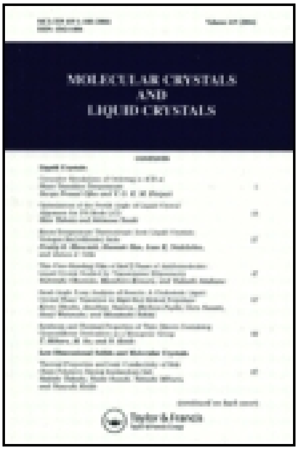

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Optical Properties of Cycloolefin Copolymers for Plastic Substrates

Keun-byoung Yoon [a], Jin Sik Choi [a], Dong-ho Lee [a], Youngjune Hur [b] & Seok Kyun Noh [c]

[a] Department of Polymer Science, Kyungpook National University, Daegu, Korea

[b] Advanced Display Manufacturing Research Center, Kyungpook National University, Daegu, Korea

[c] School of Chemical Engineering and Technology, Yeongnam University, Gyeongsan, Korea

Version of record first published: 31 Jan 2007

To cite this article: Keun-byoung Yoon, Jin Sik Choi, Dong-ho Lee, Youngjune Hur & Seok Kyun Noh (2006): Synthesis and Optical Properties of Cycloolefin Copolymers for Plastic Substrates, Molecular Crystals and Liquid Crystals, 459:1, 27/[307]-34/[314]

To link to this article: http://dx.doi.org/10.1080/15421400600930425

Mol. Cryst. Liq. Cryst., Vol. 459, pp. 27/[307]–34/[314], 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600930425

Synthesis and Optical Properties of Cycloolefin Copolymers for Plastic Substrates

Keun-byoung Yoon
Jin Sik Choi
Dong-ho Lee
Department of Polymer Science, Kyungpook National University, Daegu, Korea

Youngjune Hur
Advanced Display Manufacturing Research Center, Kyungpook National University, Daegu, Korea

Seok Kyun Noh
School of Chemical Engineering and Technology, Yeongnam University, Gyeongsan, Korea

Cycloolefin copolymers comprise a new class of polymer 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 type of cyclic monomers and polymerization methods. In ethylene/norbornene (E/NB) copolymerization, iPr(Cp)(Flu)$ZrCl_2$ catalyst exhibited more activity than Cp_2ZrCl_2 and rac-Et(Ind)$_2$$ZrCl_2$ catalysts. By the incorporation of Norbornene in copolymer, the glass transition temperature (Tg) of copolymer became higher. The Tg of copolymer increased up to 190°C. The transmission of copolymers was above 90% over 300 $\sim$ 900 nm. The RI of ethylene/tetracyclododecene (E/TCD) copolymer was higher than that of E/NB copolymer. The RI of E/NB copolymer could not changed increasing NB contents, however, the RI of E/TCD copolymer increased with increasing of TCD contents. The E/NB NB copolymer has very low birefringence and that film has very smooth surface.

Keywords: cycloolefin copolymer; polymer substrate; refractive index; thermooptic coefficient

This work was supported by the Regional Innovation Center Program (ADMRC) of the Ministry of Commerce, Industry and Energy of Korea.

Address correspondence to Prof. Keun-Byoung Yoon, Department of Polymer Science, Kyungpook National University, Sangyuk-dong, Buk-gu, Daegu 702-701, Korea (ROK). E-mail: kbyoon@knu.ac.kr

INTRODUCTION

While today's display industry is, to a very large extent, based on rigid, glass-based devices with the dominant space occupied by LCDs, there is an emerging flexible display industry which is forecast to show significant growth and which will have the opportunity to exploit the display technologies OLED and e-paper in addition to LCD [1].

Flexible displays offer substantial rewards in terms of being able to develop displays that are thinner, lighter, robust, conformable and can be rolled away when not required. Flexible displays can be built on metal foil, very thin glass coated with a polymer and a variety of plastics. To replace glass, a plastic substrate needs to be able to offer the properties of glass, i.e., clarity, dimensional stability, thermal stability, barrier, solvent resistance, low coefficient of thermal expansion coupled with a smooth surface [2].

The modification of general purpose polyolefin materials to enhance their performance characteristics to the level of practical use as optical applications 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 olefin. 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, optical clarity, low shrinkage, low moisture absorption and low birefringence [3].

With metallocene compounds of the new generation polymerization catalysts, Kaminsky discovered that cycloolefins of norbornene and its derivatives can be polymerized with keeping cyclic structure of monomer itself. By using the *ansa*-metallocene compounds as catalyst and methylaluminoxane (MAO) cocatalyst, the cyclooefin can be copolymerized with olefin to obtain the so-called cycloolefin copolymer (COC) [4]. Many efforts were devoted to the development of COC [5,6]. To prepare the high transparent polymer material for the flexible polymeric substrate of display devices, the copolymerization of ethylene and norbornene had been examined for various ansa-metallocene compounds and polymerization conditions. The effect of metallocene/MAO catalyst system and polymerization condition on the catalyst activity and composition of COC had been studied. The optical properties, refractive index and UV-visible transmission, of the obtained COC and commercial COC were also investigated.

EXPERIMENTAL

Materials

The metallocene catalysts such as Cp_2ZrCl_2 (Strem Chem., U.S.A.), *rac*-Et(Ind)$_2$ZrCl$_2$ (Strem Chem., U.S.A.) and *i*Pr(Cp)(Flu)ZrCl$_2$ (Boulder Sci., U.S.A.) were purchased and used as received. Modified methylaluminoxane (MMAO, Type-4, 6.4 wt% Al, Akzo, U.S.A.) was used without further purification. The cycloolefins such as norbornene was purchased and used after purification and drying. The commercial cycloolefin copolymer (ethylene/tetracyclododecene; E/TCD) received from Mitsui Chemical Co.

Copolymerization [7]

In glass reactor were introduced sequentially the proper amounts of toluene, cycloolefins and MMAO solutions and then the system was saturated with ethylene. With a continuous flow of ethylene, the polymerization was initiated by injecting toluene solution of metallocene. After a fixed time, the reaction mixtures were poured into the HCl-methanol solution with vigorous stirring. The precipitated polymer was filtered and washed with a plenty of methanol followed by drying under vacuum.

Characterization

The composition of the produced polymer was analyzed with ^{13}C-NMR (Varian, Unity, 500 MHz). The glass transition temperature (T_g) was estimated with DSC (TA 10). The transmission of UV-visible light for polymer film was measured with UV-Visible Spectroscopy (Shimatsu/UV-1201). The refractive index of the polymer product was measured with prism coupler (Matricon 2010). The surface roughness was measured with AFM (PSIA X-10).

RESULTS AND DISCUSSION

The copolymerization of ethylene(E) and cycloolefins such as norbornene (NB) was conducted with metallocenes such as Cp_2ZrCl_2(**1**), *rac*-Et(Ind)$_2$ZrCl$_2$(**2**) as well as iPr-(Cp)(Flu)ZrCl$_2$(**3**) and MAO cocatalysts. The results are shown in Table 1.

In the E/NB copolymerization, the catalyst activity of (**3**) was higher than that of (**1**) and (**2**).

TABLE 1 Effect of Norbornene Feed Ratio on Ethylene/Norbornene Copolymerization Initiated with Various Metallocenes and MMAO Cocatalyst

Cp_2ZrCl_2				*rac*-Et$(Ind)_2ZrCl_2$				*i*Pr(Cp)(Flu)$ZrCl_2$			
[NB]/[E]	Act[a]	Tg (°C)	Tm (°C)	[NB]/[E]	Act[a]	Tg (°C)	Tm (°C)	[NB]/[E]	Act[a]	Tg (°C)	Tm (°C)
0	1714	n.d.	133.4	0	2163	n.d.	133.4	0	325	n.d.	132.0
1	207	2.06	n.d.	5	2081	52.4	n.d.	5.0	1759	101.0	n.d.
3	53	31.3	n.d.	7.5	1265	115.5	n.d.	7.5	2469	117.2	n.d.
4	49	34.5	n.d.	10	675	131.2	n.d.	10	3057	162.2	n.d.
5	43	36.5	n.d.	20	525	164.5	n.d.	20	2334	198.5	n.d.

Polymerization condition: [Zr] = 2.5×10^{-5} mol/L, [Al]/[Zr] = 3000, 40°C, 1 atm, 1 hr.
[a]Activity: kg-Polymer/mol-Zr · h · atm.
n.d.: Not detected.

The catalyst activity of (**2**) decreased with addition of NB as comonomer. On the other hand, the catalyst activity of (**3**) increased with addition of NB as comonomer which due to the larger angle and lower steric hindrance of catalyst geometry (Ligand-Zr-Ligand).

By the incorporation of NB in copolymer, Tg of copolymer became higher. The Tg of E/NB copolymer obtained with (**3**) increased up to 190°C.

The characteristics of the commercial copolymer (ethylene/tetracyclododecene copolymer, E/TCD) and obtained copolymer (ethylene/norbornene copolymer, E/NB) were given in Table 2, which

TABLE 2 Characteristics of the Commercial and Synthesized Cycloolefin Copolymers.

	Tg (°C)	Cyclic monomer mole fraction (%)	Light transmission (%)	Refractive Index TE mode	Refractive Index TM mode
Commercial COC (E/TCD)	70	20.0	91	1.5342	1.5339
	80	21.4	91	1.5361	1.5360
	105	28.8	90	1.5405	1.5402
	129	29.6	90	1.5431	1.5428
	145	32.2	90	1.5421	1.5426
Synthesized COC (E/NB)	83	40.1	92	1.5310	1.5311
	137	48.4	92	1.5328	1.5325
	162	61.5	92	1.5331	1.5325
	190	68.5	92	1.5328	1.5321

shows the glass transition temperature, cyclic monomer mole fraction, light transmission and refractive index.

Thermal and dimensional stability are critical enabling a film to withstand the high temperatures required for deposition of barrier coatings and ITO coatings and for the multilayer device to be able to withstand cycling during its manufacture [8]. The variation of Tg with cyclic monomer content for the TCD is bigger that that of the NB, which implies that the polycyclic unit, TCD, which has bulkier structure that the bicyclic unit NB, leads to a restricted local motion of chain segments. The T_g of E/TCD copolymer increased up to 145℃ at lower content of TCD (32.2 mol%). While, T_g of E/NB copolymer was 83℃ at higher content of NB (40.1 mol%).

The clarity of the film is important for bottom-emissive displays where one is viewing through the film and a total light transmission (TLT) of $>85\%$ over $400 \sim 800$ nm coupled with a haze of less than 0.7% or typical of what is required for this application. Birefringence of these COC has very low values (below 0.001). These COC are more suitable for LCDs.

The UV-visible spectra of the COC product had been examined with the variation of polymer composition and the results are shown in Figure 1.

The TLT of copolymers was above 90% over $300 \sim 900$ nm. The transmission of E/NB copolymer was higher than that of E/TCD at lower wavelength (below 300 nm).

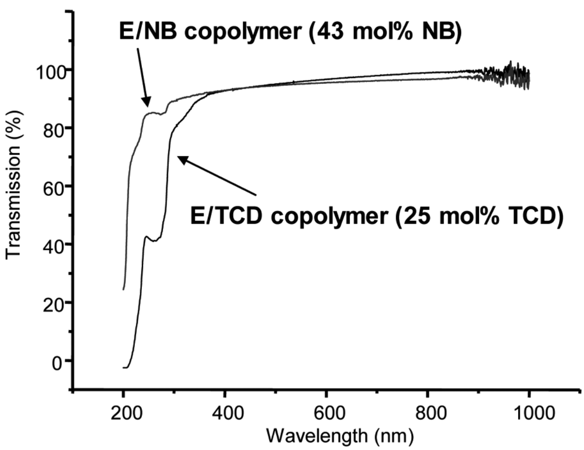

FIGURE 1 Percentage transmission of COC; E/NB and E/TCD copolymer.

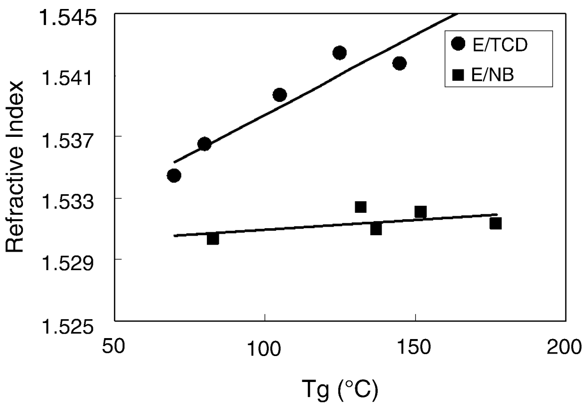

FIGURE 2 Refractive index of copolymers at various copolymer compositions.

The refractive index (RI) of COC film had been investigated with the variation of polymer composition and the experimental results are shown in Figure 2.

The RI of E/TCD copolymer was slightly higher than that of E/NB copolymer. The RI of E/NB copolymer could not changed increasing NB contents, however, the RI of E/TCD copolymer increased with increasing of TCD contents. The thermo optic coefficient (TOC) was calculated from RI of copolymers at various temperatures. TOC values ($\approx 3.0 \times 10^{-5}/^{\circ}C$) of COC were lower than other amorphous polymer.

The surface smoothness and cleanliness of the flexible substrates are essential to ensure the integrity of subsequent layers such as barrier and conductive coatings [8]. The COC film was prepared by hot press method and the surface roughness was measured with AFM (Figure 3).

Combining numerous measurements to deliver large areas ($20\,\mu m \times 20\,\mu m$) reveals low surface peak heights with resultant surface roughness values (Ra) of less than 2 nm (rms roughness = 1.7 nm). Such levels are necessary to ensure good integrity for subsequent barrier layers, conductive coatings and pixel array resolution.

CONCLUSIONS

In ethylene/norbornene copolymerization, by the incorporation of norbornene in copolymer, the glass transition temperature (Tg) of copolymer became higher. The Tg of copolymer increased up to 190°C. The transmission of copolymers was above 90% over $300 \sim 900$ nm. The refractive index of E/NB copolymer could not

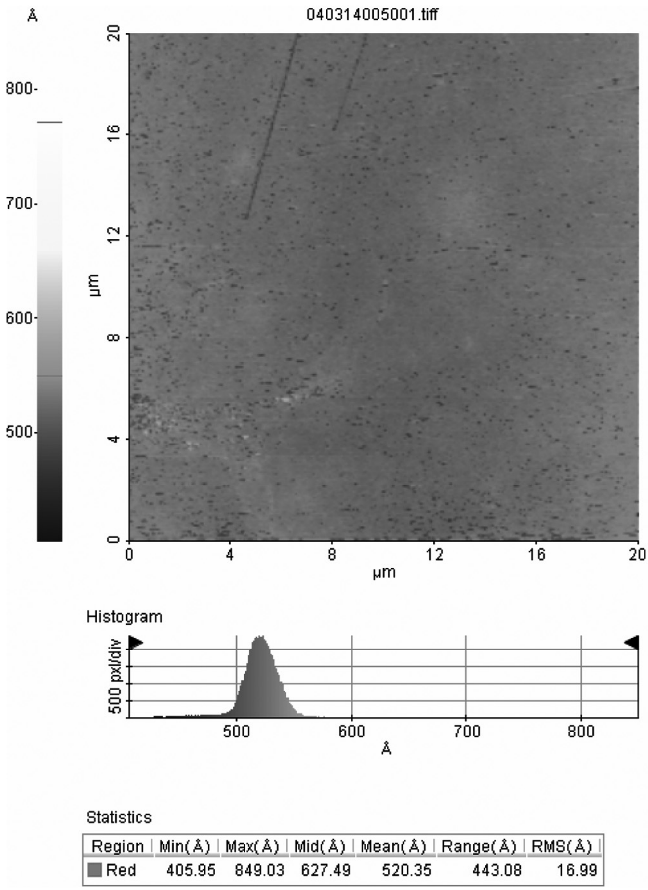

FIGURE 3 Surface smoothness of E/NB copolymer film.

changed increasing NB contents, however, the RI of E/TCD copolymer increased with increasing of TCD contents. The E/NB copolymer has very low thermo-optic coefficient and birefringence and that film has very smooth surface. These copolymers are more suitable for LCDs substrates.

REFERENCES

[1] Allen, K. & Mentlley, D. E. (2003). Flexible Displays-Emerging Display Technologies, iSuppli/Stanford Resources.
[2] Silkkerveer, P. J. (2003). *Information Displays*, *3*, 20.
[3] Khanarian, G. (2001). *Opt. Engin.*, *40*, 1024.

[4] Kaminsky, W. & Spiedhl, R. (1989). *Makromol. Chem. Phys.*, *190*, 515.
[5] Thayer, A. M. (1995). *Chem. Eng. News*, *11*.
[6] Shin, J. Y., Park, J. Y., Liu, C., He, J., & Kim, S. C. (2005). *Pure Appl. Chem.*, *77*, 801.
[7] Lee, D. H., Choi, Y. Y., Lee, J. H., Park, Y. S., & Woo, S. S. (2001). *e-Polymers*, 019.
[8] MacDonald, W. A. (2004). *J. Mater. Chem.*, *14*, 4.