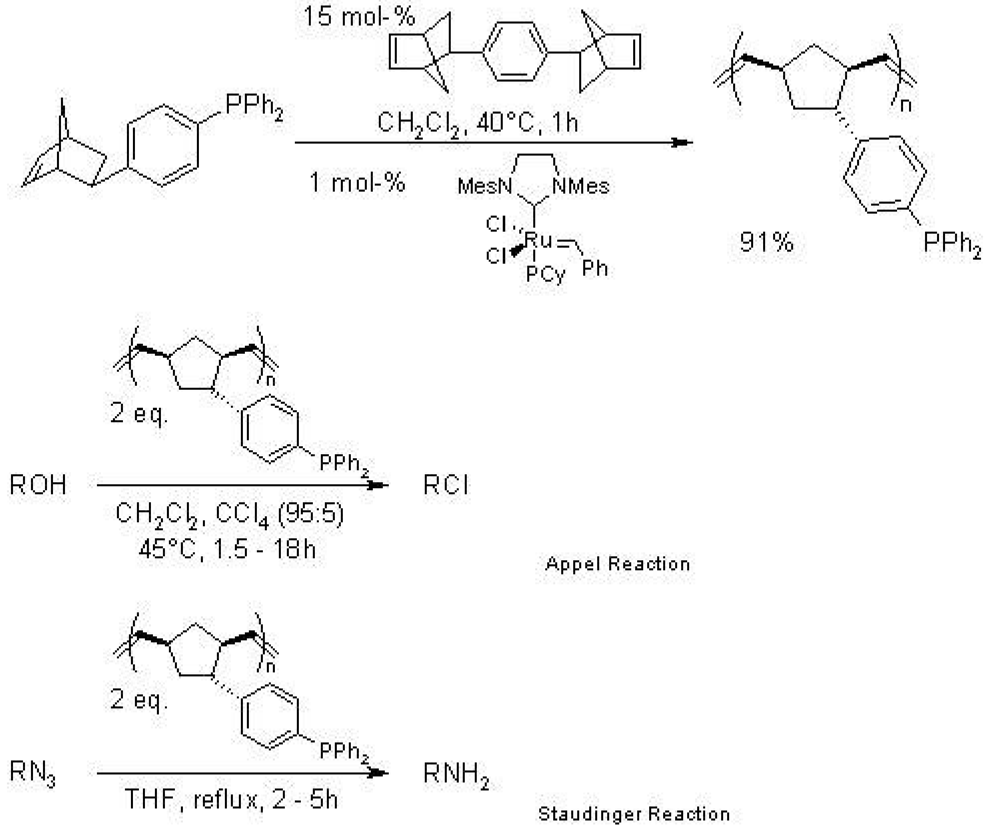


Figure 5*: Ring opening metathesis polymerization catalysis by Ruthenium catalyst [33]*

1.2.3 Practical implementation

Practically, the copolymerization of COC can be performed by many different techniques, however they are very similar like the method described thereinafter.

A clean and dry 1.5 dm^3 polymerization reactor with stirrer is flushed with nitrogen and then with ethylene and filled with 0.6 dm^3 of an 85% strength solution of norbornene in toluene. Then 60 ml of 5-vinyl-2-norbornene is added. The ethylene pressure is adjusted to 6 bar gauge. Subsequently, 180 cm^3 of hydrogen is also added and the temperature is adjusted to 70° C. Diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride in amount of 12 mg is dissolved in 20 cm^3 of a solution of methylaluminoxane in toluene (10% by weight of methylaluminoxane of molecular mass 1 300 g/mol by cryoscopic determination) and then the solution is metered into the reactor. By subsequent injection the ethylene pressure is maintained at 6 bar. After a polymerization time of one hour the reactor contents are run off into a vessel, and 5 cm^3 of isopropanol is added.

Then 10 g of Celite 545 (LuV, Hamburg) and 5 cm^3 of water are added to the solution, which is stirred at 60 ℃ for 30 min. A filtercake consisting of 10 g of Celite suspended in 0.5 dm^3 of toluene is built up on the filter mesh of a 2 l pressure suction filter. The polymer solution is filtered through the pressure suction filter, with a nitrogen pressure of about 1 bar being developed. The clear solution is introduced into 5 dm^3 of acetone using a disperser. The solid is isolated by filtration, dispersed twice in acetone and then dried at 100 ℃. and under reduced pressure (0.2 bar) for 15 hours. The amount of 99 g of polymer solid is obtained [19].

2 CHEMICAL STRUCTURE AND MORPHOLOGY

2.1 Methods of investigation

Following methods can be used for investigation of structure of cyclic olefin copolymers.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is transmitted through a specimen, then an image is formed, magnified and directed to appear either on a fluorescent screen or layer of photographic film (see electron microscope), or to be detected by a sensor such as a CCD camera. The first practical transmission electron microscope was built by Albert Prebus and James Hillier at the University of Toronto in 1938 using concepts developed earlier by Max Knoll and Ernst Ruska [5].

CARBON 13 – Nuclear Magnetic Resonance

In this method the nuclear magnetic resonance (NMR) is applied in spectroscopy with respect to carbon. It is analogous to proton NMR and allows the identification of carbon atoms in an organic molecule just as proton NMR identifies hydrogen atoms. As such carbon NMR is an important tool in structure elucidation in organic chemistry [9].

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions. DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing [10]

Gel Permeation Chromatography

This is a separation technique involving the transport of a liquid mobile phase through a column containing the separation medium, a porous material. Gel permeation chromatography (GPC), also called size exclusion chromatography and gel filtration, affords a rapid method for the separation of oligomeric and polymeric species. The separation is based on differences in molecular size in solution. It is of particular importance for research in biological systems and is the method of choice for determining molecular weight distribution of synthetic polymers [11].

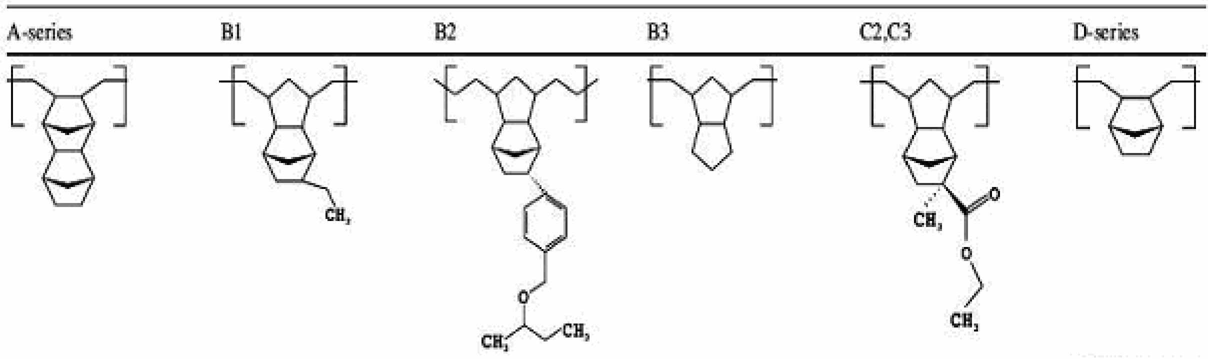
X-Ray Diffraction

X-ray Diffraction is a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy [25].

2.2 Chemical structure

By reason that many monomers are used for preparing COC, they form various types of copolymers. Several groups of different types of COC can be distiguished according to their chemical structure. These individual groups are plotted and labeled in Table 4.

***Table 4**: The types of cyclic olefin copolymers [1]*



Each series are deaply described in following text:

- **A-series -** COCs are formed by tetracyclododecane like cyclic unit and ethene like acyclic unit in this group. Every copolymers of this group are the same. Only their cyclic monomer mole fractions are different and this factor essentially influences their properties. All copolymers of A-series are produced by Vinyl polymerization.

- **B-series -** Copolymers of this group are preferably derived from cyclic and acyclic polyenes, in particular dienes, of 4-20 carbon atoms which contain conjugated and/or non-conjugated double bonds. The double bonds may be at the end in a chain, in a ring (endocyclic) or exocyclic. Every COCs of B-series are prepared by ROMP.

  Typical cyclic monomers of this series are 2,5-norbornadiene, 5-vinyl-2-norbornene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, dicyclopentadiene, 5-isopropylidene-2-norbornene, tricyclopentadiene etc [19].

- **C-series -** Every cyclic units of this series have an ester branch group in their chemical structure. COCs of this series are produced by ROMP as well as copolymers of the B-series.

- **D-series**) Copolymers of D-series are formed by norbornene like cyclic unit and ethene like acyclic unit. Every copolymers from this group are same just their cyclic monomer mole fractions are different analogously to A-series. Copolymers of this group are prepared by vinyl polymerization as well as A-series.

2.2.1 A-series

Figure 6 displays the chemical structure and 13C NMR spectra obtained for the A-series ethane-tetracyclododecene copolymer [7]. The resonances at δ= 29.8–31.8 ppm in these spectra are assigned to the ethane-1,2-diyl(ethylene) unit, and the other resonances are due to the incorporated cyclic unit. The tetracyclododecene content of A-series was determined by units following equation:

$$\text{mole fraction tetracyclododecene} = \frac{I_{C5,C10}}{I_{Et} + I_{C7,C8}} \quad (1)$$

where: $I_{C7,C8}$ = integral between 32 and 32.5 ppm, $I_{C5,C10}$ = integral between 50.8 and 51.5 ppm, and I_{Et} = integral between 29.8 and 31.8 ppm.

For all A-series, with a tetracyclododecene content of less than mole fraction 33 %, the eight resonances are considerably well separated. In Figure 6, two well-separated main resonance signals at 40.2 and 40.9 ppm are C2/C3 carbons of decahydro-1,4,5,8-dimethanonaphthalene-2,3-diyl (tetracyclododecanediyl). The resonance at 40.9 ppm can be assigned to C2/C3 carbons in alternating units along the polymer chain, and the signal at 40.2 ppm arises from C2/C3 carbons of tetracyclododecanediyl bonded to longer ethylene sequences. With increasing tetracyclododecene content, the intensity of the signal at 40.2 ppm decreases, and the signal at 40.9 ppm assigned to ethylene-tetracyclododecanediyl alternating units increases [12].

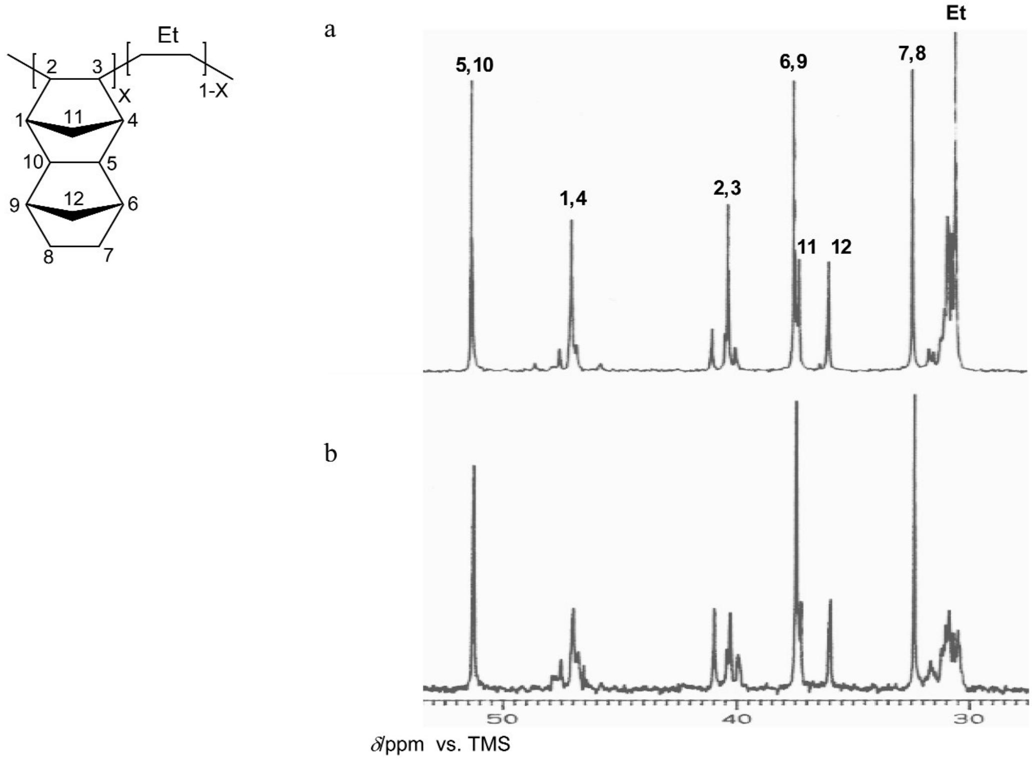


***Figure 6**: Chemical structure of A-series with cyclic monomer mole fractions, (a) 21.4 %, (b) 32.2% [12]*

2.2.2 D-series

The 13C NMR spectra and assignments of the D-series are shown in Figure 7. Between 28 and 33 ppm, the ethylene signals overlap with C5 and C6 resonances of 8,9,10-trinorbornane-2,3-diyl (norbornanediyl) [13–16]. The norbornene content of the D-series was determined by using the following equation [17]:

$$\text{mole fraction norbornene} = \frac{I_{C1,C4}}{I_{Et} + I_{C5,C6}} \qquad (2)$$

Where: I_{Et} + $I_{C5,C6}$ were calculated from signals between 28 and 33 ppm and $I_{C1,C4}$ were calculated from the signals between 37 and 44 ppm.

This method of investigation detected that the microstructure of ethene-norbornene copolymers divides into two distinct patterns depending on the norbornene content [7;18]. Ethene-norbornene copolymers with a norbornene mole fraction of less than 50 % consist mainly of blocks of alternating ethylene-norbornanediyl units and longer ethylene units, whereas copolymers of norbornene mole fraction of more than 50 % contain blocks of norbornanediyl units of varying length as well as a certain amount of alternating ethylene-norbornanediyl units. It was demonstrated that the length of norbornanediyl blocks does not exceed two norbornanediyl units when the norbornene content is less than mole fraction 50 %, whereas the length of the norbornanediyl block of copolymers with higher norbornene content exceeds two norbornanediyl units [18].

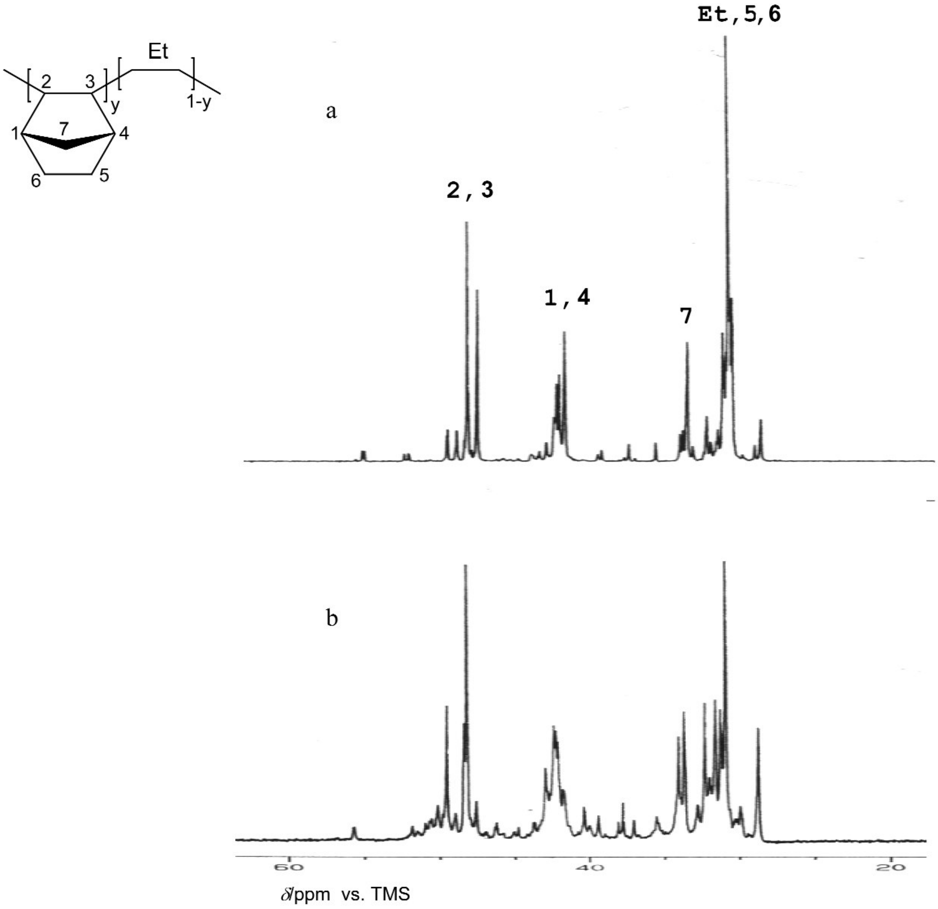


***Figure 7**: Chemical structure of D-series with cyclic monomer mole fractions, (a) 40.1%, (b) 65.9 % [12]*

Many details about the microstructure of ethene-norbornene copolymers can be obtained from the examination of the signal at 47–52 ppm. This resonance group is assigned to the C2/C3 methine carbons in the norbornanediyl unit, and four main resonances are observed in this range. The resonance at 47.4 ppm is assigned to the C2/C3 methine carbons of norbornanediyl bonded to at least two ethylene units. The signal at 48.08 ppm corresponds to the C2/C3 methine carbons of alternating units along the polymer chain. The next two resonances at 48.8 and 49.3 ppm arise from norbornanediyl dyads. As the norbornene content increases, the relative intensity of the signals at 47.4 ppm decreases owing to the decrease in the amount of the longer sequences of ethylene units, whereas the relative intensity of the signals at 49.3 ppm increases and new resonance peaks are detected between 50 and 51 ppm. From the 13C NMR spectrum of D1 with a norbornene mole fraction of 40.1 % shown in Figure 7a, this copolymer contains mainly alternating ethylene-norbornanediyl units and longer sequences of ethylene units. Copolymers with more than mole fraction 50 % norbornene must contain norbornanediyl triads. Figure 7b shows the 13C NMR spectrum of D5 with a norbornene mole fraction of 65.9 %. Compared to Figure 7a, there are new resonances at 40.6, 44.6, and 46.1 ppm. These additional signals in the spectrum of a copolymer having high norbornene content can only be explained by the presence of norbornanediyl triads and perhaps longer norbornanediyl micro blocks [12].

2.2.3 B- and C-series

Chemical structure and the 13C NMR assignments of the B- and C- series copolymers are represented in Figures 8 and 9. It can be observed that the B- and C-series, except B3, show unsymmetrical polycyclic structures with side branches attached to the ring. B1 has an ethyl branch group, B2 has a phenyl branch group, and the C-series has an ester branch group. Owing to the presence of *exo-* and *endo*-isomers in these unsymmetrical structures, 13C NMR spectra show very complex signals. In Figure 9a, the signals at 13.2 and 29.9 ppm are assigned to the carbons of the *exo*-ethyl group, whereas the signals at 13.9 and 26.0 ppm correspond to the same carbons of the *endo*-ethyl group. The C-series also show two distinct peaks owing to the effects of isomerism. Two distinct signals of carbonyl carbon 179.0 and 180.3 ppm and methyl carbon attached to the ring 23.1 and 27.1 ppm in the polymer in Figure 8 indicate the presence of *exo–endo*-isomers. In the 13C NMR spectrum of B2, the shifts appearing around 125–180 ppm correspond to the phenyl group and the shifts at 62.9 and 72.7 ppm are assigned to the carbons adjacent to the oxygen of the ether group.

The cyclic repeating unit content of the B- and C-series was calculated by following equation:

$$\text{Mole fraction cyclic repeating unit} = \frac{I_{Cl,Cn}/n}{I_{Et}/2 + I_{Cl,Cn}/n} \qquad (3)$$

Where I_{Et} of B1 = integral between 30.5 and 32 ppm, I_{Et} of B2 = integral between 29.5 and 30.5 ppm, I_{Et} of B3 = integral between 30.5 and 31.5 ppm, I_{Et} of the C-series = integral between 30 and 31.5 ppm. As It was mentioned before, the B- and C-series are synthesized by the ring-opening metathesis polymerization followed by the hydrogenation, so these polymers can be viewed conceptually as an alternating copolymer of ethene and a cyclic monomer (the alternating units are ethylene and cyclopentane-1,3-diyl). The cyclic unit mole fraction of B- and C-series is around 50 % [12].

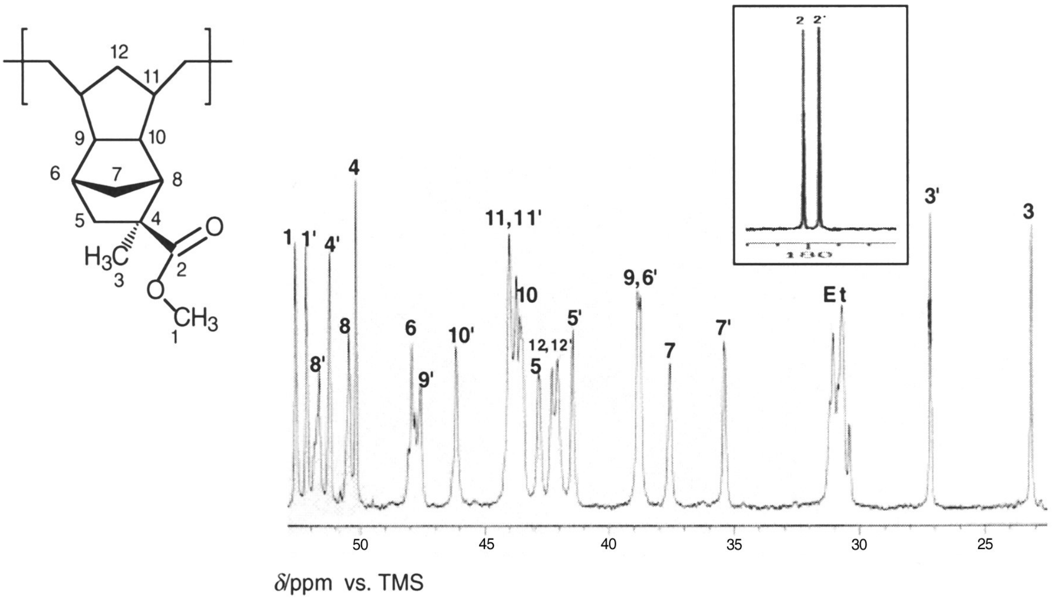


***Figure 8**: Chemical structure of C-series (specially C3) [12]*

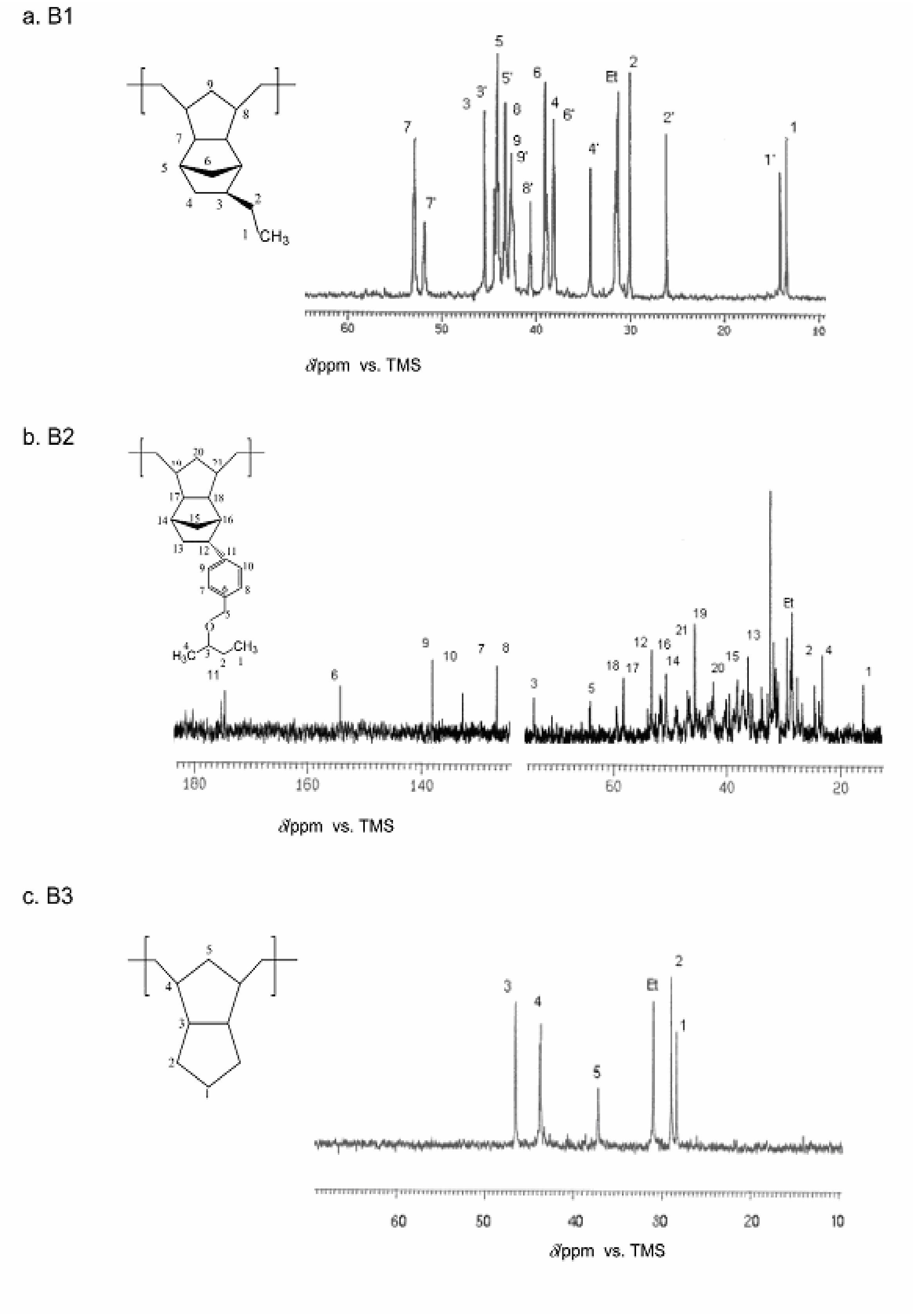


***Figure 9**: Chemical structure of B-series [12]*

Notation of individual copolymers and their cyclic monomer mole fraction are listed in Table 5.

Table 5: *Cyclic monomer mole fraction for some cyclic olefin copolymers*

COC	A1	A2	A3	A4	A5	A6	B1	B2
Cyclic monomer mole fraction[%]	20.0	21.4	28.8	29.6	32.2	32.2	52.0	50.5
COC	B3	C2	C3	D1	D3	D4	D5	-
Cyclic monomer mole fraction[%]	53.7	51.0	51.6	40.1	61.5	48.4	65.9	-

2.3 Morphological investigations

Theoretically, COC are absolutely amorphous through bulky cyclic units in the main copolymer chain or through large branch group in chemical structure of individual cyclic units. Nevertheless, It was demonstrated that some of cycloolefin copolymers can create local microstructures, it was made to detected in TEM. Applying the standard RuO_4 staining no more than local density fluctuations in the majority of the symplex investigated was registered, as shown for example in Figure 10 for the D2. Theoretical considerations predict however some crystallisation in copolymers with alternating ethylene and norbornene sequences, which was supported by DSC measurements [6]. X-ray diffraction studies have found reflections, located at different 2θ angles [7,8], but the interpretations are still ambiguous and controversial. No direct visualisation of semicrystalline structure in COCs using electron microscopy has yet succeeded.

After rather heavy staining procedure lamella-like structures was observed occasionally also in COC's comprising ramification of the norbornene comonomer. The reason for this phenomenon is not clear yet [12].

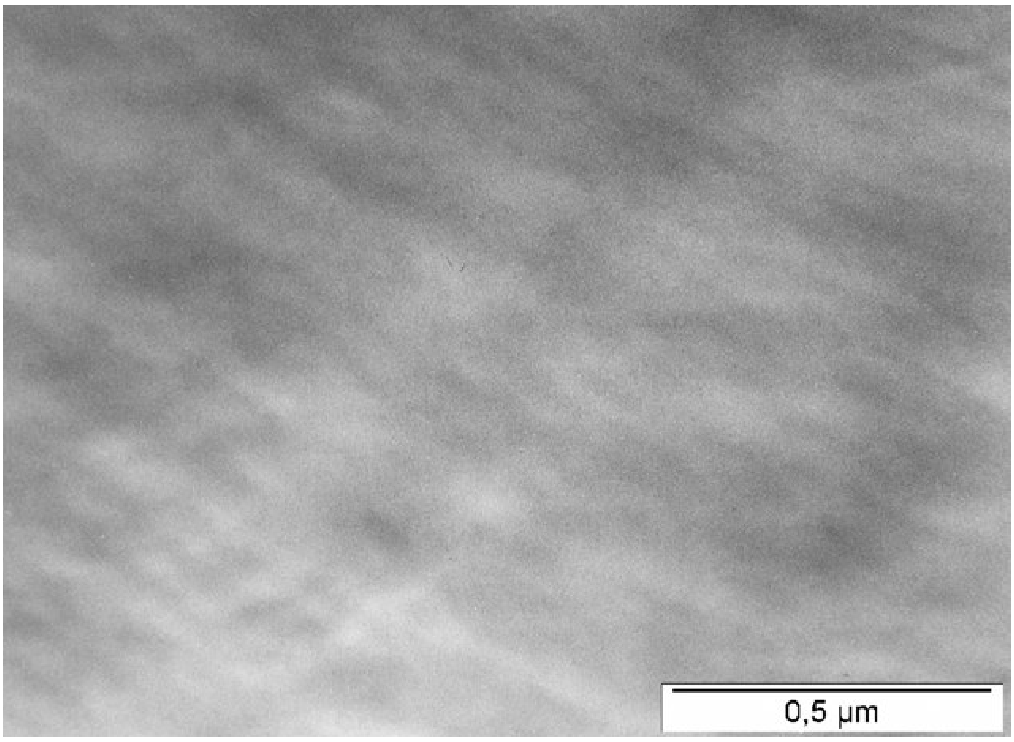


***Figure 10**: TEM-micrograph of COC D2 [12]*

3 PROPERTIES

Specific chemical structures of cycloolefin copolymers give also combination of properties that are specific only for these copolymers as is high glass-transition temperature, low density and other physical properties.

Although each group of COCs includes copolymers with different chemical structures, all copolymers possess the similar physical properties. For example, water absorption of COCs is smaller then 0.01 % per 24 hour immersion in water. Some of the properties are displayed in Table 6. In Figure 11 the relation between light transmission and light wavelength is shown. Light transmission higher than 90 % over visible spectrum and this property is better for example than in glass.

***Table 6**: Physical properies of the individual COCs.[12]*

COC	$^1T_{HD}$ [°C]	Density [g . cm^{-3}]	Light transmission [%]	Refractive index
A1	60^a	1.02	91	1.54
A2	70^a	1.02	91	1.54
A3	95^a	1.03	90	1.54
A4	115^a	1.04	90	1.54
A5	135^a	1.04	90	1.54
A6	120^a	1.04	90	1.54
B1	123^a	1.01	92	1.525
B2	122^a	1.01	92	1.53
B3	99^a	1.01	92	1.53
C2	162^a	1.08	92	1.51
C3	162^a	1.08	92	1.51
D1	75^b	1.02	92	-
D3	150^b	1.02	92	-
D4	130^b	1.02	93	1.53
D5	170^b	1.02	92	

$^1T_{HD}$ [°C]: heat deflection temperature: a: at p = 1.82 MPa, b: at p = 0.45 MPa

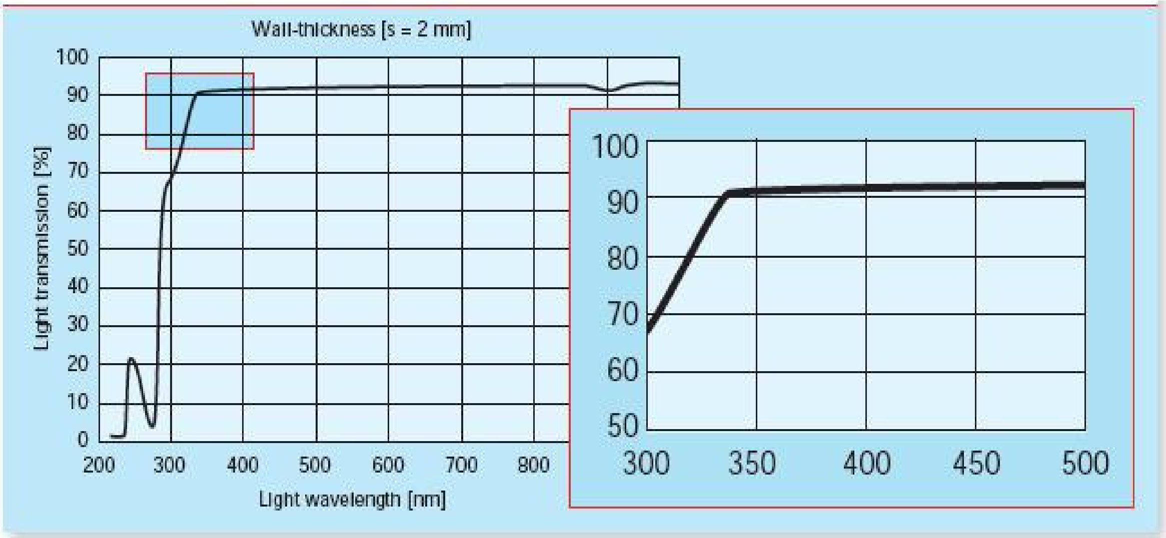


Figure 11: *The relation between light transmission and light wavelength [16]*

Other important optical property is optical birefringence and it is a critical factor which must be controlled in a range of applications; from optical storage media and lenses to films. One of the main suppliers of COC, the company Topas, which focuses on the producing of COCs D-series, confronted optical birefringence with other transparent polymers as are PMMA, PC and PS. This confrontation is graphically expressed in Figure 12. Table 7 displays the stress optical constant of these polymers.

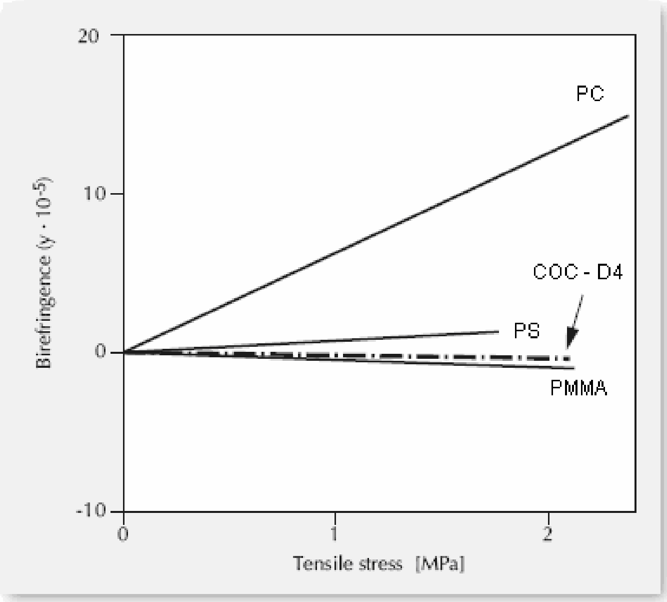


Figure 12: *Stress birefringence of various plastics. [16]*

***Table 7**: Stress optical constant [16]*

Material	C [10^{-6} mm^2/N]
COC – D4	-2 to -7
PMMA	-4.5 to -4.8
PS	4 to 7
PCA	66 to 70

3.1 Mechanical properties

Mechanical properties play an important role in the application of the materials. The mechanical properties of COCs considerably differ among the groups. In the A- and D-series the properties are dependent on cyclic monomer mole fraction: elongation and flexural modulus increase with rising cyclic monomer mole fraction. As for B-series the properties are influenced by the size of branch groups. B2 contains the largest branch group of the B-series, thus, its elongation is the lowest and the flexural modus is the highest. On the other hand, B3 does not consist of branched groups, so its elongation is the highest and flexural modulus is the lowest. The differences between copolymers of C-series are only in a methyl groups at the end of branch group. This negligible variation has almost no effect on their mechanical properties.

The main suppliers of commercial cyclic olefin copolymers are Japan Synthetic Rubber, Mitsumi Chemical Co., Ticona, Zeon Chemicals Co. and Topas [12]. Each of them generally supplies only one kind of COC, for example: Mitsumi Chemical Co. supplies COCs of A-series or Topas produces COCs of D-series. Every producer automatically offers basic information about mechanical properties of their COC. Some important data, especially tensile strength, elongation, flexural modulus and notched impact strength, of commercial COCs are displayed in Table 8.

***Table 8**: Table of mechanical properties of individual COCs* [12, 16]

COC	Tensile strength [MPa]	Elongation [%]	Flexural modulus [MPa]	Notched impact strength [J/m^2]
A1	50	100	2400	45
A2	60	60	2500	35
A3	60	3	2700	25
A4	60	3	3000	25
A5	60	3	3200	25
A6	60	3	3200	25
B1	60	40	2100	23
B2	72	10	2500	20
B3	53	60	2100	19
C2	75	15	3000	8
C3	75	15	3000	7
D1	63	4.5	2600	20
D2	63	2.7	2900	15
D3	60	2.5	3000	15
D4	46	1.7	3200	13
D5	58	2.4	3000	15

3.2 Glass-Transition Temperature

Glass-transition (T_g) temperature is another relevant property of COCs. Their T_g is significantly higher than that of others polyolefines, eventually major part of other polymers. Figure 13 shows the dependence of T_g on cyclic monomer content and chemical structure of COC. There seems to exist a linear relationship between cyclic monomer content and T_g within the composition range in the A- and D-series. For the D-series this relationship is valid after current studies of the thermal properties of ethene-norbornene copolymers [7, 18]. For the A-series this linear relationship between T_g and the tetracyclododecene mole fraction is also valid and it was demonstrated by production of ethene-tetracyclododecene copolymers (prepared by vinyl copolymerization using catalyst system known as 1,2-

ethylenebisindenylzirconocene dichloride/MAO*) [11]. An increase of 7–8 °C in T_g with every tetracyclododecene % unit increase was observed [20]. This deviation may be due to variations in the microstructure induced by a different catalyst system. The variation of Tg with cyclic monomer content for the A-series is more significant as compared to D-series, which implies that the polycyclic unit, tetracyclododecanediyl, which has bulkier structure than the bicyclic unit norbornanediyl, leads to a restricted local motion of chain segments. From a comparison of the T_g of cyclic olefin copolymers with different chemical structure but similar cyclic monomer mole fraction, about 50 %, it was observed that the C-series has the highest T_g and B3 the lowest. The B1, B2, and D4 have a T_g around 140 °C. As it was described in the chapter Chemical structure, B1, B2 and the C-series have the same cyclic structure with different sidechain substituents. It was found that the T_g of the polymers produced by ROMP of tetracyclododecene and subsequent hydrogenation of the resulting polymer is 162 °C. Therefore, it can be concluded that the tricyclic unit also leads to a higher T_g than the bicyclic unit, and the sidechain substituents attached in the ring have significant influence on the T_g of cyclic olefin polymers [12, 21]. Table 9 shows the individual COCs and their glass-transition temperature.

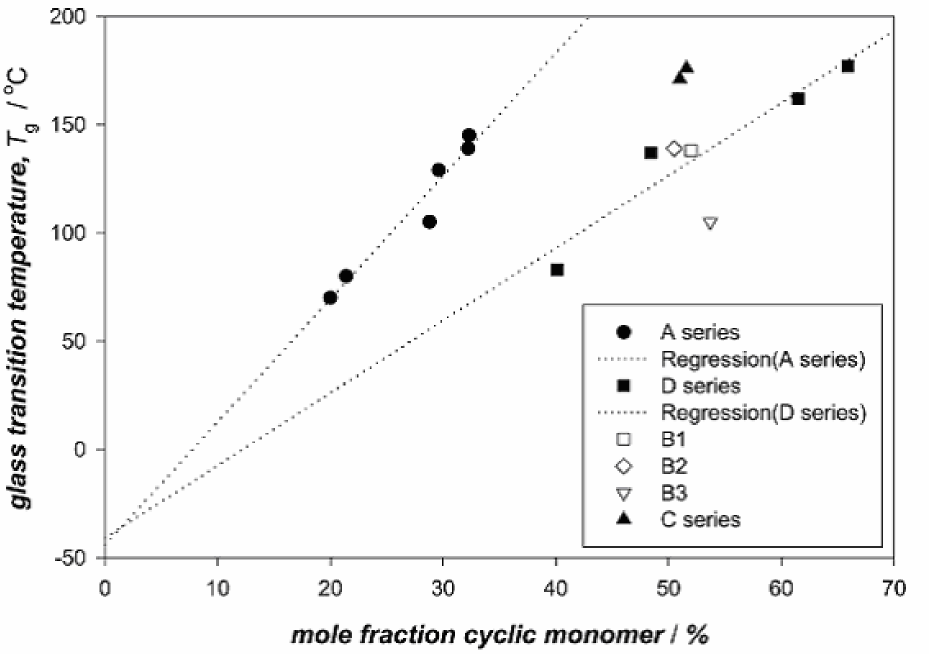


***Figure 13**: Dependence of Tg on cyclic monomer content [12]*

***Table 9**: Glass-transition temperature of some COCs*

COC	A1	A2	A3	A4	A5	A6	B1	B2	B3	C2	C3	D1	D3	D4	D5
T_g [°C]	70	80	105	129	145	139	138	139	105	171	176	83	162	137	177

3.3 Thermal stability and degradation

Thermal stability, or ability to offer resistance to high temperatures, is an important property for the processing of the material. The temperature at which the polymer starts to lose its own weight is called onset temperature (T_{onset}). Over this temperature copolymers are dissociated onto low molecular substances. This temperature is different for each COC. Following chapters deal with the thermal stability of the COCs and onset temperatures are introduced. Also the critical temperatures (T_c – inflection point of the degradation curve) are mentioned and they are compared to the temperatures of HDPE.

3.3.1 Methods of investigation

Thermogravimetric analysis (TGA) is the most suitable method for degradation determination. It is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted [2].

3.3.2 Characteristic Temperatures

The TGA curves for the four series COCs and HDPE are shown in Figures 14–16. The T_{onset} is obtained from the TGA curves by extrapolating from the curve at the peak of degradation back to the initial weight of the polymer. Similarly, the end temperature of degradation is obtained from the TGA curves by extrapolating from the curve at the peak of degradation forward to the final weight of the polymer. These characteristic temperatures are listed in Table 10. The difference of the critical temperatures and the onset temperatures of degradation is ΔT, which represents the temperature range of thermal degradation. As a reference, the data of thermodegradation of HDPE are also listed in Table 10.

It can be seen that COCs have maintained the superior thermal stability of polyolefin materials; however it shows some differencies [31]:

The onset and critical temperatures of degradation of COCs are lower than those for HDPE and are scattered at about 410 and 430 °C. It should be attributed to the chemical structure and microstructure features of COCs including the branching effect and the steric effect. The influence of the extent of branching of the main polymer chain on the reaction rate at a given temperature was reviewed [26] and it was found that the reaction rate increases with the extent of branching in the following order: HDPE<LDPE<PP<PS, which is identical with the order that the ability of substituents to stabilize macroradicals forming in chain scission (CH_3 <CH_2CH_3 <$CH(CH_3)_2$ <$C(CH_3)_3$ <benzyl) [27]. It was systematically studied the effect of ethylene-propylene content on the thermal degradation behavior of EPDM [28]. It was found that both the T_{onset} and T_c linearly increased as the ethylene content increases above 40 %. However, it was detected that the onset and critical temperatures are about 415±4 and 433±2 °C for A- and D-series copolymers except D2 of T_c value 438 °C, although there are larger change on the cyclic structure content and the T_g for these two series of COCs [31].

For B- and C-series copolymers, there are larger differences in the side substituents and the cyclic structure, which lead to that the onset temperature and critical temperatures are different. It seems that the chemical structure and microstructure features may be playing an important role in determining the degradation temperature. On the one hand, the branching of cyclic structure increases the reaction rate; on the other hand the chain stiffness of cyclic structure reduces the mobility of the chain, then decreases the reaction rate and improves thermal stability [29]. It is interesting to note that both B2 and C3 have lower T_c values 424 °C, but B3 has higher T_c value 440 °C, respectively. Contrarily, compared with other copolymers of B- and C-series COCs, B3 is absent both the sidegroup and the rigid bridge-ring structure possessing larger tension, so it has a relatively higher thermal stability [31].

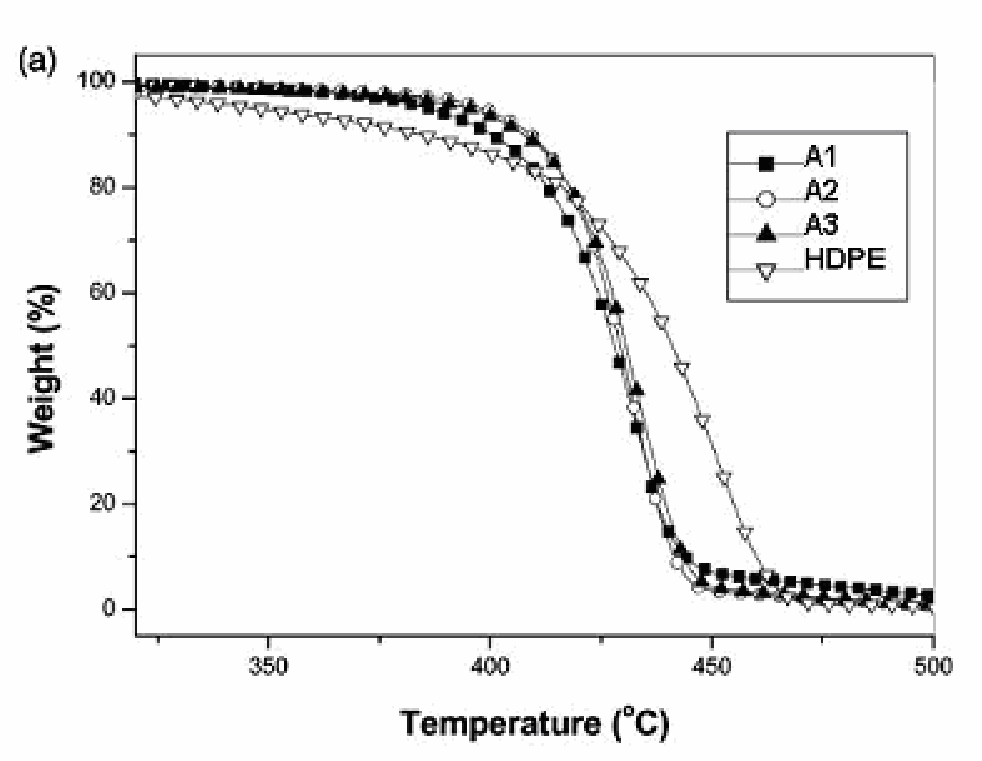


***Figure 14**: The TGA curves of A-series COCs and HDPE [31]*

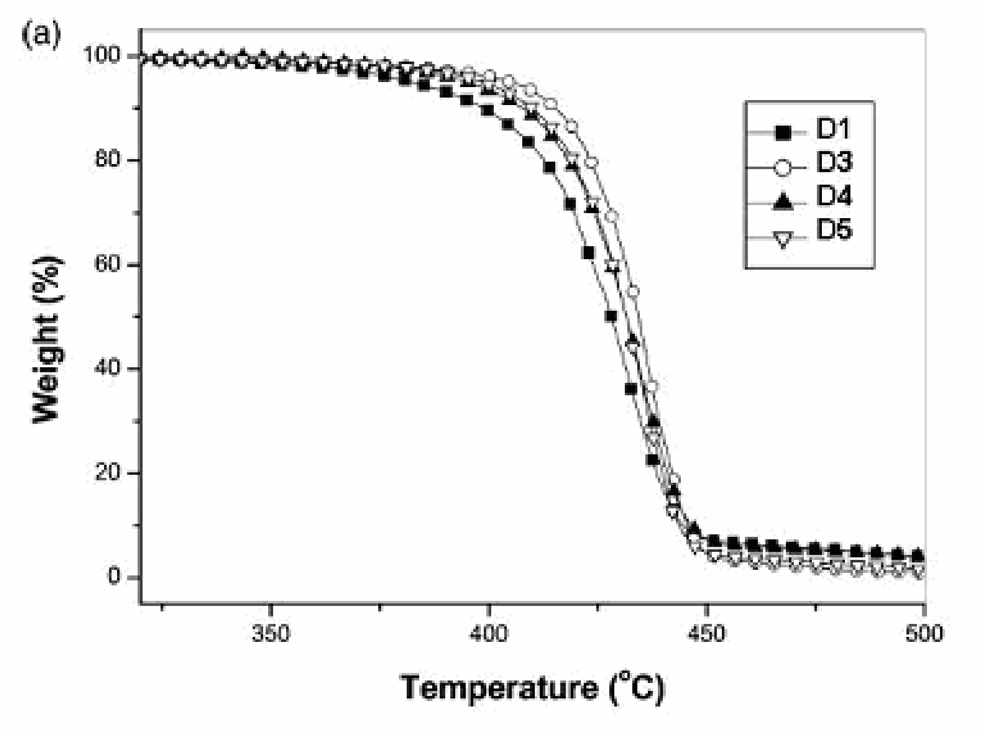


***Figure 15**: The TGA curves of D-series COCs [31]*

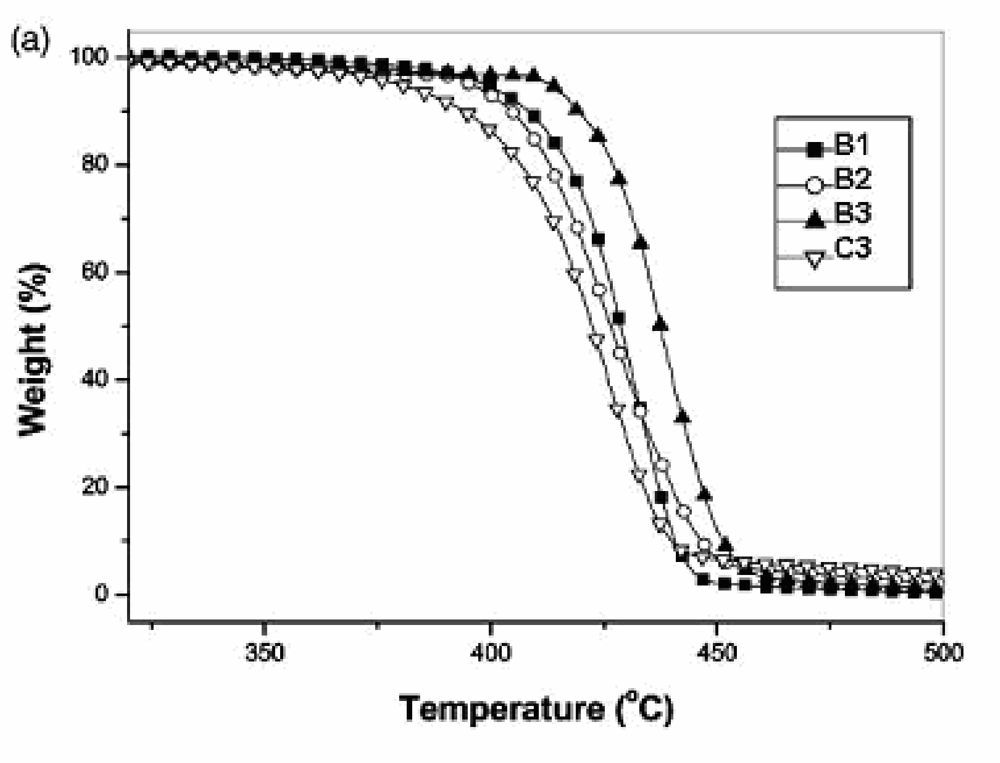


Figure 16: *The TGA curves of B- and C-series COCs [31]*

3.3.3 The Temperature Range

The temperature range of thermal degradation ΔT is equal to the difference of the critical temperatures and the onset temperatures of degradation. COCs have narrower temperature ranges of degradation than HDPE, which means the chain scission happens in shorter time. Another effect of branching is a possible change of the reaction mechanism; therefore, the bonds next to a side chain exhibit a higher breakage rate than do normal PE bonds, which lead to a more pronounced maximum in the conversion rate curve [31].

Table 10: *Characteristic temperatures and activation energies [22-24]*

COC	Onset temperatre, T_{onset} (℃)	Critical temperature T_c (℃)	ΔT (℃)
A1	413	432	19
A2	416	433	17
A3	417	435	18

B1	415	432	17
B2	407	424	17
B3	424	440	16
C3	404	424	20
D1	412	432	20
D3	422	438	16
D4	417	435	18
D5	419	435	16
HDPE	423	451	28

ΔT—The difference of T_c and T_{onset}.
Data were obtained for the constant heating rate of 2 °C/min

3.3.4 End of Degradation

Because polyolefins consist of carbon and hydrogen elements, there is usually little or no residue once the degradation of polyolefin had ended. However, from Figures 12, 13 and 14, it can be seen that COCs have 2–5 % black residual ash above the end temperature of degradation, especially for COCs with polar side-groups such as B2, C3. It is probably due to some cross linked structures formed from the reaction between radicals. The rate of formed radicals increases with their stability, and therefore, the content of the cross linked structures is higher if the radicals formed during the pyrolysis process are more stable [31].

4 APPLICATION

All properties of cycloolefin copolymers provide wide spectrum of usage especially in medicine, for process assorted optical tools or for produce bottles, films and others packaging applications.

4.1 Application in Medicine

Basic medicine tools

The combination of high transparency, greater shatter resistance than glass and superior barrier to moisture makes COC particularly attractive for prefillable primary pharmaceutical packaging; examples of this application is shown in the Figures 17 and 18. The material has also high purity and excellent biocompatibility. Therefore, it can be successfully used for prefillable syringes and vials and a wide variety of prefillable containers.

Injection molding and injection blow molding/injection stretch blow molding are typical manufacturing processes for this kind of pharma-packaging. Furthermore, COC is used increasingly for pharmaceutical blister packaging because of its high transparency, biocompatibility and excellent moisture barrier. [30]

Figure 17*: the typical application in pharmacy: Injections [30]*

***Figure 18**: the typical application in pharmacy: pharmaceutical packaging [30]*

Barrier for Long Life Pharmaceuticals

The moisture barrier helps to extend the shelf life of pharmaceuticals and solutions stored in prefillable primary packaging. It keeps the moisture away from the contents or keeps the concentration of ready-prepared solutions constant. With its remarkable property profile compared with known plastics, COC offers new options for these applications. [30]

Diagnostic Application

It was developed specifically for applications in diagnostics have excellent light transmission in the near UV region as well as high transparency in the visible region.

Excellent resistance to aqueous and polar organic media, good biocompatibility and the ability to reproduce fine structures, makes these materials of choice for innovative applications in the area of diagnostic articles. Examples of applications are microtiter plates (Figure 19) for high throughput screening, microstructured cuvettes and test tubes for clinical analysis, and containers for spectroscopic monitoring of biochemical reactions.

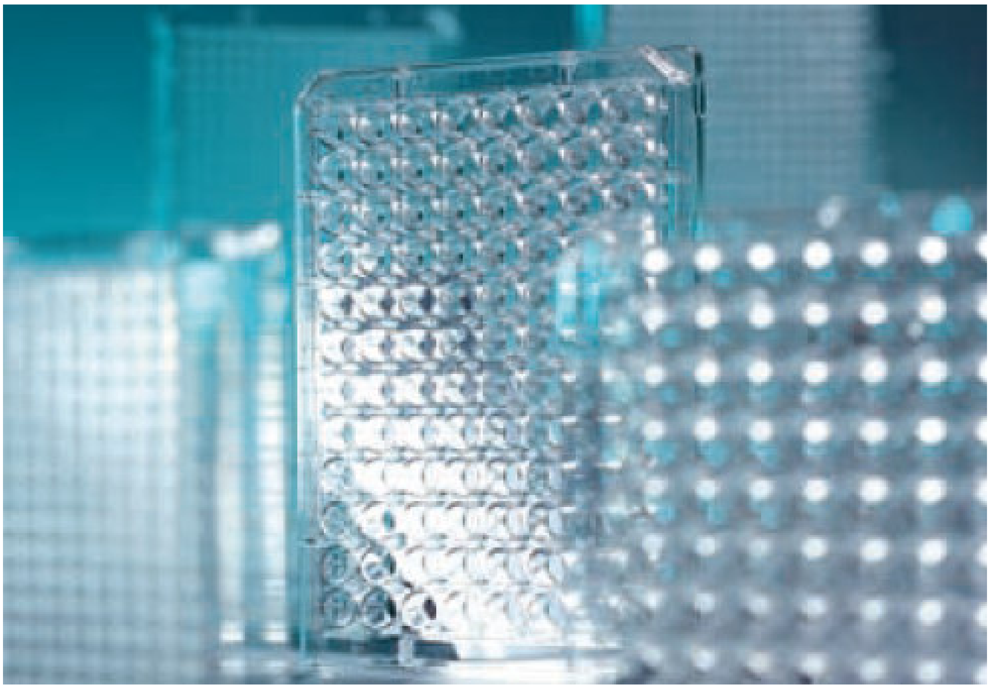


Figure 19*: Microtiter plates for diagnostic applications [30]*

4.2 Optical Application

With combination of features mentioned in previous chapters likes: high transparency, shatter resistance, low specific gravity, high heat resistance, low water absorption etc. The most common optical applications of COCs are:

- Mobile telephone lenses
- Digital still camera lenses
- Video camera lenses
- Printer lenses
- CD, DVD pick up lenses
- Projector lenses
- LED lenses
- Light guide panels for LCD

- Contact lenses
- Automotive parts
- Other optical application

Figures 20 and 21 show typical optical tools used in practice, concretely LED-diodes lenses and contact lenses used in ophthalmology.

Figure 20*: LED lenses [36]*

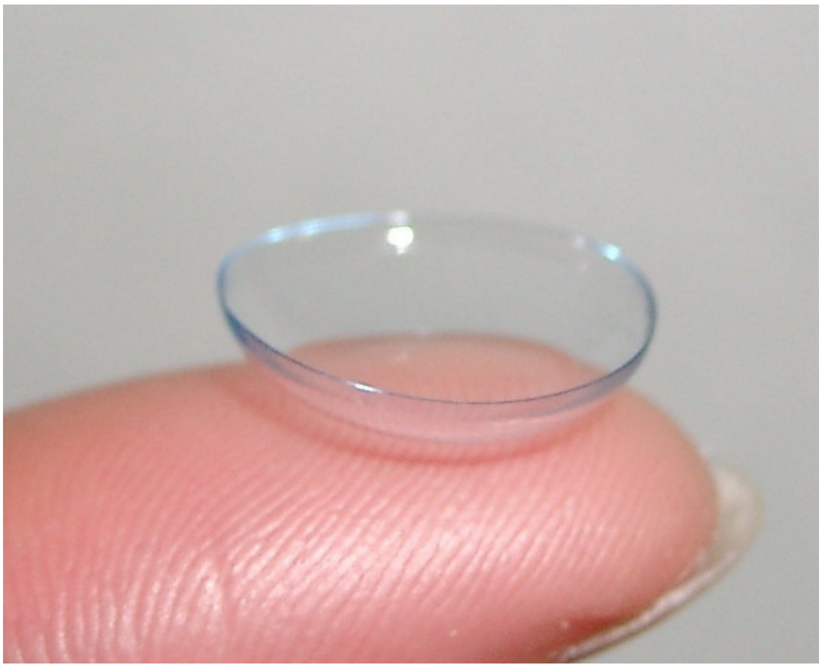


Figure 21*: Contact lens [35]*

4.3 Films

Films are produced by extrusion as in the case of any other plastic. Except of films, also the sheets and profiles can be processed. The good property of COCs is easy metal plating. In the Figure 22 the transparent and metallized films are pictured.

***Figure 22**: Transparent and mettalized films. [16]*

It meets the demanding optical application requirements and functions and can be used in the back light and image light areas of LCDs such as diffusion film, protective film, and retardation film and as an anti-glare polarizing film for high-resolution LCDs (see Figure 23).

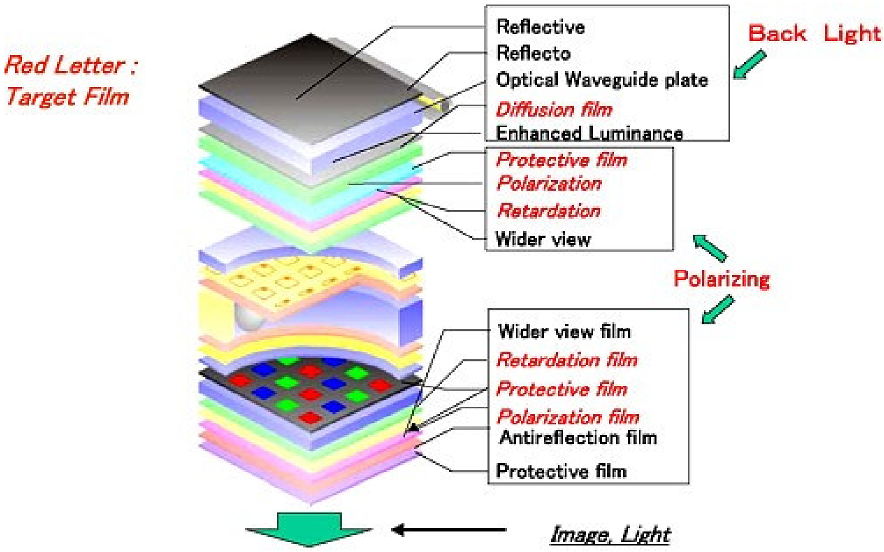


***Figure 23**: Application of COCs films in the LCDs [32]*

CONCLUSION

Cycloolefin copolymers are the relatively new class of the polymer materials. Thus, practically no complex study comprising all information as preparation, structure, morphology, processing, properties, application and degradation exists. The main aim of this Bachelor Thesis was to create such comprehensive review.

The first part of this work was focused on the manufacturing of cyclic olefin copolymers and their structure. Several types of monomers can be used for preparation of COCs, however, the most common cyclic monomer is norbornene and the linear one is ethene. The copolymerization can be performed by ring opening metathesis polymerization or vinyl copolymerization. The COCs are divided into several groups according to their chemical structure. The morphology of these materials is almost entirely amorphous.

In the second part of this work physical properties are discussed. The outstanding properties of COCs are high transparency, biocompatibility and excellent moisture barrier. They possess high glass transition temperature and shows good thermal stability.

The last part of the thesis is focused on application of these copolymers namely in pharmaceutical packaging, for various optical tools etc.

Finally, I would like to say I am delighted that I could contribute for higher knowledge of cyclic olefin copolymers and I hope that this thesis will help to those who are interested in this field of polymer science.

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REVIEW OF SYMBOLS

COC	Cyclic olefin copolymer.
ROMP	Ring Opening Metathesis Polymerization.
TEM	Transmission Electron Microscopy
13C-NMR	Carbon-13 Nuclear Magnetic Resonance
DSC	Differential Scanning Calorimetry
GPC	Gel Permeation Chromatography
X-Ray	Röntgen Rays
Ppm	Part Per Million
T_g	Glass-Transition Temperature [°C]
M_w	Weight average molar mass
M_n	Number average molar mass
T_{HD}	Heat Deflection Temperature [°C]
TGA	Thermogravimetric Analysis
T_c	Critical Temperature [°C]
T_{ONSET}	Onset Temperature of the degradation [°C]
ΔT	The difference of the critical temperature and the onset temperature of degradation [°C]
PE	Polyethylene
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
PP	Polypropylene
PS	Polystyrene
EPDM	ethylene propylene diene monomer rubber

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