Pure Appl. Chem., Vol. 77, No. 5, pp. 801–814, 2005.
DOI: 10.1351/pac200577050801

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

POLYMER DIVISION

CHEMICAL STRUCTURE AND PHYSICAL PROPERTIES OF CYCLIC OLEFIN COPOLYMERS*

(IUPAC Technical Report)

Prepared for publication by
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*Publication resulting from work carried out under the IUPAC Polymer Division Project 199-039-1-400; ***Task Group Members*****:** S. C. Kim (Korea, project leader), T. Takigawa (Japan, project co-leader), D. J. Djikstra (Germany), J. He (China), B. Z. Jiang (China), D. S. Lee (Korea), C. Liu (China), T. Masuda (Japan), G. H. Michler (Germany), K. Nakayama (Japan), K. Nitta (Japan), J. Y. Park (Korea), J. Y. Shin (Korea), S. S. Woo (Korea).

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Chemical structure and physical properties of cyclic olefin copolymers

(IUPAC Technical Report)

Abstract: Cyclic olefin copolymers comprise a new class of polymeric materials showing properties of high glass-transition temperature, optical clarity, low shrinkage, low moisture absorption, and low birefringence. There are several types of cyclic olefin copolymers based on different types of cyclic monomers and polymerization methods. In this work, we have analyzed the chemical structure of the currently commercialized cyclic olefin copolymers by ^{13}C NMR, and investigated their glass-transition temperatures and surface characteristics. It was observed that the glass-transition temperature, T_g, of cyclic olefin copolymers depended on the bulkiness of the main chain, and the number of rings had an important role in increasing the bulkiness of cyclic olefin copolymers. Cyclic olefin copolymers with polar substituents such as ester or ether groups showed high surface energy per area and peel strength.

Keywords: cyclic olefin copolymers; chemical structure; thermal property; surface energy; ^{13}C NMR; Division IV.

INTRODUCTION

The modification of general-purpose polyolefin materials to enhance their performance characteristics to the level of practical use as engineering plastics is currently a relevant topic for industrial as well as academic research. Cyclic olefin copolymers comprise one of the new classes of polymers based on cyclic olefin monomers and ethene.

Because of the bulky cyclic olefin units randomly or alternately attached to the polymer backbone, the copolymer becomes amorphous and shows the properties of high glass-transition temperature, T_g, optical clarity, low shrinkage, low moisture absorption, and low birefringence [1–3].

With these properties, the application of cyclic olefin copolymer has now been extended to production of plastic lenses and optical storage media, and is currently being produced by Mitsui Chemical Co., Ticona (formerly Hoechst Celanese), Japan Synthetic Rubber, and Zeon Chemicals Co.

There are several types of commercial cyclic olefin copolymers based on different types of cyclic monomers and polymerization methods. Cyclic olefin copolymers are produced by chain copolymerization of cyclic monomers such as 8,9,10-trinorborn-2-ene (norbornene) or 1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene (tetracyclododecene) with ethene, Ticona's TOPAS, Mitsui Chemical's APEL, or by ring-opening metathesis polymerization of various cyclic monomers followed by hydrogenation (Japan Synthetic Rubber's ARTON, Zeon Chemical's Zeonex and Zeonor). A typical polymerization scheme is shown in Fig. 1.

Recently, a considerable amount of work has been reported on the physical properties and microstructure of cyclic olefin copolymers. Most of these reports correlated the composition, microstructure, and thermal properties of ethene-norbornene copolymer [4–8]. A few studies have been made on the influence of chemical structure on the thermal properties of cyclic olefin copolymers. There is no report on the surface characteristics of these polymers.

The objective of the present work is a study of the chemical structure, microstructure, glass-transition temperature, and surface energy per area of a series of commercialized cyclic olefin copolymers and an evaluation of the correlations between the chemical structure and physical properties.

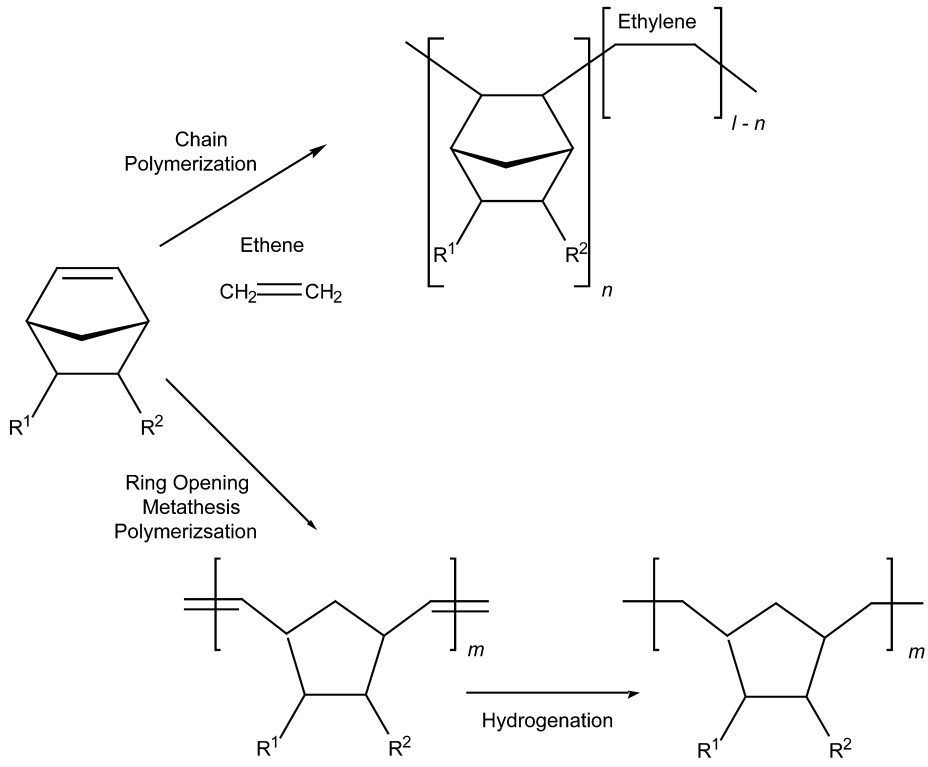


Fig. 1 Typical polymerization scheme for a cyclic olefin polymer.

EXPERIMENTAL

Materials

The commercial cyclic olefin random copolymers were supplied by Japan Synthetic Rubber, Mitsui Chemical Co., Ticona, and Zeon Chemicals Co. The characteristics of these polymers are given in Table 1, which shows the heat distortion temperature, density, light transmission, and refractive index provided by the supplier.

Table 1 Characteristics of the cyclic olefin copolymers used in this study.

Sample	$^1T_{HD}$/°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

(*continues on next page*)

Table 1 (*Continued*).

Sample	$^1T_{HD}$/°C	Density /g cm^{-3}	Light transmission/%	Refractive index
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	

$^1T_{HD}$: heat distortion temperature: a: at p = 1.82 MPa, b: at p = 0.45 Mpa.

NMR

To investigate the chemical structure and cyclic monomer content of cyclic olefin copolymers, ^{13}C NMR spectra were obtained using a Bruker AMX 500 spectrometer operating at ν_0 = 125.77 MHz. The temperature was regulated to 25 °C. Polymers were dissolved in $CDCl_3$, which was used as a lock and as reference chemical shift versus tetramethylsilane, TMS, assuming its chemical shift to be $\delta\,(CDCl_3) = 77.00 \times 10^{-6} = 77.00$ ppm.

DSC

In order to investigate the thermal behavior of various cyclic olefin copolymers, differential scanning calorimetry (DSC) TA Instruments DSC 2010, was carried out. In each experiment, 7–15 mg of sample was used and the DSC was run under dry nitrogen. All samples were first heated to 220 °C at a rate of 20 °C/min and then cooled to 0 °C. They were then scanned from 0 to 350 °C at a rate of 10 °C/min.

GPC

The molecular weight and molecular weight distribution were measured by gel permeation chromatography (GPC), Polymer Laboratory, PL-220. The operating temperature was 80 °C, and toluene was used as a solvent. For calibration and measurement, monodisperse polystyrene standards were used.

Surface energy

The surface energy per area (= surface tension) was calculated by using the values of contact angles formed by drops of different liquids, water, and ethylene glycol on the surface of these polymers. For the contact angle determination, cyclic olefin copolymers were molded into sheets of 2 mm thickness at 280 °C for 10 min. The contact angles made by drops of liquids were measured with a contact angle meter.

Peel test

The TC peel, thermo-compression bonded peel test [9,10], was performed to measure the adhesion strength of aluminum film with cyclic olefin substrate. The substrate and aluminum strip were thermo-compressed at 10 000 ton, 280 °C for 3 min. The aluminum strip was peeled away at an angle of 90° with 2 mm/min cross-head speed. The peel strength values were measured for five samples in each case.

RESULTS AND DISCUSSION

The results of the characterization of cyclic olefin copolymers used in this study are listed in Table 2, which shows the cyclic monomer content, glass-transition temperature, average molecular weight, and molecular weight distribution.

Table 2 Composition, glass-transition temperature, molecular weight, and polydispersity index of cyclic olefin copolymers.

Sample	Cyclic monomer mole fraction/%	T_g/°C	$M_w/10^4$	M_w/M_n
A1	20.0	70	13.1	2.46
A2	21.4	80	10.8	2.28
A3	28.8	105	10.2	2.45
A4	29.6	129	11.6	2.52
A5	32.2	145	11.9	2.30
A6	32.2	139	9.3	2.40
B1	52.0	138	5.4	2.26
B2	50.5	139	6.5	1.65
B3	53.7	105	4.5	1.95
C2	51.0	171	8.5	3.70
C3	51.6	176	12.0	2.79
D1	40.1	83	12.5	1.99
D3	61.5	162	9.9	1.93
D4	48.4	137	10.9	1.97
D5	65.9	177	9.6	1.93

Chemical structure of cyclic olefin copolymers

The ^{13}C NMR spectra of cyclic olefin copolymers were assigned using distortionless enhancement by polarization transfer (DEPT) and homo- and heteronuclear two-dimensional NMR techniques. The advanced chemistry development (ACD) NMR software was a good guide to the assignment of ^{13}C NMR spectra.

Figure 2 displays the chemical structure and ^{13}C NMR spectra obtained for the A series ethene-tetracyclododecene copolymer. Our assignments for the ethene-tetracyclododecene copolymer are in accordance with that of Rhodes et al. [11]. 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 using following relationship:

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

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 Fig. 2, two well-separated main resonance signals at 40.2 and 40.9 ppm are C2/C3 methine 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

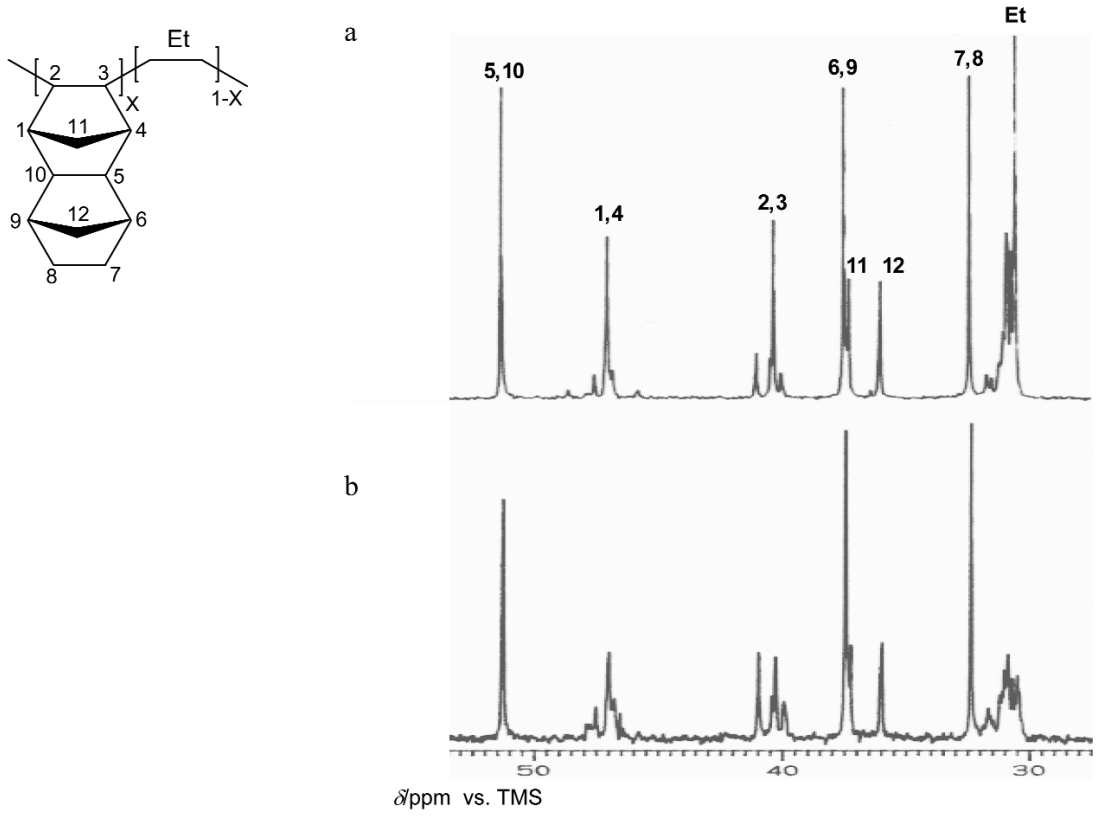


Fig. 2 ^{13}C NMR spectrum assignments and the chemical structure of A series with cyclic monomer mole fractions, (a) 21.4 %, (b) 32.2 %. Vertical axis: relative intensity; horizontal axis: chemical shift δ/ppm vs. TMS.

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. Comparison of a series of spectra shows that the intensity of these resonances changes with increasing tetracyclododecene content, but new resonances and splitting of existing signals, which would indicate the presence of tetracyclododecanediyl blocks, do not appear in the ^{13}C NMR spectrum. Therefore, it is concluded that the A series contained only isolated and alternating tetracyclododecanediyl units.

The ^{13}C NMR spectra and assignments of the D series studied in this work are shown in Fig. 3. Between 28 and 33 ppm, the ethylene signals overlap with C5 and C6 resonances of 8,9,10-trinorbornane-2,3-diyl (norbornanediyl) [8,12–14]. The norbornene content of the D series was determined by using the following relationship: [15]

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

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

Results of ^{13}C NMR investigations of the microstructure of ethene-norbornene copolymers supplied by Hoechst Celanese were recently reported by Rische et al. [6] and Delfolie et al. [16]. Rische et al. divided ^{13}C NMR spectra into two distinct patterns depending on the norbornene content. Ethene-

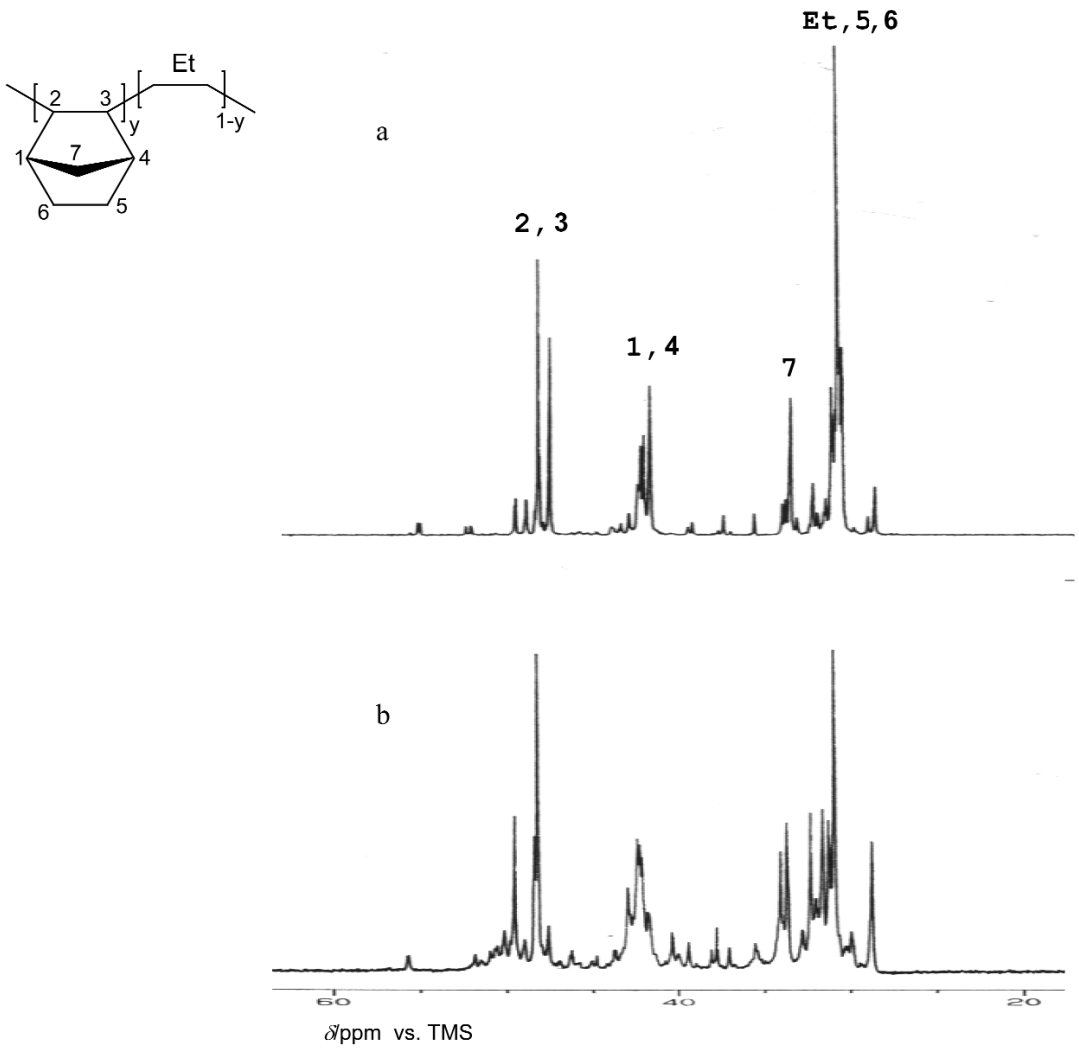


Fig. 3 ^{13}C NMR spectrum assignments and the chemical structure of D series with cyclic monomer mole fractions, (a) 40.1 %, (b) 65.9 %. Vertical axis: relative intensity; horizontal axis: chemical shift δ/ppm vs. TMS.

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. Delfolie et al. 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.

Many details about the microstructure of ethene-norbornene copolymers can be obtained from the examination of the signals 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 ^{13}C NMR spectrum of D1 with a norbornene mole fraction of 40.1 % shown in Fig. 3a, it can be concluded that 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 3b shows the ^{13}C NMR spectrum of D5 with a norbornene mole fraction of 65.9 %. Compared to Fig. 3a, 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 microblocks. From these results, we found that the D series studied in this work are made up of a random mixture of isolated and alternating sequences, dyads, and blocks of three or more norbornanediyl units.

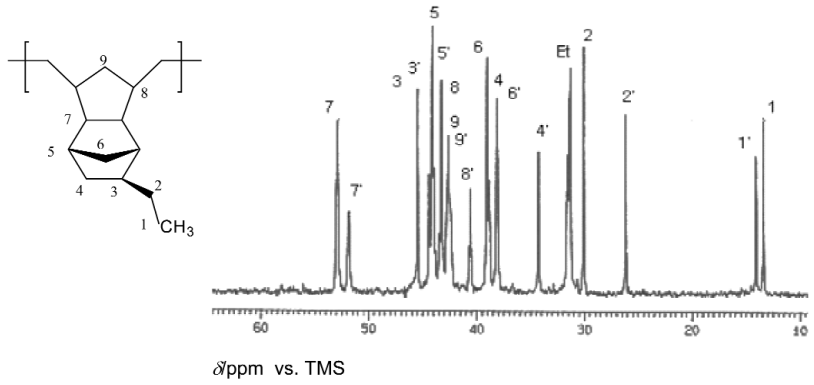
The ^{13}C NMR assignments and the chemical structure of B and C series copolymers are represented in Figs. 4 and 5. It was observed that the B and C series, except B3, show unsymmetrical polycyclic structures with side branches attached to the ring. B1 has an ethyl branch group, B2 has a phenyl branch group, and the C series has an ester branch group. Owing to the presence of *exo*- and *endo*-isomers in these unsymmetrical structures, ^{13}C NMR spectra show very complex signals. In Fig. 4a, 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 Fig. 5 indicate the presence of *exo–endo*-isomers. In the ^{13}C 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. However, the complicated NMR spectrum prevented us from further investigation of the isomerism of this polymer. The cyclic repeating unit content of the B, C series was calculated by following equation:

$$\text{mole fraction cyclic repeating unit} = \frac{I_{C_1\ C_n}/n}{I_{Et}/2 + I_{C_1\ C_n}/n} \tag{3}$$

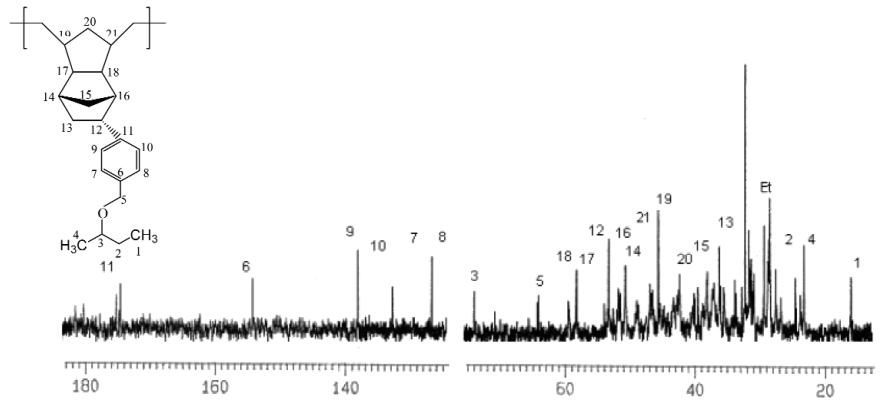
where I_{Et} of B1 = integral between 30.5 and 32 ppm, I_{Et} of B2 = integral between 29.5 and 30.5 ppm, I_{Et} of B3 = integral between 30.5 and 31.5 ppm, I_{Et} of the C series = integral between 30 and 31.5 ppm.

As we mentioned before, the B and C series are synthesized by the ring-opening metathesis polymerization (ROMP) 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 will be 50 %. From the calculation for the composition, it was confirmed that B and C series have a cyclic monomer mole fraction of around 50 %.

a. B1



b. B2



c. B3

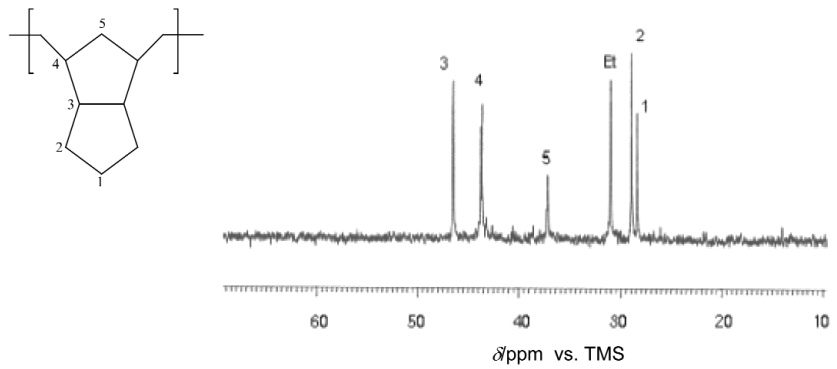


Fig. 4 ^{13}C NMR spectrum assignments and the chemical structure of B series. Carbon assignment scheme: The unprimed numbers in the spectrum correspond to the same numbers in the formula when the configuration at that position is exo; the primed numbers in the spectrum correspond to the same when the configuration is endo. Vertical axis: relative intensity; horizontal axis: chemical shift δ/ppm vs. TMS.

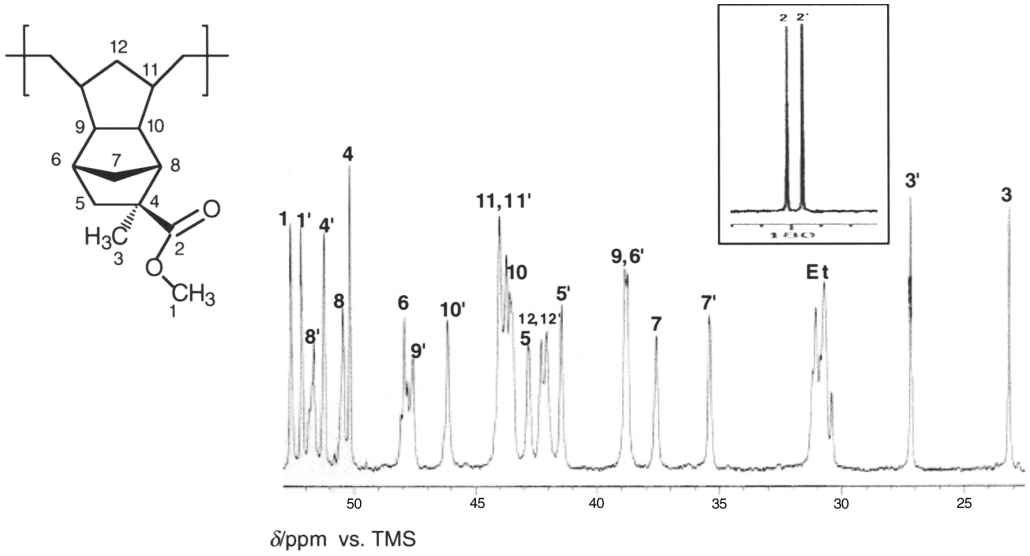


Fig. 5 ^{13}C NMR spectrum assignments and the chemical structure of C series C3. Carbon assignment scheme: The unprimed numbers in the spectrum correspond to the same numbers in the formula when the configuration at that position is exo; the primed numbers in the spectrum correspond to the same when the configuration is endo. Vertical axis: relative intensity; horizontal axis: chemical shift δ/ppm vs. TMS.

GLASS-TRANSITION TEMPERATURE

Figure 6 shows the dependence of the glass-transition temperature, T_g, on cyclic monomer content and chemical structure of cyclic olefin copolymers studied in this work. There seems to exist a linear relationship between cyclic monomer content and T_g within the investigated composition range in the A and D series. For the D series, this relationship is in accordance with the results obtained by Rische et al. [6] and Delfolie et al. [16], who studied the thermal property of ethene-norbornene copolymers supplied by Hoechst Celanese. Rhodes et al. [11] reported a linear relationship between T_g and the tetracyclododecene mole fraction in ethene-tetracyclododecene copolymers prepared using the catalyst system known as 1,2-ethylenebisindenylzirconocene dichloride/MAO*, and they observed an increase of 7–8 °C in T_g for every unit increase in amount % in tetracyclododecene. Our result is slightly different from theirs: an increment of 5–6 °C in T_g was found. This deviation may be due to variations in the microstructure induced by a different catalyst system. The variation of T_g with cyclic monomer content for the A series is bigger than that for the 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 shown in the results of ^{13}C NMR, B1, B2, and the C series have the same cyclic structure with different side-chain substituents. In ref. [17], we 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 side-chain substituents attached in the ring have significant influence on the T_g of cyclic olefin polymers.

*The catalyst in this system is dichloro{1,1'-ethane-1,2-diyldi[(1,2,3,3a,7a-η)-1*H*-inden-1-yl]}zirconium. The cocatalyst is a complex mixture of linear and cyclic oligomeric aluminoxanes known as MAO (from the common name methylaluminoxane not recommended by IUPAC).

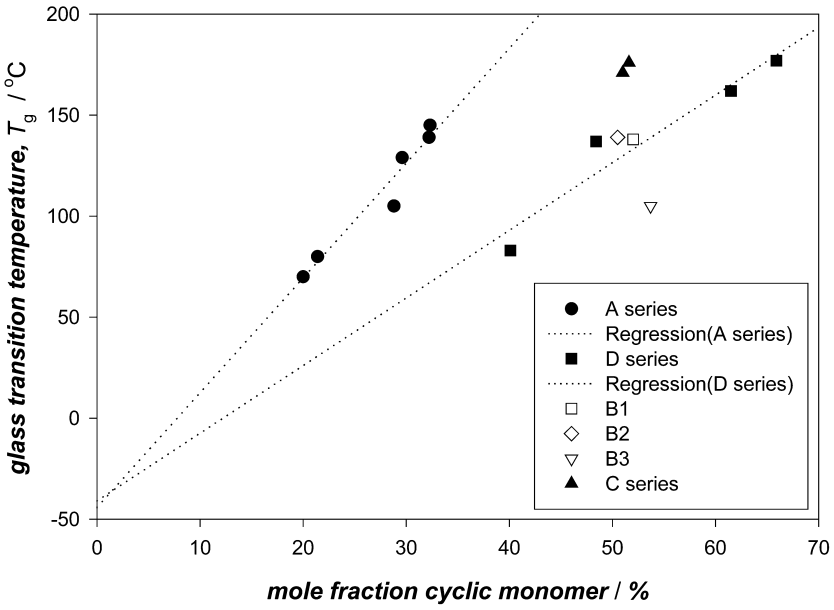


Fig. 6 Dependence of T_g/°C upon cyclic monomer content.

MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

Recently, Bergström et al. [18,19] reported the results of molecular weight and polydispersity index of ethene-norbornene copolymers determined by GPC in 1,2,4-trichlorobenzene. They observed the GPC peak area decreased with increasing norbornene content and the signal disappeared at a norbornene mole fraction close to 29 %. At higher norbornene content, the polarity of the signal was reversed. This phenomenon is due to refractive index changes caused by the composition in ethene-norbornene copolymer. The refractive index of a polyethylene solution is lower than that of 1,2,4-trichlorobenzene. The higher the norbornene content in the ethene-norbornene copolymer, the smaller the difference in refractive index between the polymer solution and the pure solvent. We found similar trends in the A and D series from GPC analysis using 1,2,4-trichlorobenzene, but the critical composition at which no signal is observed varies with the chemical structure of the cyclic monomer. In this study, we used toluene as a solvent to obtain an accurate result for the molecular weight and molecular weight distribution of cyclic olefin copolymers. Because the refractive index of toluene is lower than that of polyethylene, cyclic olefin copolymers show distinct signals regardless of the composition. The GPC analysis results are listed in Table 2. The average molecular weights of the B series are lower than those of the other cyclic olefin copolymers. From comparison of the molecular weight distributions, it was observed that the B and D series have a relatively low polydispersity index compared to the A and C series.

SURFACE CHARACTERIZATION

Surface energy is a direct manifestation of intermolecular forces. The molecules at the surface of a liquid or a solid are influenced by unbalanced molecular forces and therefore possess additional energy, in contrast with the molecules inside the liquid or solid. The surface of a solid possesses additional Gibbs energy, but owing to the lack of mobility at the surface of solids, this Gibbs energy is not directly observable, but must be measured by indirect methods. Often two different nonpolar liquids are used, and this has been commonly called the two-liquid technique of determining the surface Gibbs energy

components of polymeric solids [20]. The surface energy per area (= surface tension) of the cyclic olefin copolymer was calculated from contact angle measurements using ethylene glycol and water as the liquid component. The surface tension of two liquids at 25 °C is as follows.

For ethylene glycol,

γ^{d}_{GV} = 33.8 mN/m, γ^{p}_{GV} = 14.2 mN/m, γ_{GV} = 48 mN/m

For water,

γ^{d}_{WV} = 21.8 mN/m, γ^{p}_{WV} = 50.0 mN/m, γ_{WV} = 72.8 mN/m

where superscripts d and p refer to the dispersion and polar components.

The surface tension of the solid surface (energy per area), γ_{SV}, was obtained by the following equation.

$$\gamma_{SV} = \gamma_{SW} + \gamma_{VW} + 4\left(\frac{\gamma^{d}_{SW}\gamma^{d}_{VW}}{\gamma^{d}_{SW} + \gamma^{d}_{VW}}\right) + 4\left(\frac{\gamma^{P}_{SW}\gamma^{P}_{VW}}{\gamma^{P}_{SW} + \gamma^{P}_{VW}}\right)$$

where γ_{sw} is the interfacial tension between the solid and water, γ^{d}_{sw} and γ^{p}_{sw} are the dispersion and polar components of the interfacial tension between the solid and water.

To investigate the effect of chemical structure on the surface characteristics, A6, B series, C2, and D4 were selected. Table 3 presents the calculated values for the surface energies per area of various cyclic olefin copolymers. As shown in the results of NMR Figs. 2–5, the C series, which has pendant ester groups, shows the highest surface energy per area among the cyclic olefin copolymers studied. B2, with ether groups, shows relatively high surface energy per area. The A and D series and B1, B3, with no polar substituents, show values similar to polyethylene. Correlation of the surface energy per area with peel strength is represented in Fig. 7. It was observed that when surface energy per area increased, the peel strength increased. We could deduce that the ester or ether pendant groups play an important role for determining the adhesion force between aluminum and the cyclic olefin copolymer.

Table 3 Contact angles and calculated surface tensions (surface energies per area) for various cyclic olefin copolymers.

	θ_1	θ_2	γ^{p}_{SW}/mN m^{-1}	γ^{d}_{SW}/mN m^{-1}	γ_{SW}/mN m^{-1}	γ_{SV}/mN m^{-1}
A6	131	97	4.92	24.32	29.24	38.11
B1	130	100	5.11	19.86	24.97	37.62
B2	135	100	4.19	22.89	27.08	39.72
B3	125	103	6.14	14.18	20.42	36.79
C2	137	116	3.85	9.54	13.40	45.31
D4	120	93	7.27	22.39	29.66	32.83

θ_1: angle of ethylene glycol–air–solid, θ_2: angle of water–air–solid.

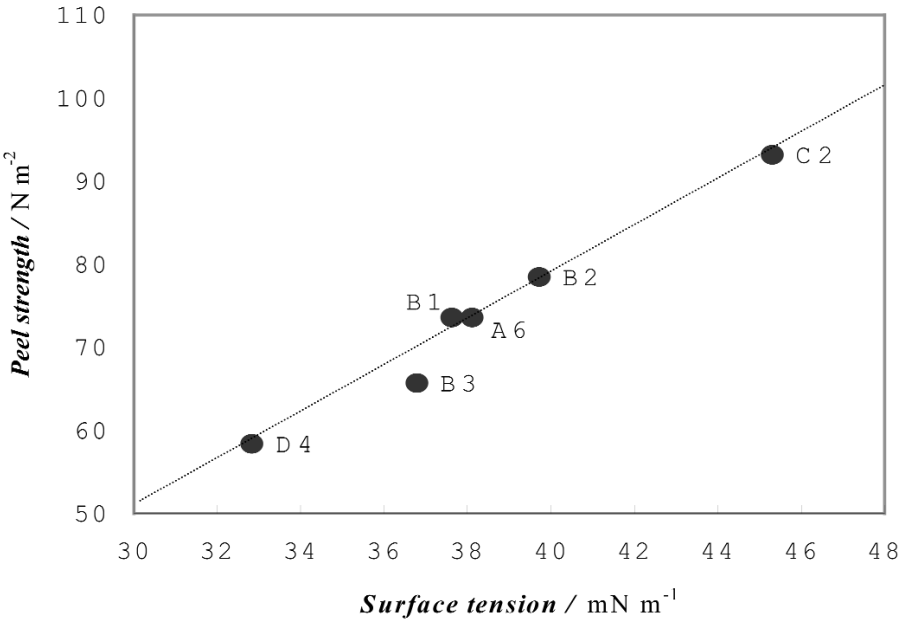


Fig. 7 Surface tension vs. peel strength for various cyclic olefin copolymers.

SUMMARY AND CONCLUSION

The chemical structure and thermal and surface properties of a series of commercialized cyclic olefin copolymers were investigated. Structural analysis of cyclic olefin copolymers was performed using NMR, and we found different chemical structures. The relation between thermal properties and the chemical structure of various cyclic olefin copolymers was studied. The T_g of the cyclic olefin copolymers linearly increased with cyclic monomer content, and it was observed that the T_g of cyclic olefin copolymers depends heavily on the bulkiness of the main chain; the number of cyclic rings has an important role in increasing the bulkiness of the cyclic olefin copolymers. The surface characteristics were also analyzed. Cyclic olefin copolymers C series and B2 in this work with ester or ether groups show high surface energy per area in cyclic olefin copolymers. Ethene-norbornene copolymers D series, ethene-tetracyclododecene copolymer A series and B1, B3 composed entirely of hydrocarbons show values similar to those for polyethylene. A linear correlation was found between the surface energy and the peel strength when the aluminum was sputtered on the cyclic olefin copolymer substrate.

ACKNOWLEDGMENTS

We would like to thank Japan Synthetic Rubber, Mitsui Chemical Co., Ticona, and Zeon Chemicals Co. for providing the materials.

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