

Characterization of Ethylene Homo- and Copolymers*
V. Molecular Characterization of (Norbornene Ethylene) Copolymers
by Size Exclusion Chromatography, Viscosimetry and Osmometry

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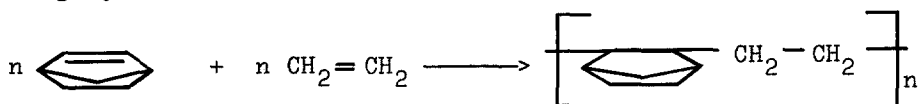
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Summary

For the estimation of molecular mass distribution and average molecular masses of (norbornene ethylene) copolymers a size exclusion chromatography method is described. The validity of the universal calibration function of Benoit et al. based on polystyrene molecular mass standards was confirmed by comparing with the number average molecular masses obtained by osmometry. The constants of the Mark-Houwink equation are $a \approx 0.535$, $K = 1.00 \cdot 10^{-1}$ (Xylene, 90 °C) and $a \approx 0.589$, $K = 4.93 \cdot 10^{-2}$ (diethylbenzene, 120 °C, $[\eta]$ in $\text{cm}^3 \text{g}^{-1}$).

Introduction

(Norbornene ethylene) copolymers (NEC) can be polymerized by means of a modified ZIEGLER catalyst [1]. In this case the norbornene is polymerized as a vinyl compound and its ring system is conserved.



The obtained copolymers preferably have an alternating structure and contain approximately 50 mole-% ethylene and norbornene as found by using nuclear magnetic resonance spectroscopy [2,3], differential scanning calorimetry [4] and differential refractometry [4], although the composition of the two monomers in the polymerization step varies widely.

We did not find any publications about the molecular characterization of such copolymers. The application of size

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exclusion chromatography seems successful, because the alternating structure of copolymer excludes a heterogeneity of chemical composition as far as possible. In order to calculate the molecular mass distribution from the chromatograms we had to elaborate a useful calibration method, which had finally to be tested by osmometric and viscosimetric measurements on the same specimens.

Experimental

Distilled xylene (a mixture of 50 % m-, 16% p- and 11 % o-isomers and 23 % ethylbenzene) and vacuum distilled diethylbenzene (a mixture of 35 % p-, 64 % m- and 1 % o-isomers) were tested as eluents in size exclusion chromatography. Chromatograms were obtained from the analytical part of a WATERS ANA-PREP Gel permeation chromatograph. A 4 x 1.2 m (10^6 , 10^5 , 10^4 and 500 Å) styragel column set was used with a 1 cm³/min flow rate of xylene (90 °C) respectively diethylbenzene (120 °C). The samples were dissolved to obtain a concentration of 0.15 mass-% of copolymer and 0.05 mass-% diphenylamine as inhibitor and filtered over Krueger asbestos filters. 2 cm³ of solution were injected. For the correction of chromatographic peak broadening we used our previously published method [6].

The universal calibration function of Benoit et al. [5] was determined by means of WATERS polystyrene standards. The intrinsic viscosities of solutions with a concentration of 1 mg/cm³ in the same solvents were measured in a Berger-Deckert high temperature viscosimeter at the same temperatures. Diphenylamine (0.05 mass-%) was added to all solutions. The intrinsic viscosity $[\eta]$ was calculated by the method of Schulz and Blaschke [7], using the constant 0.28.

For all osmometric measurements the Hewlett-Packard high temperature Membrane Osmometer HP 502 equipped with Schleicher and Schuell 08 membranes was used. In each case five concentrations in the range 1...5 mg/cm³ were measured in xylene at 60 °C.

In order to check the validity of the universal calibration function and to determine the $[\eta]$ -M relation we used 10 specimens of NEC with relatively narrow molecular mass distributions, polymerized with a one-step addition of the catalyst [1] and various reaction times (KMR 3.1...KMR 3.9, TVBO in table 1).

The usefulness of the method was proved by examination of five samples synthesized in the laboratory (KMR 30, KMR 31, KMR 70, KMR 72 and KMR 76). The broader molecular mass distribution of these specimens was obtained by a stepwise dosage of catalyst and simultaneous addition of a chain length regulator during the synthesis [1].

Results and discussion

In order to calculate the average values of molecular masses and their distributions from the size exclusion chromatography data the viscosity-molecular mass relations had to be found. Following a proposal of Belenki et al.[8] and supposing that the universal calibration function is also valid for NEC, the agreement between the measured intrinsic viscosity values ($[\eta]_{\text{exp}}$) and those calculated from the chromatograms ($[\eta]_{\text{calc}}$) was used as a criterion also for the validity of the $[\eta]$ -M relation used. The constants a and K of this relation were varied by an iterative procedure to fulfil the condition

$$\sum_1^n \left[\frac{[\eta]_{\text{exp}} - [\eta]_{\text{calc}}}{[\eta]_{\text{exp}}} \right]^2 \longrightarrow \text{minimum}$$

The following values for the constants were obtained ($[\eta]$ in cm^3/g).

$$\begin{aligned} a &= 0.535 & K &= 1.00 \cdot 10^{-1} & \text{for xylene at } 90^\circ \text{C} \\ a &= 0.589 & K &= 4.93 \cdot 10^{-2} & \text{for diethylbenzene at } 120^\circ \text{C} \end{aligned}$$

Table 1 summarizes the average molecular masses including the viscosity averages \bar{M}_v for the samples with a narrow molecular mass distribution, we also give the ratios \bar{M}_w/\bar{M}_n and \bar{M}_z/\bar{M}_w and the results for the number average molecular masses \bar{M}_n , obtained by membrane osmometry. These results agree well with those obtained by size exclusion chromatography. The deviations are in most cases less than 10 %. In summary the data demonstrate the validity of the universal calibration function for the specimens of (norbornene ethylene) copolymers here tested. The sample KMR 3.1 contains macromolecules with $M < 10^4$ g/mole and these molecules will permeate through the osmotic membrane.

Table 1 further represents the good agreement between the values calculated from the chromatograms and the measured ones for the intrinsic viscosity. The deviations are mostly less than 5 % and confirm the correctness of the procedure for the calculation of the constants a and K of the $[\eta]$ -M relation. Also the average values of the molecular masses obtained by application of various eluents agree well. The discrepancy at the specimen TVOB suggests that the molecular mass distribution of this sample had changed over some months. We observed similar effects in other specimens not described here.

Table 1: Molecular parameters for (norbornene ethylene) copolymers with narrow molecular mass distribution

| Sample | $\bar{M}_n \cdot 10^{-3}$ [g/mol] | $\bar{M}_n \cdot 10^{-3}$ SEC [g/mol] | $\bar{M}_w \cdot 10^{-3}$ [g/mol] | $\bar{M}_z \cdot 10^{-3}$ [g/mol] | $\bar{M}_v \cdot 10^{-3}$ [g/mol] | $\frac{\bar{M}_w}{\bar{M}_n}$ | $\frac{\bar{M}_z}{\bar{M}_w}$ | $[\eta]_{calc}$ [cm ³ /g] | $[\eta]_{exp}$ [cm ³ /g] | SEC |
|---------|--------------------------------------|---|--------------------------------------|--------------------------------------|--------------------------------------|-------------------------------|-------------------------------|---|--|-----------------|
| KMR 3.1 | 28.4 | 22.7 | 27.8 | 32.5 | 26.1 | 1.23 | 1.17 | 23.4 | 23.3 | xylene, 90 °C |
| KMR 3.2 | 33.5 | 31.8 | 37.8 | 43.3 | 36.5 | 1.19 | 1.15 | 27.6 | 27.7 | " |
| KMR 3.3 | 37.7 | 37.5 | 44.9 | 51.7 | 43.3 | 1.20 | 1.15 | 30.3 | 30.8 | " |
| KMR 3.4 | 44.3 | 45.4 | 54.4 | 62.1 | 52.5 | 1.20 | 1.14 | 33.5 | 31.8 | " |
| KMR 3.5 | 51.2 | 51.7 | 64.3 | 74.3 | 61.8 | 1.25 | 1.16 | 36.6 | 38.1 | " |
| KMR 3.6 | 69.6 | 69.1 | 95.0 | 111 | 90.6 | 1.38 | 1.17 | 44.9 | 42.9 | " |
| KMR 3.7 | 80.7 | 87.9 | 123 | 147 | 118 | 1.41 | 1.18 | 51.6 | 49.4 | " |
| KMR 3.8 | 95.0 | 105 | 148 | 175 | 141 | 1.40 | 1.18 | 56.9 | 52.8 | " |
| KMR 3.9 | 113.1 | 117 | 174 | 210 | 170 | 1.48 | 1.20 | 61.7 | 62.3 | " |
| TVOB | 221 | 225 | 368 | 461 | 343 | 1.64 | 1.25 | 91.6 | 94.6 | " |
| KMR 3.1 | 21.1 | 21.1 | 27.4 | 33.1 | 26.2 | 1.30 | 1.21 | 19.7 | 19.4 | diethylbenzene, |
| KMR 3.2 | 32.5 | 32.5 | 38.1 | 43.4 | 37.1 | 1.17 | 1.14 | 24.2 | 24.0 | 120 °C |
| KMR 3.3 | 38.8 | 38.8 | 45.2 | 51.2 | 44.0 | 1.17 | 1.13 | 26.8 | 25.5 | " |
| KMR 3.4 | 45.0 | 45.0 | 54.3 | 62.5 | 52.6 | 1.21 | 1.15 | 29.8 | 29.5 | " |
| KMR 3.5 | 53.3 | 53.3 | 65.4 | 75.9 | 63.3 | 1.23 | 1.16 | 33.2 | 34.3 | " |
| KMR 3.6 | 72.6 | 72.6 | 96.2 | 113 | 92.2 | 1.32 | 1.17 | 41.4 | 43.0 | " |
| KMR 3.7 | 87.2 | 87.2 | 123 | 147 | 117 | 1.41 | 1.20 | 47.7 | 47.9 | " |
| KMR 3.8 | 107 | 107 | 152 | 180 | 145 | 1.42 | 1.19 | 54.2 | 50.6 | " |
| KMR 3.9 | 122 | 122 | 175 | 212 | 166 | 1.44 | 1.22 | 58.6 | 57.9 | " |
| TVOB | 185 | 185 | 371 | 519 | 338 | 2.04 | 1.40 | 90.6 | 89.1 | " |

* membrane osmometry

The test results presented here show that both eluents are useful for the size exclusion chromatography of NEC. Nevertheless the higher temperature of 120 °C in the application of diethylbenzene is to be preferred. Parts of very high molecular mass are soluble better and faster, because under these conditions the quality of solvent is higher according to the higher value of α . Moreover the specimens may contain small parts of very high molecular, linear polyethylene (mostly less than 1 %). This is not completely soluble at 90 °C and these microgels can clog the chromatograph.

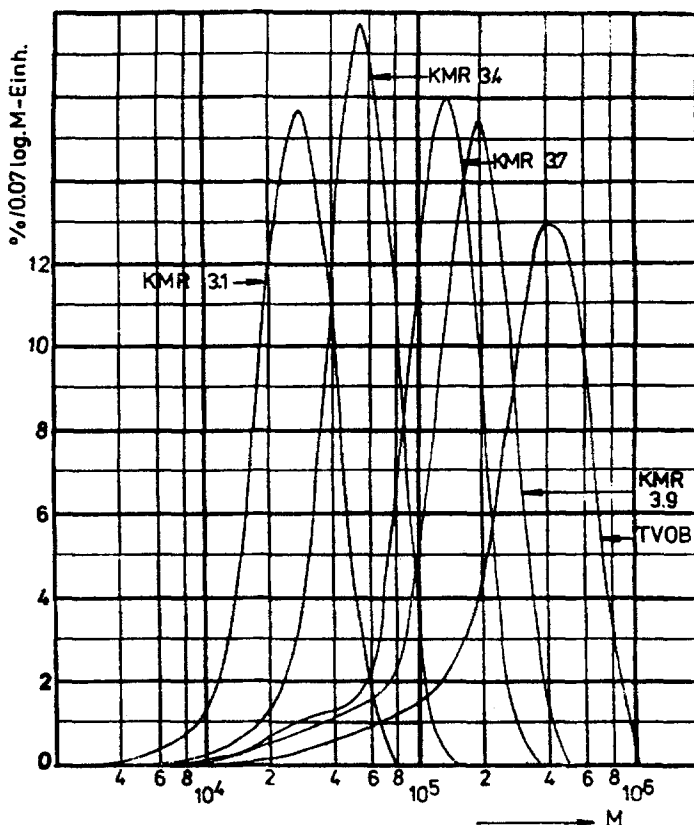


Fig. 1: Molecular mass distribution of samples with narrow distribution

Fig. 1 shows the molecular mass distribution for some samples of NEC with narrow distribution. All these curves show a tailing in the low molecular region. This tailing depends on the synthesis and can be found to a varying degree also for (norbornene ethylene) copolymers with a broader molecular mass distribution. Fig. 2 presents results due to this fact, especially in the case of the molecular mass distribution of laboratory synthesized copolymer samples. The average molecular masses of these samples are summarized in

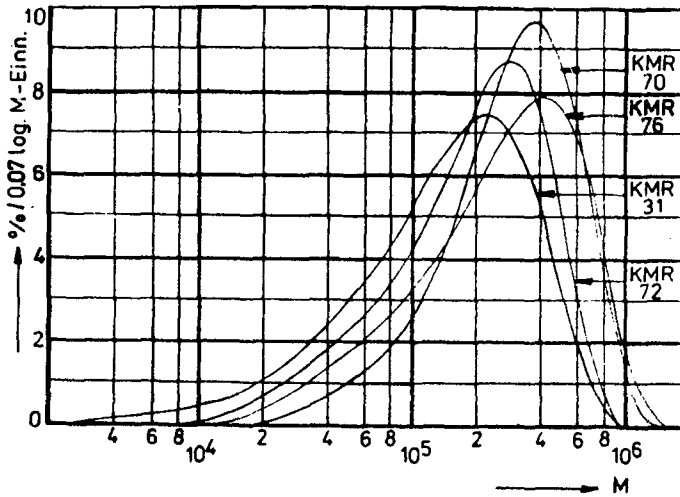


Fig. 2: Molecular mass distribution of samples with broader distribution

Table 2. The degree of low molecular tailing can be estimated from the difference between the quotients \bar{M}_w/\bar{M}_n and \bar{M}_z/\bar{M}_w . The two quotients are equal for symmetric distribution types, i. e. logarithmic normal distribution.

Table 2: Molecular parameters for (norbornene ethylene) copolymers with broad molecular mass distribution (laboratory polymerized samples)

| Sample | $\bar{M}_n \cdot 10^{-3}$ [g/mol] | $\bar{M}_w \cdot 10^{-3}$ [g/mol] | $\bar{M}_z \cdot 10^{-3}$ [g/mol] | $\frac{\bar{M}_w}{\bar{M}_n}$ | $\frac{\bar{M}_z}{\bar{M}_w}$ | $[\eta]_{\text{calc}}$ [cm ³ /g] | $[\eta]_{\text{exp}}$ [cm ³ /g] |
|--------|--------------------------------------|--------------------------------------|--------------------------------------|-------------------------------|-------------------------------|--|---|
| KMR 30 | 79.9 | 191 | 299 | 2.39 | 1.57 | 62.1 | 61.3 |
| KMR 31 | 72.0 | 192 | 306 | 2.66 | 1.59 | 62.0 | 70.8 |
| KMR 70 | 197 | 342 | 477 | 1.74 | 1.40 | 85.2 | 85.7 |
| KMR 72 | 116 | 236 | 347 | 2.04 | 1.47 | 67.8 | 69.4 |
| KMR 76 | 151 | 338 | 519 | 2.23 | 1.54 | 83.0 | 87.5 |

KMR 30 and 31: in xylene at 90 °C

KMR 70, 72, and 76: in diethylbenzene at 120 °C

The above mentioned constants of the $[\eta]$ -M relations are successfully applicable even for copolymers with a composition slightly deviating from the 50/50 mole ratio, in our special case for a ratio of norbornene/ethylene = 54/46 mol-%.

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