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Review

Industrialization and application development of cyclo-olefin polymer

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Abstract

Since its establishment in 1950, ZEON Corporation has contributed to the advancement of Japanese industry, as a chemical company focused on the manufacture of synthetic rubber. Some of our specialty rubber products hold 40–70% of the worldwide market share. ZEON's exclusive technology is the source of a number of breakthroughs and continues to contribute to today's polymer industry. In order to maintain the position as a leading company in synthetic rubber business, ZEON strategically planned industrialization of polyisoprene rubber to compete with natural rubber. The main raw material for polyisoprene rubber is isoprene monomer, which was not yet available on the market. ZEON had to first develop isoprene extraction technology from C5 fraction of naphtha successfully. The issue then was C5 fraction contained only 10–15% of isoprene monomer. In order to reduce the total isoprene monomer cost, we had to utilize other components. The components are 1,3-pentadiene (1,3-PDE), dicyclopentadiene (DCPD), and others. So along with polyisoprene business, we launched the 1,3-PDE resins business and DCPD resins business for adhesives and traffic paints in 1970. To fully utilize these extracted components, we still had to develop unique products using residual 1,3-PDE and DCPD. Our cyclo-olefin polymer business was born from this basic strategy to fully utilize those components. This report discusses the development and current status of cyclo-olefin polymer and its precision molding business, including optical film business, realized by the ZEON's comprehensive utilization of C5 fraction.

Keywords: Cyclo-olefin polymer; ROMP; Hydrogenation; Optical properties; Molding process

1. Development of cyclo-olefin polymers

In 1983, as a result of our experimental work with norbornene polymer, we discovered cyclo-olefin polymer synthesized from ring-opening polymerization. This polymer was difficult to mold because of its extremely low heat stability and low melt flow rate. We thought in order to prevent the color change during molding, hydrogenation of double bonds in polymer main chain could be effective. Beyond our expectation, we discovered that glass clear plastics was created when the polymer was hydrogenated [1].

The polymer structure after hydrogenation was undoubtedly cyclic olefin, and therefore we named it cyclo-olefin polymer (Fig. 1).

2. Cyclo-olefin polymer production process

Norbornene ring-opening metathesis polymerization and an additional polymerization process represent the current production processes for cyclo-olefin polymer. Combinations of different monomers can produce polymers with varying structures and properties.

ZEON's cyclo-olefin polymer is an amorphous polyolefin with a bulky ring structure in the main chain, based on DCPD as the main monomer saturating the double bond in norbornene ring-opening metathesis polymer with a substituent (R) by hydrogenation. Improved transparency and heat resistance (glass transition temperature, T_g) result from changing the substituent (R), with suitability for various molding conditions being controlled through molecular weight and distribution. T_g can be enhanced by forming the ring structure that connects R_1 and R_2 ([2], Table 1).

In addition to conventional norbornene ring-opening metathesis polymerization, and hydrogenation, we also apply process similar to semiconductor chemical products. These processes are: a smaller than 100 μm particles

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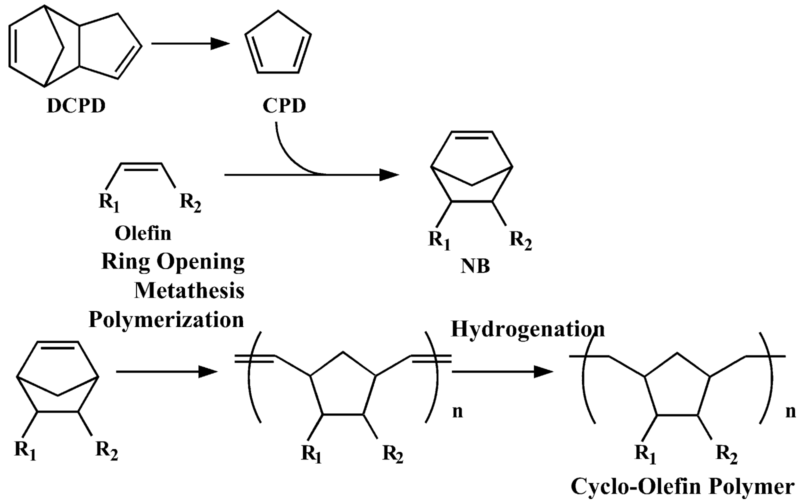
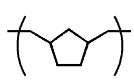
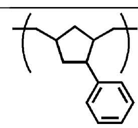
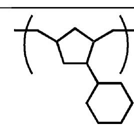
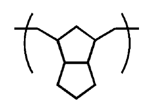
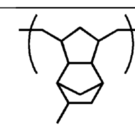
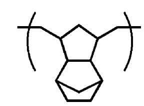


Fig. 1. Cyclo-olefin polymer synthesis.

Table 1
Properties of cyclo-olefin polymer synthesized by ring-opening metathesis polymerization and hydrogenation

Cyclo-olefin polymer	A	B	C	D	E	F
Chemical structure						
Crystallinity	Crystalline	Amorphous	Amorphous	Amorphous	Amorphous	Amorphous
Transparency	Opaque	Transparent	Transparent	Transparent	Transparent	Transparent
T_g (°C)	Tm: 134	75	86	95	150	162

removing process, a residual metal content reduction process, and a residual chemical substances removal process. Finally, the products emerge from the closed process are handled in clean rooms (Fig. 2).

3. Characteristics of cyclo-olefin polymers

ZEON has two cyclo-olefin polymer products: ZEONEX®, marketed in 1991, and ZEONOR®, marketed in 1998. Both

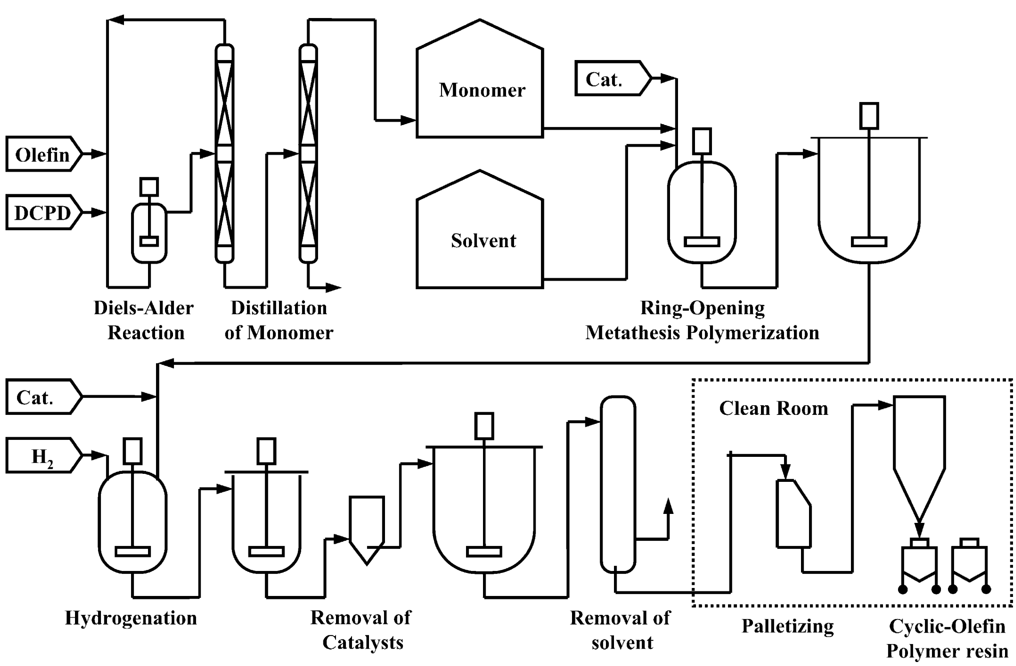


Fig. 2. Cyclo-olefin polymer manufacturing process.

Table 2
Characteristics comparison of cyclo-olefin polymer

Properties	ZEONEX® 480R	PC[a] Optical grade	PMMA[b] Optical grade		
(1) ZEONEX®					
Light transmittance (t: 3 mm) (%)	92	90	92		
Refractive index (n_D)	1.525	1.59	1.49		
Abbe's number	56	30	58		
Photoelastic constant (cm^2/dyne)	6.5×10^{-13}	72×10^{-13}	6.0×10^{-13}		
Specific gravity	1.01	1.20	1.19		
Water absorption (23 °C, 24 h) (%)	<0.01	0.2	0.3		
Glass transition temperature (°C)	140	145	105		
Heat distortion temp. (18.6 kgf/cm^2) (°C)	123	121	90		
Tensile strength (MPa)	63	63	72		
Tensile modulus (MPa)	2400	2400	3000		
	ZEONOR®			PC	PP[c]
	1020R	1420R	1600R		
(2) ZEONOR®					
Light transmittance (t: 3 mm) (%)	92	92	92	89	Opaque
Specific gravity	1.01	1.02	1.03	1.2	0.90–0.91
Water absorption (23 °C, 24 h) (%)	<0.01	<0.01	<0.01	0.15	<0.01
Heat distortion temperature (18.6 kgf/cm^2) (°C)	101	136	161	132	54
Tensile strength (MPa)	53	61	73	66	31–41
Tensile modulus (MPa)	2100	2400	2700	2100	1100–1500
Tensile elongation (%)	100	20	10	110	100–600
Izod impact strength (3.2 mm, Notched) (kJ/m)	6	3	3	75–100	2–5
Dielectric constant (1 MHz)	2.3	2.3	2.3	3	2.3
Dielectric loss tangent (1 MHz)	0.0002	0.0002	0.0002	0.01	0.0003

[a] PC: polycarbonate.
[b] PMMA: polymethylmethacrylate.
[c] PP: polypropylene.

exhibit such properties as high transparency, low specific gravity, low water absorbency, good insulating property, low birefringence, high heat resistance, and excellent precision molding. The essential difference between these two products is that ZEONEX® is expected to be used for optical products, such as optical lenses and prisms for fourth-decimal-place refractive index accuracy, while ZEONOR® provides improved molding product strength by reinforcing mechanical strength and elongation in tension for second-decimal-place refractive index accuracy at reduced cost to support a wider range of applications (Table 2).

3.1. Optical properties

Light transmission in the visible light range (400–800 nm) is as high as for polymethylmethacrylate (PMMA), exhibiting 90% or more throughout the whole visible light range. The refractive index of cyclo-olefin polymer is 1.53 and is placed midway between PMMA and polycarbonate (PC). Its Abbe's number of 56 is greater than PC and closer to PMMA. It exhibits the characteristics of a ring structure polymer with a relatively great Abbe's number considering its refractive index, giving this material a small chromatic aberration. Since its photoelastic coefficient is one less figure than PC and closer to PMMA, molding is easier for optical components with small birefringence (Fig. 3).

3.2. Heat resistance

The glass transition temperature varies by product type. ZEONEX® with T_g of 140 °C demonstrates 122 °C of deflection temperature under load, which is almost the same as PC and higher than PMMA by over 20 °C. Therefore, molded products made with this material can be used across a wide range of temperatures.

3.3. Electric property

Over a broad frequency range up to 1 GHz, it exhibits a low dielectric constant and dielectric dissipation tangent, with no fluctuation against changes in temperature and humidity. It also demonstrates an excellent insulation property.

3.4. Other properties

Furthermore, cyclo-olefin polymer is a unique polymer. Its volatile chemical content, which causes molecular contamination, is extremely low at 1/200–1/300 compared to conventional polymers, and it also exhibits a dry-down (desorption) rate as fast as that for stainless steel [3], and extremely low residual metal. Its only shortcoming is the possible occurrence of solvent cracks when touched by greasy hands because of residual stress. For applications

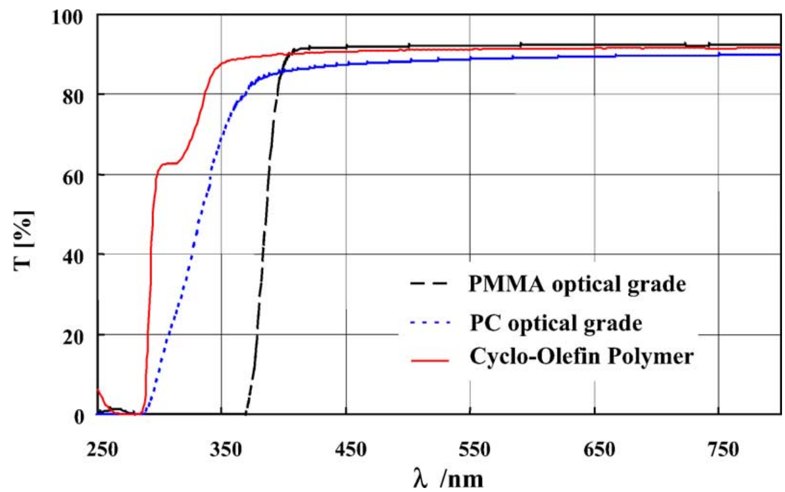


Fig. 3. The light transmittance of cyclo-olefin polymer.

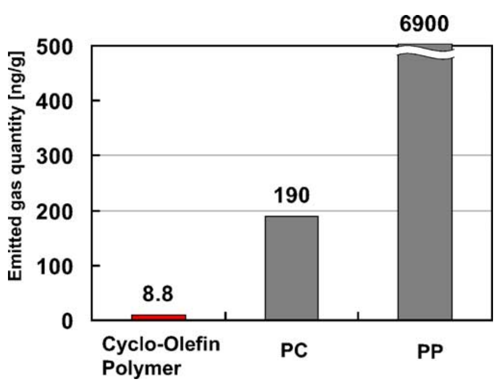


Fig. 4. Volatile chemical content of cyclo-olefin polymer.

requiring direct handling, the residual strain must be eliminated at the time of molding (Figs. 4 and 5).

4. Molding processes

Cyclo-olefin polymer features outstanding molding processability. Most molding processes can be applied, including injection molding, extrusion molding, press molding, blow molding, and calendar molding. Since cyclo-olefin polymer exhibits high fluidity and facilitates the precise transferring of submicron patterns, information patterns for digital home appliances, which will come into wider everyday use, can be precisely transferred and molded, and a wider range of applications is therefore being developed.

Use of a nitrogen seal is recommended to prevent the yellowish stain that can be produced at the time of molding due to the “burn” caused by exposure of cyclo-olefin polymer to oxygen at high temperatures. Since water absorbed by pellet surfaces or air entrapped in pellets may cause color defects or undesirable coloration, it is recommended that the material be dried at temperatures around 20 °C lower than glass transition temperature for 4–12 h [4,5] prior to molding. As mentioned above, it is important to control molding conditions because subjecting molded products to residual stress may cause solvent cracks or breaks induced by grease from hands.

Injection molding molded products can be reproduced to nearly precise specifications due to the small molding shrinkage of the cyclo-olefin polymer, approximately 0.3–0.5%. Please see [2,4,5] for details.

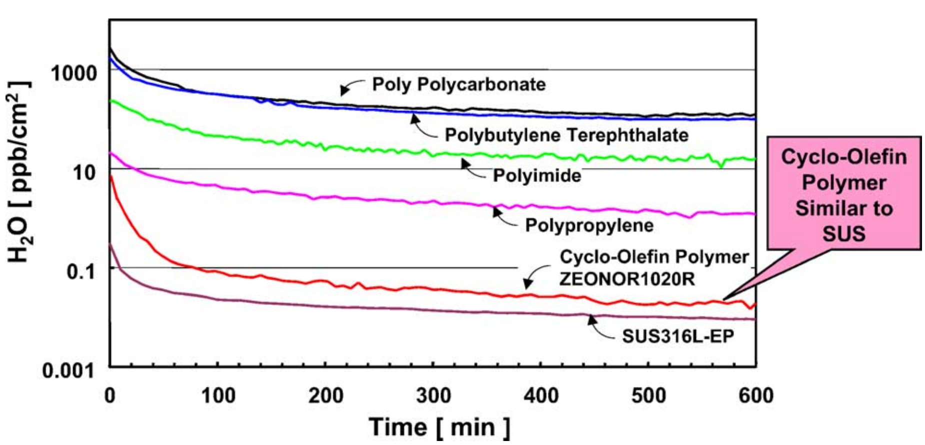


Fig. 5. Water drydown property comparison based on API-MS [3].

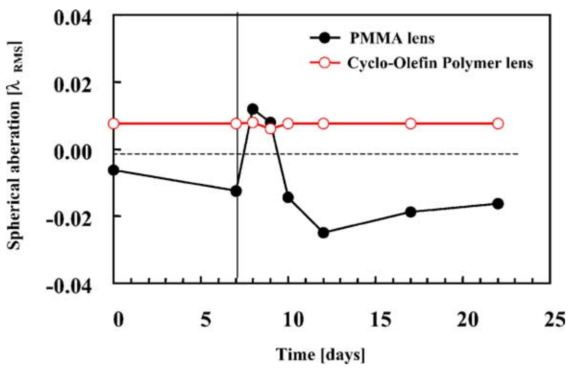


Fig. 6. Changes of spherical aberration of optical lenses under high humidity and high temperature condition.

5. Applications of cyclo-olefin polymer

Cyclo-olefin polymer resins are used in a variety of applications according to the above-mentioned properties and costs.

5.1. Optical applications for lenses and prisms

These products must exhibit stable optical properties under diverse environments at varying temperatures and humidity levels. ZEONEX® properties such as excellent transparency, high heat resistance, low water absorbency, stable and guaranteed refractive index, and low birefringence are fully utilized in these applications. ZEONEX® has become the de-facto standard material, especially for camera lenses/prisms, lenses for cameras incorporated into mobile phones, pick-up lenses, and Fq lenses for laser beam printers. As an illustrative example, Fig. 6 compares spherical aberration with PMMA showing the time transition under the following condition: After allowing optical lenses to absorb water under high temperature and humidity for a week, they are returned to normal room temperature and humidity. Changes in spherical aberration of PMMA lenses are rather drastic since they absorb and release water depending on changes in environment conditions. Moreover, they never recover their original spherical shape even when returned to normal temperature and humidity. Lenses by ZEONEX®, in contrast, exhibit almost no such changes, and they demonstrate high reliability.

5.2. Medical and food container use

With excellent transparency, low impurity content, low water permeability, low water absorbency, and strength comparable to glass, cyclo-olefin polymer is used in such applications as medical vials, syringes, optical lab test cells, syringes pre-filled with pharmaceutical content, and packaging (Press Through Pill Pakage) that also serves to protect tablet pharmaceuticals. Cyclo-olefin polymer is especially suitable for use in medical devices that undergo autoclave sterilization at 121 °C. Recently, many problems have been identified relating to the impact on human health of substances that are suspected of disrupting endocrine action. Since cyclo-olefin polymer does not contain such substances and has a low outgas property (low content of extremely volatile chemicals). Thus, the ZEONOR® brand is now well recognized and used as a clean material for infant feeding bottles, tableware for school children.

5.3. Semiconductors

Semiconductor applications take advantage of the same cyclo-olefin polymer characteristics that make the product practical for medical uses, including its status as a clean material with low degassing, low metal content, and good dry-down property (a desorption rate as fast as that of metals). Therefore, cyclo-olefin polymer began to appear in silicone wafer containers used in production and shipment, and in materials for clean room interiors as an important component in semiconductor manufacturing in response to the trend for increasing refinement.

5.4. Liquid crystal display components

Liquid crystal displays (LCDs) are replacing conventional cathode-ray tubes (CRTs) in the IT industry, with rapid growth in demand in large markets for such everyday applications as mobile phones, car navigation systems, laptop computers, monitors, and LCD TVs. These LCDs rely on optical components such as light guide plates and diffusers that evenly disperse light, polarizing plates that control the screen, brightness-improving films that make the screen more brilliant, and wide viewing films that broaden the viewable angle for screens. Cyclo-olefin polymer characteristics, such as transparency, low birefringence, lightweight, and a precision molding property, are highly suitable for precision-molded components that include light guide plates and diffusers. More components made with cyclo-olefin polymer continue to be used in personal computers and LCD TVs with large-size screens. The use of ZEONOR® particularly for light guide plates in mobile laptop computers is becoming the de-facto standard because of its lightweight, precision-molding properties.

6. Production of optical films by the sheet extrusion process

We successfully developed cyclo-olefin polymer optical film produced through the sheet extrusion process in October 2002, and began to widely provide it for its application in LCDs [6,7]. ZEONOR FILM® is produced with an exclusive polymer design by a sheet extrusion process previously thought to be utterly impossible for optical uses, because of the difficulty of controlling thickness and eliminating streak-like flaws (die lines) on the surface of film caused by die surface imperfections, die deposits or foreign particles. The sheet extrusion process excels in cost performance compared to the conventional solution cast process, and it is expected to contribute to the future growth of the LCD market. The use for LCDs, especially, requires strictly precise thickness in order to prevent unevenness in phase difference. Whereas conventional products were able to achieve accuracy of ±2 μm at a thickness of 100 μm, ZEON successfully achieved an accuracy of ±1 μm by reconsidering the formation of cyclo-olefin polymer, its molecular weight, and its distribution. Die lines on our products are also within just 30 nm, nearly the same measurement as that for the conventional solution cast process. As LCD screens increase in size and brightness, the requirements for optical film precision is expected to rise. We plan to further improve ZEONOR FILM® resins, providing the market with the ultimate optical film (Fig. 7).

6.1. Optical films

Cyclo-olefin polymer is starting to enjoy wide application in such products as polarizing plate protection films, broadband 1/4 wavelength plates, retardation films for VA, and plastic substrates, all of which take advantage of its high transparency, optical isotropy, small light elasticity, small wavelength dispersion in birefringence, extremely low water absorbency and excellent dimensional stability, creation of birefringence by elongation, and high mechanical strength. Information shown in parentheses summaries areas in which the use of ZEONOR FILM® could improve performance. For instance, cyclo-olefin polymer's properties of dimensional stability, low light elasticity, and optical isotropy would be especially advantageous for polarizing plates protection films and plastic substrates. Superior performance in retardation films for VA mode LCDs and broadband 1/4 wavelength plates for reflective TFT-LCDs could also be achieved by taking advantage of intentionally

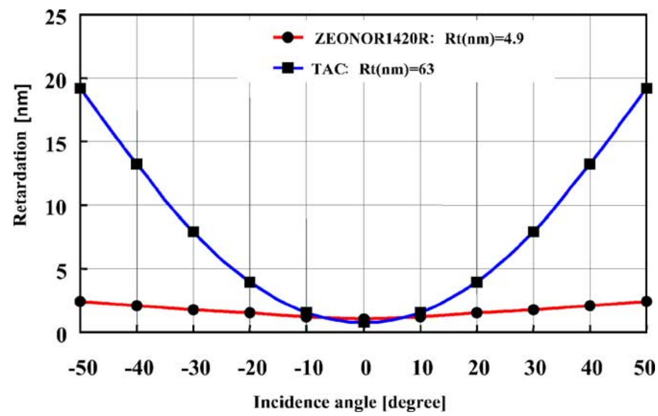


Fig. 8. The incidence angle dependence of the retardation of ZONOR film.

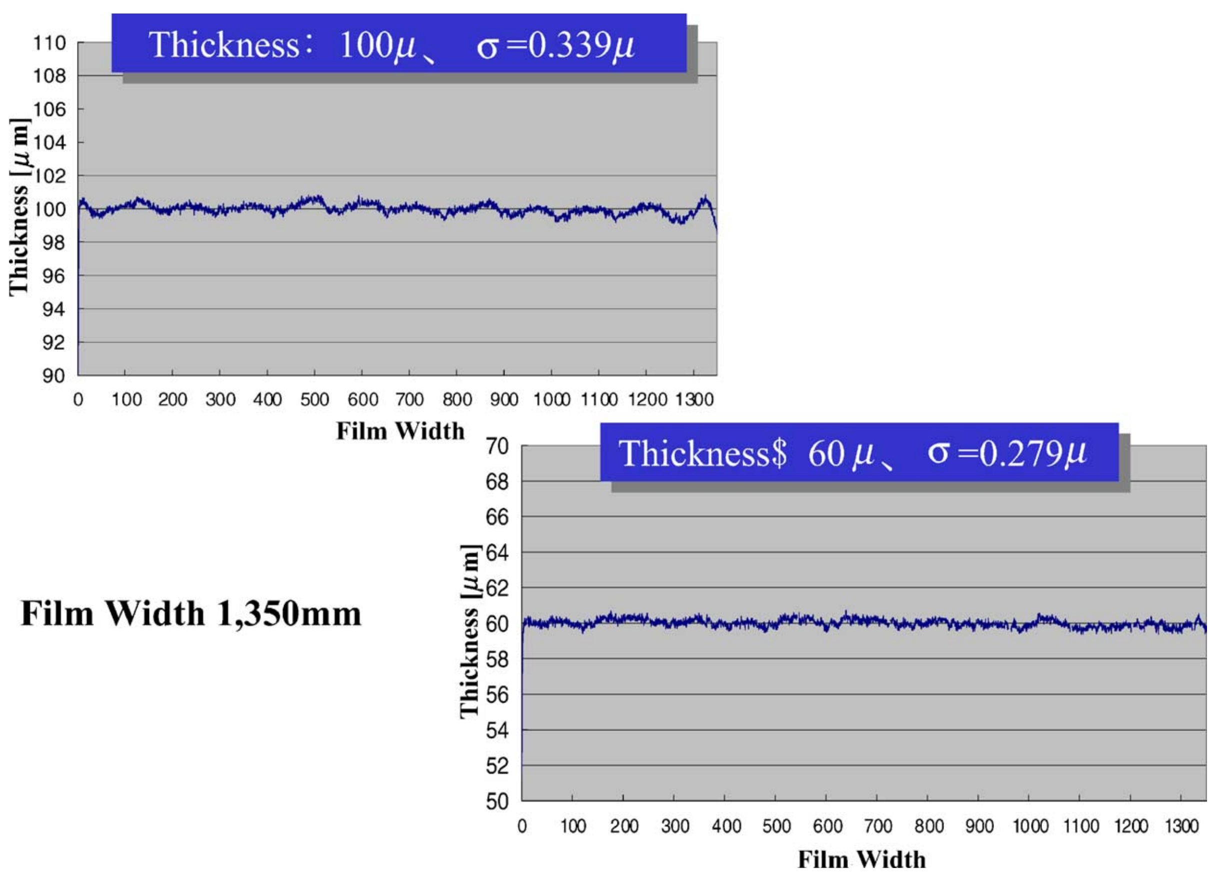


Fig. 7. Thickness of cyclo-olefin polymer film.

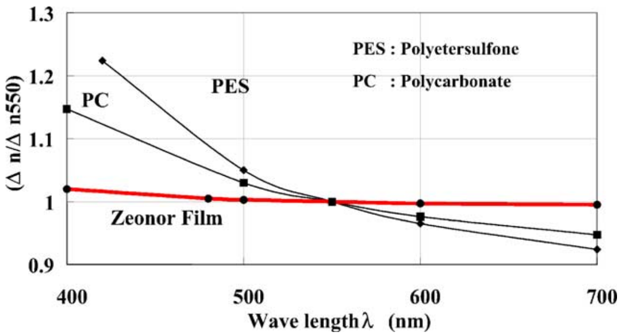


Fig. 9. ZEONOR film wave dispersion properties.

applying elongation to produce birefringence, as well as such cyclo-olefin polymer properties as low light elasticity and small dispersion (Figs. 8 and 9).

7. Conclusion

Twelve years have passed since ZEON, the pioneer in cyclo-olefin polymer development, first marketed it as an optical specialty resin and began releasing applications in 1991. Today, the plastic ZEON introduced to the world is finally receiving its due recognition as a leading optical material with uniquely effective properties supporting the dramatic dissemination of compact cameras, digital cameras, and laser beam printers, and the exploding popularity of CDs and DVDs utilizing laser beams, laptop computers, car navigation systems, mobile phones with color screens, and LCD TVs. A new paradigm is emerging in the display industry: cathode-ray tubes will soon be replaced by LCDs, organic EL displays, and PDP flat panel displays. Although cyclo-olefin polymer consumption remains relatively limited and is therefore still categorized as a specialty polymer, its applications are gradually expanding even as costs come down and new functions are added. Our current cyclo-olefin polymer production capacity is 5300 t per year, with a new plant expansion under construction increasing production to 10,300 t per year. The initial development of applications for insulation material appears promising, as cyclo-olefin polymer insulation material with good high-frequency insulating property is well suited for the widening use of broadband in the 21st century. The market for cyclo-olefin polymer is growing every year because of its excellent properties, primarily in optical applications. We believe the demand for plastic cyclo-olefin polymer will increase by thousands of tons, and we eagerly anticipate the day when the exciting potential of this material will be fully realized.

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