

Determination of Mark–Houwink Parameters of Ethylene–Norbornene Copolymers and Molecular Characteristics Estimation

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ABSTRACT: Ethylene–norbornene copolymers (ENC) with ~ 50%, ~ 25% and ~ 15% norbornene (NB) fraction in a wide range of molecular weight were produced by metallocene catalysts. By coupling the gel permeation chromatography (GPC) with the intrinsic viscosity data in 1,2,4-trichlorobenzene (TCB) at 150°C, the Mark–Houwink parameters of ENC were determined and compared with previous classical analysis using polyethylene's relative parameters. The results indicated that parameter *K* was con-

siderably increased with decreasing NB fraction in ENC but parameter α was only increased slightly. Furthermore, the structure characteristics and correlative rheological parameters of resultant ENC were also calculated and discussed by the Stockmayer–Fixman analysis. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 4010–4014, 2008

Key words: cyclic olefin copolymer; Mark–Houwink parameters; metallocene catalysts; norbornene; ethylene

INTRODUCTION

Cyclic olefin copolymer (COC) is an amorphous thermoplastic polymer endowed with excellent properties such as outstanding optical clarity, moisture barrier, and chemical resistance, etc.¹ It has been promisingly used in optical, electrical, and medical apparatus fields. COC was firstly synthesized by Kaminsky et al. using metallocene catalysts in 1989.² Since then, synthesis of COCs, especially for ethylene–norbornene copolymers (ENC), has obtained more and more attentions.^{3–10}

However, little work on Mark–Houwink parameters of ENC has been reported because of its novelty. The molecular weights of ENC published in literatures^{11–14} were usually calculated using the Mark–Houwink constants of polyethylene (PE). Ruchatz and Fink⁶ and Kaminsky and coworkers¹⁰ measured the molecular weights of ENC by coupling a gel permeation chromatography (GPC) with a viscosity detector in combination with the help of the universal calibration. However, the assuring parameters of

Mark–Houwink equations was not presented. The Mark–Houwink expressions of polynorbornene (PNB) in 1,2,4-trichlorobenzene (TCB) ($K = 9.872 \times 10^{-5}$ dL/g, $\alpha = 0.6793$, 135°C),¹⁵ chlorobenzene ($K = 5.97 \times 10^{-4}$ dL/g, $\alpha = 0.56$, 25°C),¹⁶ and cyclohexane ($K = 9.58 \times 10^{-4}$ dL/g, $\alpha = 0.51$, 25°C)¹⁶ had been evaluated by the combination of GPC with online light scattering and intrinsic viscosity measurements.

Based on intrinsic viscosities and molecular weights of the polymers, the unperturbed chain dimensions can be estimated by the Burchard–Stockmayer–Fixman approach. This evaluation of the unperturbed chain dimension allows estimation of the plateau moduli and entanglement molecular weights via the application of the packing length concept. These parameters are not accessible from the usual melt state measurements because chain degradation and the glass transition temperatures overlap.¹⁶

In this article, we attempted to determinate the Mark–Houwink parameters of ENC with different NB fraction in TCB at 150°C by coupling a GPC with a viscosity detector. Furthermore, the structure characteristics of the obtained ENC have been estimated and discussed.

EXPERIMENTAL

Materials

Ethylene (99.95%) was dried by passing through columns filled with 3 Å molecular sieve and Cu

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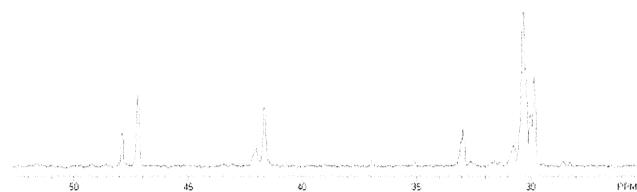


Figure 1 ^{13}C NMR spectrum of the typical ENC produced in this work (25.7 mol % NB).

catalyst. Norbornene (NB) was dried over CaH_2 and distilled for 6 h before use. Toluene was dried over a sodium/potassium alloy and distilled for 6 h before use. Metallocene catalysts used in this work, *rac*-[En(Ind) $_2$]ZrCl $_2$, were purchased from ACROS (Geel, Belgium). The cocatalyst, methylaluminoxane (MAO), was provided by AKZO NOBEL (Amsterdam, Holland) in the form of 10 wt % solution in toluene.

General polymerization procedure¹⁷

All polymerization were carried out in a 100 mL glass flask under atmospheric pressure. The reaction temperature was varied from 40 to 70°C. In all the experiments, Al/Zr mole ratio was kept constant at 1500. Before polymerization, the reactor was evacuated and charged with nitrogen alternatively for three times. Then, ethylene, certain amount of NB/toluene solution, and MAO/toluene suspension were added to the reactor sequentially. The polymerization was started by the addition of the metallocene/toluene solution. During the polymerization process, ethylene was continuously fed into the reactor for maintaining the atmospheric pressure. To minimize the composition drift, the reaction time was limited to 10 min. The polymerization was stopped by the acidified ethanol. The reaction mixture was slowly poured into dilute HCl/ethanol solution. The precipitated polymer was filtered and washed with ethanol, and was then dried under vacuum at 60°C.

Determination of NB fraction in copolymer

To calculate the NB fraction of ENC, Varian Unity-400 nuclear magnetic resonance (NMR) instrument

was used. ^{13}C NMR spectra of the copolymers were recorded at 120°C. The polymer samples were dissolved in deuterated *o*-dichlorobenzene with a concentration of 10%. At least 3000 scans were applied for each acquisition to obtain a good signal-to-noise ratio. The polymer chemical shift assignments and calculations followed the analysis method of Ruchatz and Fink.⁴ Figure 1 shows a typical ^{13}C NMR spectrum of the ENC produced in this work.

Determination of Mark-Houwink parameters

The molecular weight and molecular weight distribution of the resulting polymers were determined at 150°C with TCB as solvent using a Waters GPCV 2000 with three separate columns (10⁶ Å, 10⁴ Å and 10³ Å). The instrument equipped with a combined refractive index and viscosity detector, which allows the estimation of Mark-Houwink constants for copolymer with different copolymer compositions.^{6,10} The estimation procedure can be described as follows: First, a least-square objective function is constituted for the difference between intrinsic viscosity calculated by Mark-Houwink equation using GPC data and the one measured by viscosity detector, and then the Mark-Houwink parameters K and α can be estimated through minimization of the objective function.

RESULTS AND DISCUSSION

Effects of NB content on Mark-Houwink parameters

The Mark-Houwink parameters K and α of the obtained ENC with different NB fraction and their parent polymers were exhibited in Table I. K was considerably increased, but α was only changed slightly when the NB fraction in resultant ENC was decreased. α is the reflection of polymer configuration in solvent. TCB is a good solvent for ENC at 150°C. The chain configurations of polymers with different NB fraction should be similar. Consequently, variety of α was small. On the other hand, when the NB fraction in ENC was decreased, the

TABLE I
 K and α Values of the ENCs with Different NB Fraction

Polymers	NB (mol %)	Temperature (°C)	$K \times 10^4$ (dL/g)	A	References
ENC	~ 50	150	1.74	0.66	This work
	~ 25	150	3.40	0.67	
	~ 15	150	3.97	0.68	
PE	0	150	5.91	0.69	18
		135	5.10	0.706	19
PNB	100	135	0.987	0.679	15

TABLE II
 $[\eta]^v$ Compared with $[\eta]^{GPC}$ for the Obtained ENCs with (a) $\sim 50\%$ NB Fraction (NB% = 48.7 \sim 51.8 mol %); (b) $\sim 25\%$ NB Fraction (NB% = 23.5 \sim 25.7 mol %); and (c) $\sim 15\%$ NB Fraction (NB% = 13.1 \sim 17.6 mol %)

$\sim 50\%$ NB fraction (NB% = 48.7 \sim 51.8 mol %)				
Samples	1	2	3	4
$[\eta]^v$ (dL/g)	0.8417	0.7497	0.5924	0.4037
$[\eta]^{GPC}$ (dL/g)	0.8728	0.7098	0.6058	0.4045
Error (%)	3.69	-5.32	2.26	0.20
$\sim 25\%$ NB fraction (NB% = 23.5 \sim 25.7 mol %)				
Samples	5	6	7	8
$[\eta]^v$ (dL/g)	0.8882	0.7613	0.5214	0.3657
$[\eta]^{GPC}$ (dL/g)	0.8556	0.7809	0.5487	0.3548
Error (%)	-3.67	2.57	5.24	-2.98
$\sim 15\%$ NB fraction (NB% = 13.1 \sim 17.6 mol %)				
Samples	9	10	11	12
$[\eta]^v$ (dL/g)	0.7738	0.7412	0.6606	0.4741
$[\eta]^{GPC}$ (dL/g)	0.8095	0.7080	0.6363	0.4903
Error (%)	4.61	-4.48	-3.68	3.42

flexibility of polymer chain was increased because the NB unit should be more rigid than the ethylene unit. Then the chains would extend adequately. Therefore, hydrodynamics volume of the ENC with lower NB fraction should be bigger and measured intrinsic viscosity should be higher. According to the Mark-Houwink equation $[\eta] = KM^\alpha$, K would become larger with decreasing the NB fraction in ENC. Furthermore, the evolution of both K and α parameters for the obtained ENC with different NB fraction was reasonable in comparison with published Mark-Houwink parameters of their parent polymers.^{15,18,19}

Furthermore, the comparison between the $[\eta]^{GPC}$ calculated with the determined Mark-Houwink parameters and the $[\eta]^v$ measured by viscosity detector was listed in Table II to validate the determined Mark-Houwink parameters. It was obvious that the maximal error was 5.32% and the average error was $\pm 2.86\%$ for the obtained ENC with $\sim 50\%$ NB fraction. For the obtained ENC with $\sim 25\%$ NB fraction, the maximal error was 5.24% and the average error was $\pm 3.62\%$. For the obtained ENC with $\sim 15\%$ NB fraction, the maximal error was 4.61% and the average error was $\pm 4.05\%$. The results indicated that the determined K and α should be believable.

Molecular weight calculated by determined Mark-Houwink Parameters

The molecular weights calculated by the resulting Mark-Houwink parameters for all samples were

TABLE III
 The Molecular Weights of the Obtained ENCs with (a) $\sim 50\%$ NB Fraction Calculated Using Estimated K and α Values; (b) $\sim 25\%$ NB Fraction Calculated Using Estimated K and α Values; (c) $\sim 15\%$ NB Fraction Calculated Using Estimated K and α Values

$\sim 50\%$ NB fraction				
Samples	1	2	3	4
M_n ($\times 10^{-4}$) ^a	19.94	14.26	11.57	5.99
M_w ($\times 10^{-4}$) ^a	41.29	30.34	23.79	13.07
M_n ($\times 10^{-4}$) ^b	8.08	5.81	4.72	2.47
M_w ($\times 10^{-4}$) ^b	16.39	12.09	9.52	5.28
$\sim 25\%$ NB fraction				
Samples	5	6	7	8
M_n ($\times 10^{-4}$) ^c	5.37	5.02	3.27	1.43
M_w ($\times 10^{-4}$) ^c	13.38	11.74	6.75	3.62
M_n ($\times 10^{-4}$) ^d	3.44	3.21	2.10	0.93
M_w ($\times 10^{-4}$) ^d	8.39	7.37	4.27	2.30
$\sim 15\%$ NB fraction				
Samples	9	10	11	12
M_n ($\times 10^{-4}$) ^e	3.49	2.60	2.35	1.21
M_w ($\times 10^{-4}$) ^e	8.97	7.37	6.30	4.41
M_n ($\times 10^{-4}$) ^f	2.54	1.90	1.72	0.89
M_w ($\times 10^{-4}$) ^f	6.43	5.30	4.53	3.18

^a $K = 1.74 \times 10^{-4}$ dL/g, $\alpha = 0.66$ (estimated).

^b $K = 5.91 \times 10^{-4}$ dL/g, $\alpha = 0.69$ (PE).

^c $K = 3.40 \times 10^{-4}$ dL/g, $\alpha = 0.67$ (estimated).

^d $K = 5.91 \times 10^{-4}$ dL/g, $\alpha = 0.69$ (PE).

^e $K = 3.97 \times 10^{-4}$ dL/g, $\alpha = 0.68$ (estimated).

^f $K = 5.91 \times 10^{-4}$ dL/g, $\alpha = 0.69$ (PE).

shown in Table III. For the obtained ENC with ~ 50 mol % NB, the average number molecular weight (M_n) was varied from 5.99×10^4 to $19.94 \times$

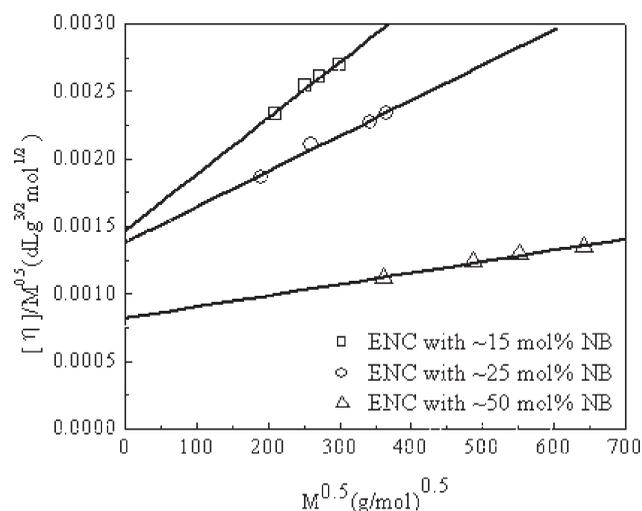


Figure 2 Stockmayer-Fixman plots for the obtained ENCs with different NB fraction.

TABLE IV
Unperturbed Chain Dimension Data And Polymer-Solvent Interaction Parameter

Polymers	NB (mol %)	$\frac{K_\theta \times 10^3}{(\text{dL g}^{-3/2} \text{ mol}^{1/2})}$	$\frac{\langle R^2 \rangle_0 / M}{(\text{\AA}^2 \text{ mol/g})}$	χ	Solvent
ENC	~ 50	0.823	0.477	0.474	TCB
	~ 25	1.380	0.673	0.419	TCB
	~ 15	1.470	0.702	0.373	TCB
PE	0	4.000	1.368	0.376	TCB
PNB	100	0.675	0.418	0.485	TCB

10^4 . For the obtained ENC with ~ 25 mol % NB, the variation of M_n was from 1.43×10^4 to 5.37×10^4 . For the obtained ENC with ~ 15 mol % NB, the M_n was in the range of 1.21×10^4 and 3.49×10^4 . It could be found that the molecular weight was decreased when the NB fraction in ENC was decreased. This phenomenon was consistent with the findings of Ruchatz and Fink.⁶ Furthermore, the molecular weights of resultant ENC calculated by the above Mark-Houwink parameters were clearly higher than that calculated by the PE's Mark-Houwink parameters, especially for the ENC with higher NB fraction.

Calculated structure characteristics

Based on Stockmayer-Fixman analysis,²⁰ the K_θ , which is the Mark-Houwink parameter K in the theta condition, could be calculated by the molecular weight and the intrinsic viscosity data. This analysis process was illustrated in Figure 2 for the obtained ENC with different NB fraction. The results demonstrated that no deviations from the expected behavior could be observed within the limits of experimental data. The intercept of this plot yielded the θ -condition parameter K_θ .

According to Flory intrinsic viscosity theory, K_θ can be calculated from the following expression.

$$K_\theta = [\eta]_\theta / M^{0.5} = \phi [\langle R^2 \rangle_0 / M]^{1.5} \quad (1)$$

Where ϕ denotes the universal hydrodynamic constant which is equal to $2.5 \times 10^{23} \text{ mol}^{-1}$. With the resulting K_θ , the unperturbed chain dimensions ($\langle R^2 \rangle_0 / M$) can be estimated. Furthermore, the given slopes of the Stockmayer-Fixman plots, calculated from the following equation, can be used to deter-

mine a polymer-solvent interaction parameter χ at near zero polymer concentration.

$$\text{slope} = 0.51\phi_0 \left(\frac{v_p^2}{V_s N_A} \right) (1 - 2\chi) \quad (2)$$

Where v_p is the specific volume of the polymer, which is taken to be $9.804 \times 10^{-4} \text{ m}^3/\text{Kg}$; V_s is the molar volume of TCB solvent, which is given to be $1.251 \times 10^{-4} \text{ m}^3/\text{mol}$; and N_A is the Avogadro number. The estimated results were compared with the parameters of parent polymers in Table IV. It could be seen that both K_θ and $\langle R^2 \rangle_0 / M$ were decreased as the NB fraction in ENC was increased. Moreover, the χ parameter was increased with increasing the NB fraction.

The pack length (p) is defined as follows,²¹

$$p = [\langle R^2 \rangle_0 \rho N_A / M]^{-1} \quad (3)$$

Where ρ is the mass density. The entanglement molecular weight (M_e), the plateau modulus (G_N^0) and the occupied volume of a chain (V_e) can be expressed²² by p .

$$G_N^0 = k_B T / (n_t^2 p^3) \quad (4)$$

$$M_e = \rho N_A n_t^2 p^3 \quad (5)$$

$$V_e = n_t^2 p^3 \quad (6)$$

Where k_B is the Boltzman constant and n_t denotes the number of entanglement strands present per cube of the tube diameter and is equal to $21.3\% \pm 7.5\%$.²³

TABLE V
Calculated Molecular Characteristics and Rheological Parameters at 298 K

Polymers	NB (mol %)	ρ (g/cm ³)	p (Å)	M_e (10 ⁻³ g/mol)	$V_e \times 10^{-3}$ (10 ⁻³ Å ³)	G_N^0 (MPa)	ρ_e (nm ⁻³)
ENC	~ 50	1.02	3.41	11.1	17.99	0.23	0.056
	~ 25	1.02	2.42	4.0	6.43	0.64	0.156
	~ 15	1.02	2.32	3.5	5.67	0.73	0.176
PE	0	0.96	1.27	0.5	0.93	4.48	1.08
PNB	100	0.99	4.01	17.4	29.3	0.14	0.034

Then the entanglement density (ρ_e) can be obtained,

$$\rho_e = 1/V_e \quad (7)$$

The craze resistance of glassy polymers can be seen from the value of ρ_e , because the number of entanglements per chain is closely connected with the crazing of polymers. Polymers with high values of ρ_e will display high craze resistance.²⁴ The calculated characteristic values for the obtained ENC with different NB fraction were displayed in Table V. It could imply that the craze resistance of ENC was enhanced when the incorporating ethylene was increased.

CONCLUSIONS

Mark–Houwink parameters of the obtained ENC with different NB fraction in TCB at 150°C were estimated in this work based on coupling GPC and intrinsic viscosity data. It had been found that K was considerably increased with decreasing NB fraction but α was only increased slightly. The estimated structure characteristics indicated that the craze resistance of the ENC was enhanced when the incorporating ethylene was increased.

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