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Koichi Ute^a; Ryo Niimi^a; Koichi Hatada^a; Andrew C. Kolbert^{b,c}

^a Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan ^b DSM Copolymer, Baton Rouge, LA, USA ^c AlliedSignal Inc., Morristown, NJ, USA

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Characterization of Ethylene–Propylene–Diene Terpolymers (EPDM) by 750 MHz On-line SEC-NMR

KOICHI UTE^a, RYO NIIMI^a, KOICHI HATADA^{a,*}
and ANDREW C. KOLBERT^{b,†}

^a*Department of Chemistry, Graduate School of Engineering Science,
Osaka University, Toyonaka, Osaka 560-8531, Japan;*

^b*DSM Copolymer, Baton Rouge, LA 70821-2591, USA*

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Chemical compositions of ethylene–propylene–(2-ethylidene-5-norbornene) terpolymers were investigated by size exclusion chromatography coupled directly to 750 MHz ¹H NMR (on-line SEC-NMR). Comparison of the chromatograms obtained by monitoring the CH₂ and CH₃ resonances in a terpolymer sample showed clearly that ethylene/propylene ratio depends on molar mass. The measurements were carried out with continuous flow of eluent (chloroform-*d*, 0.2 mL/min). Molar mass dependence of a small amount (0.6–1.1 mol%) of 2-ethylidene-5-norbornene units in a terpolymer was determined by SEC-NMR using the stop-and-flow technique.

Keywords: SEC; NMR; LC-NMR; Molecular weight distribution; Chemical composition; Ethylene–propylene rubber

INTRODUCTION

Ethylene–propylene–diene terpolymers, produced by the polymerization with Ziegler–Natta catalysts, constitute an important class of

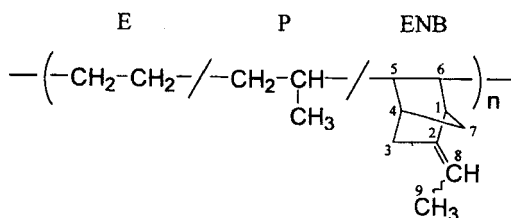
* Corresponding author.

† Present address: AlliedSignal Inc., 101 Columbia Road, Morristown, NJ 07962, USA.

hydrocarbon elastomers known as EPDM.^[1-3] Many parameters contribute to the properties of these materials. The comonomer ratio of ethylene and propylene influences the crystallinity. The vulcanization properties and mechanical properties depend on the type and amount of diene monomer. The polymerization conditions determine the molar mass and its distribution which have large effects on the viscosity and processibility.

Knowledge of the molar mass dependence of chemical composition supplies information about the polymerization mechanism and leads to a better understanding of the relationship between polymer structure and material properties. However, it is laborious and time-consuming to investigate the molar mass dependence by conventional methods such as fractional precipitation followed by spectroscopic measurements. As shown in previous papers,^[4-10] the use of ¹H NMR as a detector of size exclusion chromatography (on-line SEC-NMR) is a quick and efficient method to determine the molar mass dependence of comonomer composition^[5] or tacticity^[7] in a polymer sample. The high sensitivity and high spectral resolution of 750 MHz ¹H NMR in SEC-NMR experiments has recently been demonstrated by end-group analysis of isotactic poly(methyl methacrylate).^[10]

In the present work, several samples of ethylene-propylene-(2-ethylidene-5-norbornene) terpolymers (Scheme 1) were analyzed by 750 MHz on-line SEC-NMR operating in the continuous-flow mode or stop-and-flow mode to determine the ethylene (E), propylene (P), and diene (ENB) monomer content as a function of molar mass.



SCHEME 1

TABLE I EPDM samples subjected to SEC-NMR experiments

Sample	$M_n/10^4$ ^a	M_w/M_n ^a	Chemical composition/mol%		
			E	P	ENB
A	9.5	2.52	79.8	19.1	1.1
B	1.9	1.74	53.4	46.6	0.0
C ^b	3.2	4.41	67.9	31.5	0.6
D	7.0	2.97	65.9	33.2	0.9

^a Determined by SEC calibrated with standard polystyrene.

^b A blend of A and B (50:50).

EXPERIMENTAL

EPDM Samples

Table I shows the molar mass averages and comonomer compositions of EPDM samples A–D. M_n and M_w/M_n were determined by conventional SEC measurements using standard polystyrenes as molar mass references. The SEC measurements were carried out on a JASCO PU-980 chromatograph equipped with an SEC column Shodex K-805L (8 mm i.d. \times 300 mm, maximum porosity 4×10^6) and a refractive-index detector JASCO RI-930. Chloroform-*d* (> 99.8 at.%, stabilized with silver foil, ISOTEC Inc.) was used as the eluent. Comonomer compositions were determined by 750 MHz ¹H NMR spectroscopy. A test sample C was prepared by blending two EPDM samples (A and B) with different average molar mass and different P and ENB content. All samples dissolved completely in chloroform-*d* at room temperature.

SEC-NMR Measurements

On-line SEC-NMR were performed on a Varian Unity-INOVA 750 spectrometer using an ¹H{¹⁵N–³¹P} inverse-geometry LC-NMR probe with pulsed field gradient (PFG) coils. The flow cell in the probe had a detection volume of approximately 60 μ L. The sample inlet of the probe was connected to the above mentioned chromatograph via a PEEK tubing (0.25 mm i.d. \times 2.4 m). The temperatures of SEC column and flow cell were kept at 23°C.

Continuous-flow SEC-NMR measurements were carried out at a flow rate of 0.2 mL/min. The residence time of an analyte in the flow cell is 18 s at this flow rate. The amount of sample used for a measurement was 0.50 mg. Increasing the amount caused appreciable broadening of elution peaks. A total of 50 spectra were collected every 36 s in an elution period from 27 to 57 min. Each spectrum was obtained by the accumulation of 8 scans using 90° pulses (7.7 μs) with a pulse repetition time of 4.5 s, and stored into 65536 data points covering a spectral width of 7490 Hz. These acquisition conditions ensure quantitative measurements of the ¹H NMR resonances due to EPDM.^[10] Digital signal processing with an oversampling factor of 40 was applied. Prior to Fourier transformation, an exponential apodization function was applied to the free induction decays (FIDs) corresponding to a line broadening of 2.0 Hz. Chemical shift values were calibrated against the resonance at 7.255 ppm due to residual CHCl₃ in the eluent.

Two-dimensional Heteronuclear Correlation Spectroscopy

PFG-heteronuclear multiple quantum coherence (HMQC) experiments on EPDM samples were carried out using a 5 mm o.d. PFG ¹H{¹⁵N-³¹P} inverse-geometry probe. The spectra were recorded with a spectral width of 23995.2 Hz in the F1 dimension (¹³C) and 5070.4 Hz in the F2 dimension (¹H). Zero-filling of the original 512 × 2048 matrix gave final resolution of 11.7 Hz per point for F1 and 2.5 Hz per point for F2. Sixty transients were accumulated for each 512 increments. Prior to Fourier transformation, an apodization function of sine bell type was applied to the FIDs.

RESULTS AND DISCUSSION

¹H NMR Spectra of EPDM Samples

Figure 1 shows the 750 MHz ¹H NMR spectra of EPDM samples A and B in chloroform-*d* at 23°C. The CH₃ and CH resonances due to P units are designated by the symbol P. The CH₂ resonances due to E and P units are resolved into three regions: the CH₂ group adjacent to tertiary carbons (α-CH₂), the CH₂ group of propylene *meso* dyads

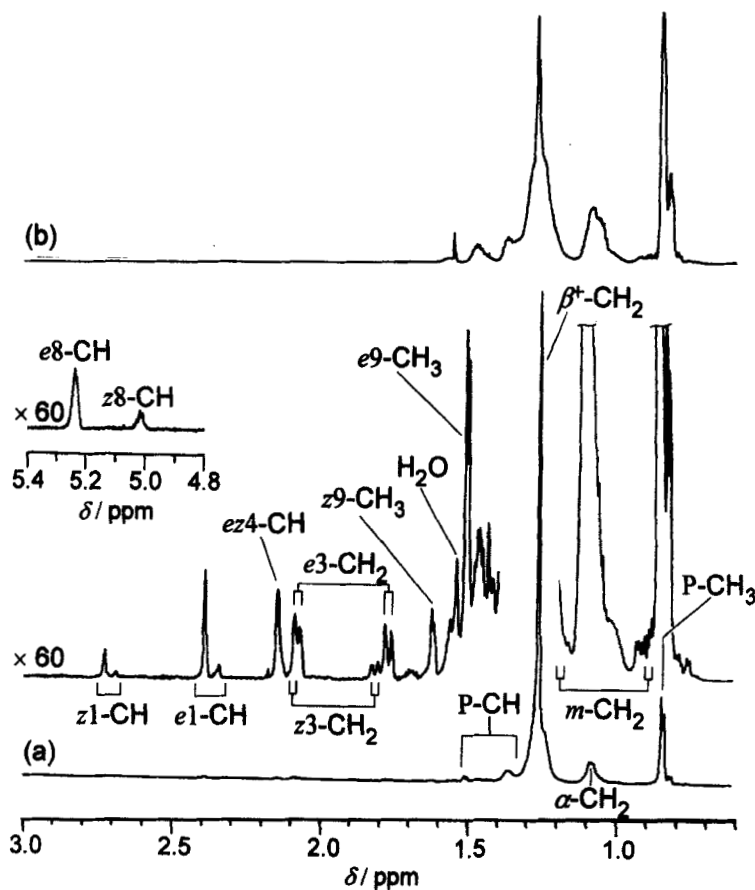


FIGURE 1 750 MHz ^1H NMR spectra of EPDM samples A (a) and B (b) measured in chloroform- d at 23°C.

($m\text{-CH}_2$), and the other CH_2 groups ($\beta^+\text{-CH}_2$). The resonances arising from ENB isomer units are indicated by e (*entgegen*) and z (*zusammen*), accompanied by the position numbers shown in Scheme 1.

The assignments for the resonances were made by means of PFG-HMQC experiments (Figure 2). Since the assignments of ^{13}C NMR spectra of E-P-ENB terpolymers have been reported in the literature,^[11-12] each ^1H resonance can be assigned automatically via

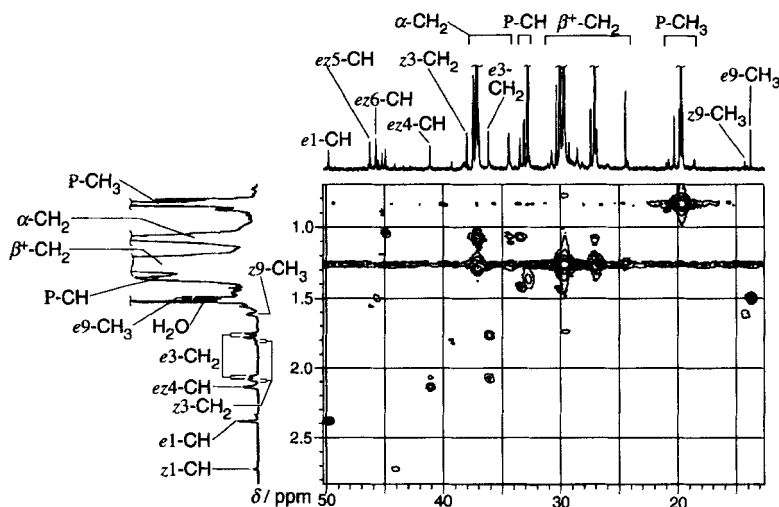


FIGURE 2 PFG-HMQC spectrum of EPDM sample A. Assignments for ^{13}C resonances are based on the literature.^[11,12]

correlation peaks in the HMQC spectrum. The assignments for the ^1H resonances due to E and P units agreed essentially with those described in the 220 MHz ^1H NMR study of E-P copolymers in *o*-dichlorobenzene at 145°C.^[13]

Olefinic ^1H resonances have been used to determine the diene content in EPDM.^[2,14] However, the *e*8-CH and *z*8-CH resonances of E-P-ENB terpolymers were unsuitable for the intensity measurements in the present work because those ^1H nuclei had relatively long spin-lattice relaxation times (T_1 's: *e*8-CH 1.87 s, *z*8-CH 2.06 s). Among the well-resolved resonances due to ENB units, *e*1-CH, *z*1-CH, and *ez*4-CH resonances showed T_1 of 1.00, 1.03, and 0.85 s, respectively, and therefore can be used for the quantitative SEC-NMR measurements under the conditions described in the experimental part. The small splitting of each *e*1-CH and *z*1-CH resonance should be ascribed to the stereoisomerism at the 5 and 6 positions in ENB units. According to the literature,^[12] ENB is incorporated into EPDM predominantly in the 5-exo-6-exo fashion. T_1 of the other ^1H species were as follows: P-CH₃ 0.81 s, P-CH 0.96 s, α -CH₂ 0.69 s, β^+ -CH₂ 0.83 s.

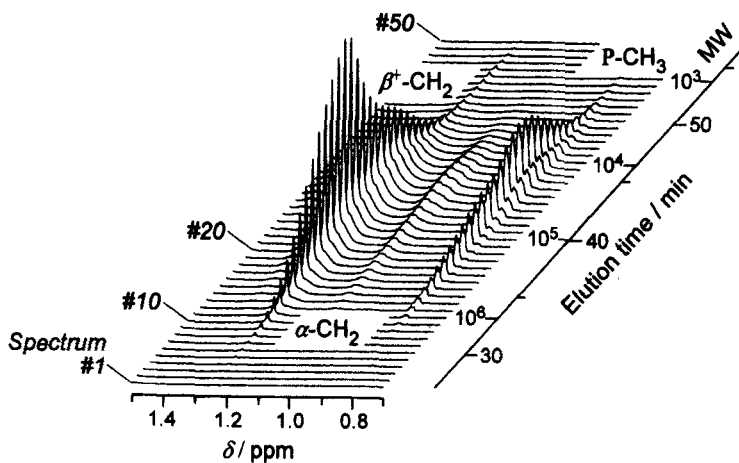


FIGURE 3 A stacked trace plot of the 750 MHz continuous-flow SEC-NMR spectra for sample C. A series of 50 spectra obtained in an elution period from 27 to 57 min are plotted against elution time. Eluent, chloroform-*d*; flow rate, 0.2 mL/min; sample amount, 0.5 mg; data acquisition per spectrum, 90° pulse/4.5 s interval/8 scans.

Determination of Ethylene/Propylene Composition by SEC-NMR in the Continuous-flow Mode

Figure 3 shows a stacked trace plot of the continuous-flow SEC-NMR data for EPDM sample C. A series of 50 spectra covering a spectral region of 0.7–1.5 ppm was plotted against elution time from 27 to 57 min. The elution time axis was converted into a scale of molar mass by the calibration procedure using standard polystyrenes. Cross sections of the stacked plot at 1.25 ppm (β^+ -CH₂) and 0.83 ppm (P-CH₃) gave the ¹H NMR-detected SEC curves indicating E and P compositions as a function of molar mass. The curves are shown in Figure 4 together with those obtained for samples A and B. As expected from the fact that sample C is a 50 : 50 blend of samples A and B (Table I), the ¹H NMR-detected SEC curves clearly indicated that the high molar mass part of sample C had a higher E content than the low molar mass part.

Although the ¹H NMR-detected SEC curves provide a simple and straightforward method to visualize the chemical composition across molar mass distribution, quantitative information of the chemical

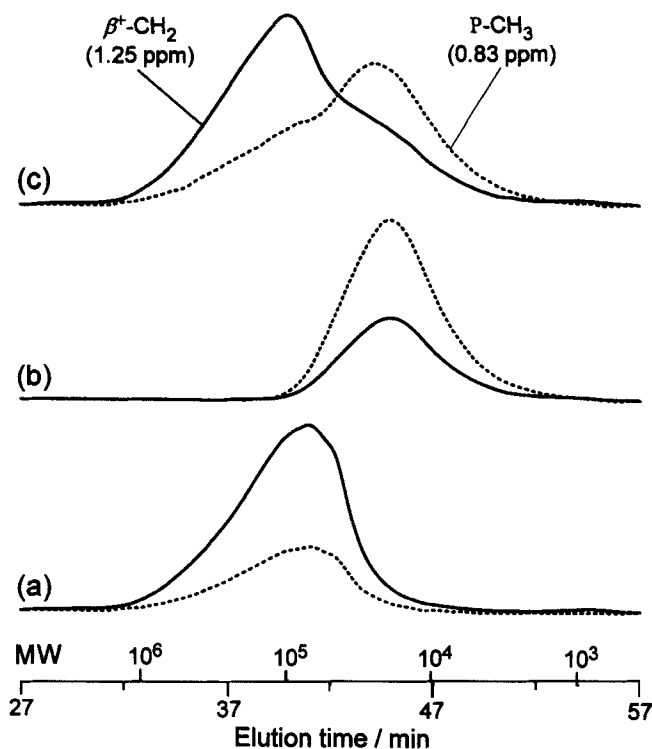


FIGURE 4 ^1H NMR-detected SEC curves of EPDM samples A (a), B (b) and C (c). The solid lines and dotted lines are obtained by plotting the signal heights of $\beta^+\text{-CH}_2$ (1.23 ppm) and P-CH_3 (0.82 ppm) resonances, respectively. The height ratio of P-CH_3 resonance to $\beta^+\text{-CH}_2$ resonance was doubled.

composition should be obtained from relative intensity of the resonances rather than the height ratio. The intensities of P-CH_3 , $\alpha\text{-CH}_2$, and $\beta^+\text{-CH}_2$ resonances in each spectrum of the SEC-NMR data [$I(\text{P-CH}_3)$, $I(\alpha\text{-CH}_2)$, and $I(\beta^+\text{-CH}_2)$] were measured by integrating the spectral regions of 0.70–0.85, 0.85–1.12, and 1.12–1.32 ppm, respectively. The molar fractions of E units ($[\text{E}]$, in mol%) were calculated by the following equations:

$$I_p = I(\text{P-CH}_3)/3$$

$$I_e = [I(\alpha\text{-CH}_2) + I(\beta^+\text{-CH}_2) - 2I_p]/4$$

$$[\text{E}] = 100I_e/(I_e + I_p).$$

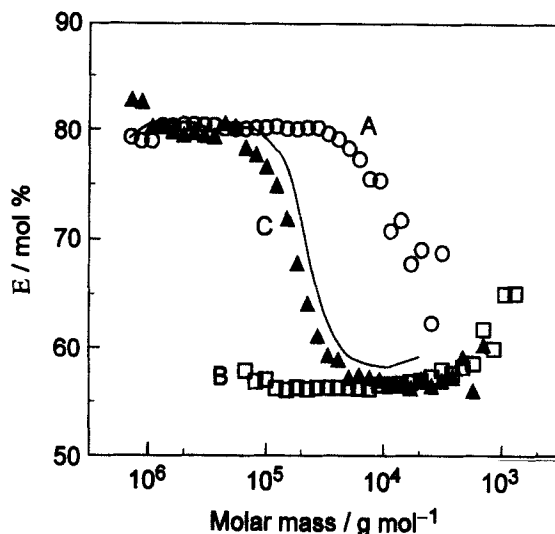


FIGURE 5 Molar mass dependence of ethylene (E) content in EPDM samples A–C. The expected curve for Sample C, a 50:50 blend of samples A and B, is shown as a solid line.

The resonances due to a small amount of *m*-CH₃, *ez*5-CH, and *ez*6-CH groups, which may overlap the above spectral regions, were neglected. The E content thus determined for samples A–C was plotted against the molar mass (Figure 5). The E content of sample A was 81 mol% in the molar mass region from 1.0×10^6 to 2×10^4 g/mol, and decreased to about 65 mol% with decreasing molar mass below 2×10^4 g/mol. However, the E content of sample B was found to increase slightly from 56 to about 60 mol% in the molar mass region below 1.0×10^4 g/mol. Sample C showed a steep decrease in the E content with decreasing molar mass from 1.0×10^5 to 2×10^4 g/mol. The variation in the E content of sample C was consistent with that expected from the mathematical superposition of the results for samples A and B.

Determination of ENB Content by SEC-NMR in the Stop-and-flow Mode

As illustrated in Figure 6(a), the ¹H NMR spectra obtained by continuous-flow SEC-NMR had high resolution almost comparable to

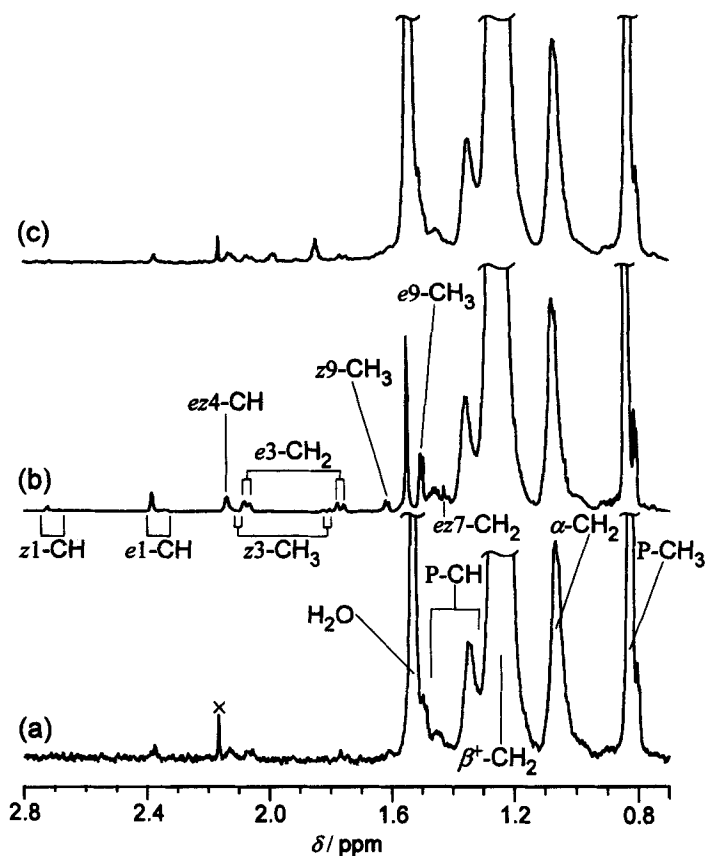


FIGURE 6 750 MHz ^1H NMR spectra of EPDM sample A in chloroform-*d*. (a) Recorded at the elution maximum (41.1 min) in the continuous-flow SEC-NMR experiment, (b) recorded by the use of a normal probe and a 5-mm o.d. sample tube, (c) recorded at the elution maximum in the stop-and-flow SEC-NMR experiment (188 scans, 90° observation pulses, 4.5 s pulse interval).

those recorded under normal conditions (Figure 6(b)). The signal-to-noise ratios (S/N 's) for P-CH₃, α -CH₂, and β^+ -CH₂ resonances in the SEC-NMR spectra were sufficient for quantitative intensity measurements. However, intensity measurements of the resonances due to a small amount of ENB units were difficult in the continuous-flow SEC-NMR experiments even at the elution maximum (Figure 6(a)).

The ENB content in EPDM samples as a function of molar mass was determined by SEC-NMR operating in the stop-and-flow mode.

In the stop-and-flow SEC-NMR experiment, the flow of mobile phase was halted at several points during the chromatographic separation, and NMR scans were accumulated in each point until an enough S/N (>10) was obtained for $e1$ -CH, $z1$ -CH, and $ez4$ -CH resonances. In the experiment on sample A for an example, the flow was halted at 5 points corresponding to the elution times of 33.6, 39.0, 41.4, 43.8 and 46.2 min in the continuous-flow mode, and 600, 220, 188, 220, and 600 transients were accumulated at those points, respectively, with a pulse repetition time of 4.5 s. Figure 6(c) shows the stop-and-flow SEC-NMR spectrum of sample A recorded at the elution maximum. The S/N of stop-and-flow SEC-NMR spectra allowed the determination of ENB content from the intensity measurement of $ez4$ -CH resonance as well as the determination of the isomeric ratio (e/z) in ENB units from the relative intensity of $e1$ -CH and $z1$ -CH resonances.

Based on the above, the ENB content of EPDM samples was determined as a function of molar mass. The results for sample D are shown in Figure 7, together with the molar mass dependence of E content as determined by continuous-flow SEC-NMR. Sample D is a typical

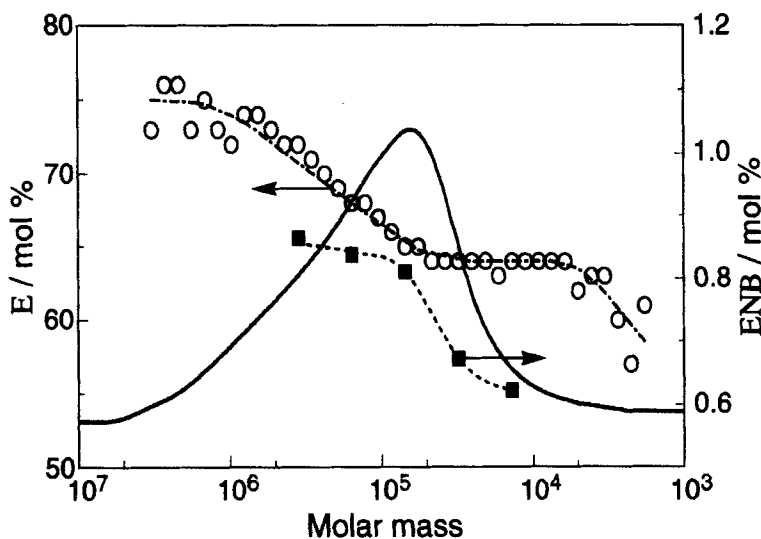


FIGURE 7 The molar mass dependence of chemical compositions as determined by SEC-NMR experiments on EPDM sample D. SEC curve of sample D recorded by a refractive index detector is also shown.

commercial EPDM having a broad molar mass distribution ranging from 10^7 to 10^3 g/mol. The ENB content in sample D was found to decrease with decreasing molar mass, and this tendency coincided with the drift to lower E content with lower molar mass. This coincidence of molar mass dependence of E and ENB contents is in conformity with the spectroscopic evidence that ENB in EPDM should be adjoined by long methylene sequence.^[12] The e/z ratio in ENB units was determined to be 72/28 and was constant throughout the whole molar mass range. A similar value for the e/z ratio in ENB units ($e/z = 3/1$) was reported in the literature.^[12]

It should be noted that SEC is a separation according to molecular size and not necessarily the same as a molar mass separation. This is a general problem in the SEC separation of copolymers. Cinquina *et al.*^[15] have reported that the SEC using *o*-dichlorobenzene as eluent at 135°C separates EPDM mainly as a function of its molar mass. It may therefore be preferable to carry out the SEC-NMR experiments using *o*-dichlorobenzene at 135°C in order to assess detailed molar mass dependence of comonomer composition in EPDM. The use of deuterated eluent is not a prerequisite for modern LC-NMR,^[16–18] and an SEC-NMR study using non-deuterated eluent will be published elsewhere.^[19]

CONCLUSIONS

On-line SEC-NMR is quite useful for the composition analysis of EPDM as a function of molar mass. Quantitative measurements of ethylene and propylene units can be carried out quickly and continuously across the molar mass distribution by SEC-NMR operated in the continuous-flow mode. Not only the diene monomer content which is small in quantity but also the isomeric ratio in diene units are successfully determined by the stop-and-flow SEC-NMR technique.

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