# Influence of Chain Microstructure on Ethylene–Norbornene Copolymer Film Properties

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**ABSTRACT:** The effects of copolymer composition, copolymer composition distribution, and polar α-olefin incorporation on transparency, refractive index, and hydrophilicity of resultant ethylene–norbornene copolymer films were investigated. It has been found that the transparency is mainly determined by the copolymer composition distribution. The samples having uniform compositions gave better transparency. However, the copolymer composition distribution had little effect on refractive index. The refractive index increased linearly with increasing norbornene content. Furthermore, the incorporation of polar α-olefin with long carbon chain improved refractive index and hydrophilicity of the films. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 707–710, 2011

**Key words:** ethylene–norbornene copolymer; polar α-olefin; composition drift; transparency; refractive index; hydrophilicity

## INTRODUCTION

Cyclic olefin copolymers (COCs) are a promising type of optical materials for their excellent performance in applications. The effects of copolymer composition, sequence distribution, and molecular weight on thermal properties of COC have been studied by many groups in the past decade.[1–17] However, there are few reports on the relationships between chain microstructure and optical/surface properties. Ou and Hsu[18] prepared COC/$SiO_2$ nanocomposites containing 1, 5, 10, and 15 wt % $SiO_2$ nanoparticles through solution blending and studied addition of $SiO_2$ on light transparency of composites. The results showed that the light transparency of composites was as high as 85% even though the $SiO_2$ content was up to 10 wt %. Shiono et al.[19] investigated the copolymerization of norbornene with higher 1-alkene (1-decene, 1-octene, and 1-hexene) and found transparency of the copolymer increased with increasing length of 1-alkene. Ban et al.[20] reported that introducing styrene into ethylene–norbornene copolymer could reduce birefringent magnitude of the COC. The birefringence of COC was even close to zero when the styrene content was controlled at an optimum value. The transparency of obtained terpolymer films was also as high as that of PMMA or PC.

In this work, the effects of copolymer composition, copolymer composition distribution (CCD), molecular weight, and polar α-olefin (P) incorporation on the optical and surface properties of ethylene(E)–norbornene(NB) copolymer were studied. We characterized the transparency, refractive indexes, and contact angles of COCs and discussed the relationships between chain microstructure and these properties.

## EXPERIMENTAL

### Materials

The preparation of the E-NB copolymer and E-NB-P terpolymer samples used in this work had been reported in literature.[21–24] The composition, molecular weight, and PDI data were cited from the sources.

### Measurement of the light transparency

The samples were dissolved in toluene with 1 wt % concentration and then poured into a glass mold to volatilize the solvent under atmospheric temperature and pressure. After the film was formed, it was

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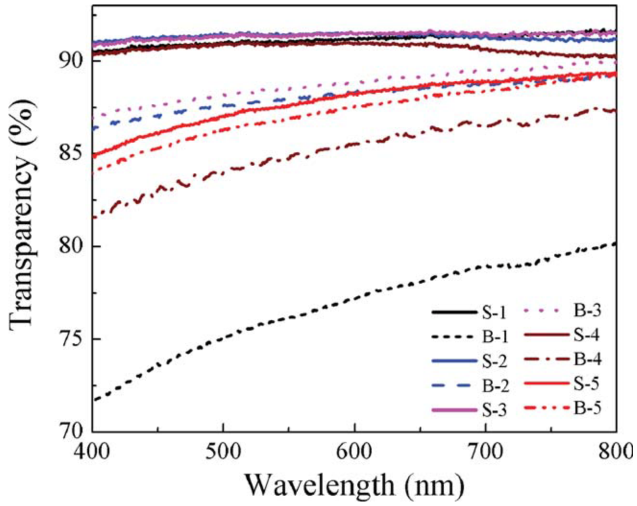


**Figure 1** UV–VIS spectra of the E-NB copolymers prepared by batch process and semibatch process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dried at 80°C under vacuum for 8 h. The light transparency of the film was measured using UV–VIS spectrometer (Varian Cary-100) with wavelengths ranging from 200 to 800 nm.

### Measurement of the refractive index

The film was prepared by spin coating 1 wt % polymer solution in toluene onto silicon wafer and dried at 80°C under vacuum for 8 h. The refractive indexes were determined by an ellipsometer (J.A.Woollam M-2000).

### Measurement of the contact angle

Polymer films used for measuring contact angles were prepared in following method: pressing polymer powders to films with the molding test press (GT 7014-A50C) under 180°C and 150 bar. After dried 8 h at 80°C under vacuum, the contact angle measurement (water, 298 K) was carried out using the video-based optical contact angle measuring instrument (OCA 20, Dataphysics), and the average of five tests was used.

**TABLE I**
**Effects of Copolymer Composition and Its Distribution on the Transparency and Refractive Index of E-NB Copolymers**

| Entry | NB content in copolymer (mol %) | Polymerization process | Transparency (%) (at 550 nm) |
|---|---|---|---|
| S-1 | 18.3 | Semibatch | 91.1 |
| B-1 | 20.4 | Batch | 76.1 |
| S-2 | 34.7 | Semibatch | 91.4 |
| B-2 | 34.1 | Batch | 87.9 |
| S-3 | 44.1 | Semibatch | 91.4 |
| B-3 | 43.6 | Batch | 88.4 |
| S-4 | 52.8 | Semibatch | 90.9 |
| B-4 | 53.3 | Batch | 84.7 |
| S-5 | 59.1 | Semibatch | 87.6 |
| B-5 | 59.8 | Batch | 86.9 |

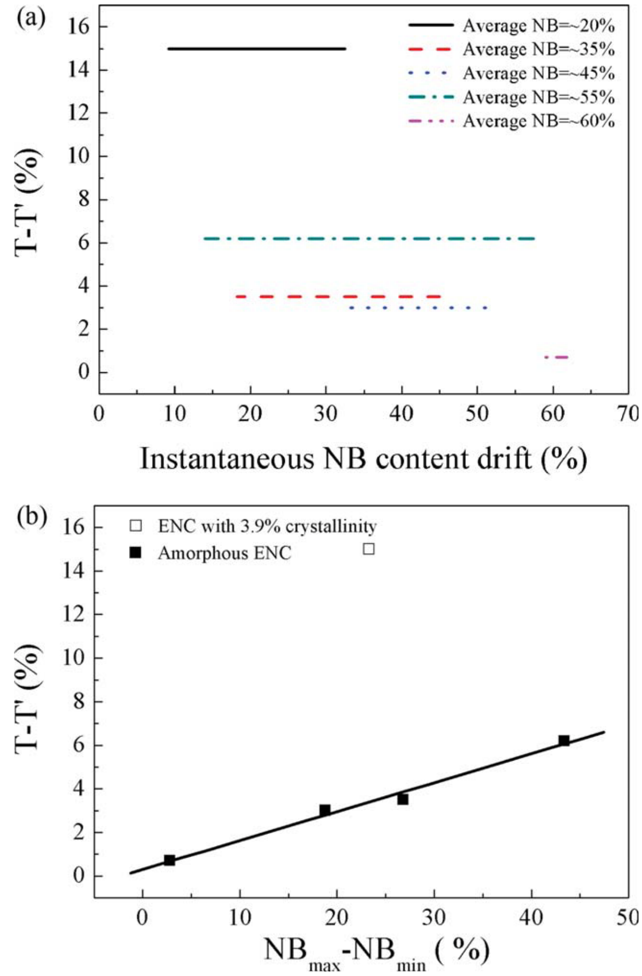


**Figure 2** Effect of NB content drift on the transparency of E-NB copolymers. ($T - T'$: The transparency difference between uniform composition copolymer and broad composition distribution copolymer with the same average NB content; $NB_{max}$: NB content of copolymer fraction with instantaneous maximum NB composition drift based on the model calculation[23]; $NB_{min}$: NB content of copolymer fraction with instantaneous minimum NB composition drift based on the model calculation[23]). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## RESULTS AND DISCUSSION

To study the effects of copolymer composition and its distribution (CCD) on optical properties of E-NB copolymers, the transparency and refractive index of E-NB copolymers with five different NB contents (20, 35, 45, 55, and 60 mol %) were compared. These copolymers were obtained from our previous work.[23]

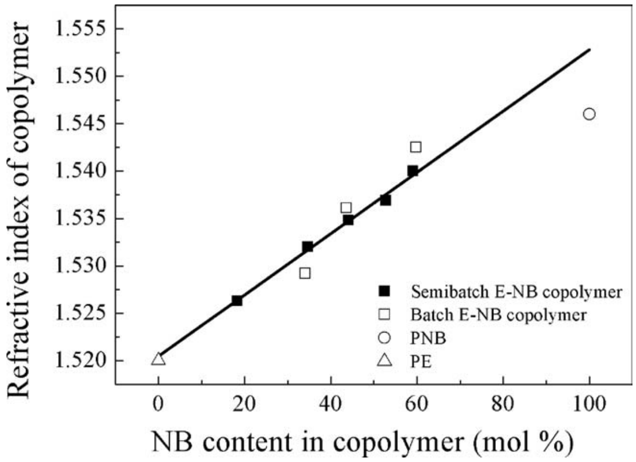


**Figure 3** The relationship of NB content and refractive index of E-NB copolymers.

There were two kinds of the samples for each composition: one with uniform composition prepared by semibatch process and the other with broad CCD prepared by batch process. In the batch process, all NB was added to the reactor before polymerization. In the semibatch process, a part of NB was charged before polymerization and the additional NB was continuously added during polymerization based on the designed NB feeding profile using a peristaltic pump. The UV–VIS spectra of these samples were shown in Figure 1. In the visible light region (400–800 nm), the light transmittance increased with the wavelength. We used the value at 550 nm to denote the transparency of the film. The results were summarized in Table I. It could be seen that CCD has significant effects on the transparency. For the same NB content, the transparency of the semibatch sample with uniform composition was better than that of the batch sample with broad CCD. This was also clearly seen from Figure 2. In this Figure, $T - T'$ meant the transparency difference between uniform composition copolymer and broad CCD copolymer having the same average NB content. The instantaneous NB content drifts were estimated by the model calculation combined with the thermal properties.[23] Their values denoted the breadth of CCD. The larger this value is, the broader the CCD is. It could be seen that the transparency decreased with increasing CCD, especially when a significant level of crystallinity was present (Entry B-1, its crystallinity 3.9%). For the uniform samples, the transparency data of the copolymers having different NB contents were similar, as high as ∼ 91%. Therefore, CCD should be the main factor to determine the uniformity of the E-NB copolymer films.

For E-NB copolymers, it had been reported that the refractive index increases with the NB content.[25] In this work, we examined the effect of CCD on the reflective index and aimed at establishing their quantitative relationship. All the refractive indexes were measured three times, and their average values were used. With an increase in the NB content, the refractive index of the uniform E-NB copolymer linearly increased between those of PE and PNB (see Fig. 3). It was also evident that the broad CCD samples agreed with the same trend as the narrow CCD samples. This finding suggested that the CCD has little effect on the refractive index of the E-NB copolymers.

Moreover, we tried to introduce polar α-olefin to the E-NB copolymer to improve their refractive index, as an alternative to increasing the NB content. Effect of the polar α-olefin incorporation on the optical properties of E-NB copolymer could be seen from Table II. The used polar α-olefin was 3-buten-1-ol, 5-hexen-1-ol, and 10-undecen-1-ol, respectively. Both NB and polar α-olefin contents were similar in the three terpolymers. However, the films of Entry T-1 and T-2 were too brittle to be removed from glass mould possibly because of their low molecular weight and low polar α-olefin content. Further studies demonstrated that films with polar α-olefin content higher than 4 mol % could not be removed due to high adhesion. When the polar α-olefin content was moderate (Entry T-2), the film was successfully removed from the mould and its transparence was thus obtained. Compared to the E-NB copolymers with similar NB contents (Entry C-1, C-2, and C-3 in Table II), the incorporation of polar α-olefin appeared to have little effect on the transparency.

**TABLE II**
**Optical Property and Contact Angle of E-NB Copolymers and E-NB-P Terpolymers with Similar NB Content**

| Entry | Polymer[a] | NB content (mol %) | OH content (mol %) | $M_n \times 10^{-4}$ | Transparency (%) (at 550 nm) | Refractive index | Contact angle (°) |
|---|---|---|---|---|---|---|---|
| C-1 | E-NB Copolymer | 48.6 | 0 | 5.99 | 89.3 | 1.5392 | 99.4 |
| C-2 | E-NB Copolymer | 47.6 | 0 | 11.57 | 88.6 | 1.5338 | 99.1 |
| C-3 | E-NB Copolymer | 48.7 | 0 | 14.26 | 89.7 | 1.5446 | 99.0 |
| T-1 | E-NB-B Terpolymer | 52.7 | 1.8 | 4.32 | – | 1.5381 | 93.6 |
| T-2 | E-NB-H Terpolymer | 52.2 | 2.6 | 15.30/0.97 | 89.2 | 1.5349 | 94.3 |
| T-3 | E-NB-U Terpolymer | 53.4 | 1.8 | 0.74 | – | 1.6025 | 94.7 |

[a] NB, norbornene; E, ethylene; B, 3-buten-1-ol; H, 5-hexen-1-ol; U, 10-undecen-1-ol.

When the polar α-olefin with low carbon numbers (3-buten-1-ol or 5-hexen-1-ol) was incorporated, the refractive indexes of the terpolymers were close to those of the E-NB copolymers having the similar NB contents. However, the introduction of higher polar α-olefin (10-undecen-1-ol) resulted in higher refractive index.

An additional advantage of the polar α-olefin incorporation is to improve the adhesion of polymer materials. The contact angle of the E-NB-P terpolymer should be lower than that of the E-NB copolymer. As shown in Table II, the contact angles of the terpolymer films with 1.8–2.6 mol % OH group were about 5° lower than those of the copolymer films with similar NB contents.

## CONCLUSIONS

In this work, we demonstrated that the films of uniform ethylene-norbornene copolymers had better transparency than that of samples with broad copolymer composition distributions. The transparency reached as high as ~ 91%. Broad copolymer composition distribution showed little effect on the refractive index. The refractive index increased with an increase in the norbornene content. The incorporation of polar α-olefin with long carbon chain could also increase the refractive index.

## References

1. Ruchatz, D.; Fink, G. Macromolecules 1998, 31, 4681.
2. Park, S. Y.; Choi, K. Y.; Song, K. H.; Jeong, B. G. Macromolecules 2003, 36, 4216.
3. Park, S. Y.; Choi, K. Y.; Jeong, B. G. Ind Eng Chem Res 2005, 44, 6496.
4. Bergström, C. H.; Vänäänen, T. L.; Seppälä, J. V. J Appl Polym Sci 1997, 63, 1071.
5. Kaminsky, W.; Noll, A. Polym Bull 1993, 31, 175.
6. Kaminsky, W.; Beulich, I.; Arndt, R. M. Macromol Symp 2001, 173, 211.
7. Kaminsky, W.; Tran, P.; Werner, R. Macromol Symp 2004, 213, 101.
8. Donner, M.; Fernandes, M.; Kaminsky, W. Macromol Symp 2006, 236, 193.
9. Wendt, R. A.; Mynott, R.; Fink, G. Macromol Chem Phys 2002, 203, 2531.
10. Wendt, R. A.; Angermund, K.; Jensen, V.; Thiel, W.; Fink, G. Macromol Chem Phys 2004, 205, 308.
11. Tritto, I.; Marestin, C.; Boggioni, L.; Sacchi, M. C.; Brintzinger, H. H.; Ferro, D. R. Macromolecules 2001, 34, 5770.
12. Tritto, I.; Boggioni, L.; Ferro, D. R. Coord Chem Rev 2006, 250, 212.
13. Huang, W. J.; Chang, F. C.; Chu, P. J. J Polym Res 2000, 7, 51.
14. Rische, T.; Waddon, A. J.; Dickinson, L. C.; MacKnight, W. J. Macromolecules 1998, 31, 1871.
15. Harrington, B. A.; Crowther, D. J. J Mol Catal A: Chem 1998, 128, 79.
16. Forsyth, J.; Perena, J. M.; Benavente, R.; Perez, E.; Tritto, I.; Boggioni, L.; Brinzinger, H.; Macromol Chem Phys 2001, 202, 614.
17. Ekizoglou, N.; Thorshaug, K.; Cerrada, M. L.; Benavente, R.; Pérez, E. J Appl Polym Sci 2003, 89, 3358.
18. Ou, C. F.; Hsu, M. C. J Polym Res 2007, 14, 373.
19. Shiono, T.; Sugimoto, M.; Hasan, T.; Cai, Z. G.; Ikeda, T. Macromolecules 2008, 41, 8292.
20. Ban, H. T.; Hagihara, H.; Nishii, K.; Tsunogae, Y.; Nojima, S.; Shiono, T. J Polym Sci Part A: Polym Chem 2008, 46, 7395.
21. Yao, Z.; Lv, F.; Liu, S. J.; Cao, K. J Appl Polym Sci 2008, 107, 286.
22. Yao, Z.; Liu, S. J.; Lv, F.; Cao, K. J Appl Polym Sci 2008, 109, 4010.
23. Liu, S. J.; Cao, K.; Yao, Z.; Li, B. G.; Zhu, S. P. AIChE J 2009, 55, 663.
24. Liu, S. J.; Yao, Z.; Cao, K.; Li, B. G.; Zhu, S. P. Macromol Rapid Commun 2009, 30, 548.
25. McKnight, A. L.; Waymouth, R. M. Macromolecules 1999, 32, 2816.