

**Title:** Application of high-temperature size exclusion chromatography coupled with dual detection for measuring the distribution of unsaturation in EPDM terpolymers

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**References:**

- Reference 1: Zhou, Z.; Janco, M.; Cong, R.; Lee, D.; Shan, C. L.P.; Boopalachandran, P.; Shi, Z.; Miller, M. D.; Winniford, B.; Huang, T.; Herceg, E.; Salazar, I.; Pangburn, T.; Sandlin, A.; Fan, L.; Wu, J. Simultaneous measurement of the molecular weight distribution and 5-ethylidene-2 norbornene content across the molecular weight distribution of ethylene-propylene-diene terpolymer via a new size exclusion chromatography-ultraviolet-refractive index method. *J. Appl. Polym. Sci.* 133, 2016, 43911-43921
- Reference 2: Micheli, R.A.; Applewhite, T.H.; Measurements on isolated double bond systems: ultraviolet absorption spectra of steroids and triterpenoids. *J. Org. Chem.* 27, 1962, 345-353
- Reference 3: Ute, K.; Niimi, R.; Hongo, S.; Hatada, K. Direct determination of molecular weight distribution by size exclusion chromatography with 750 MHz <sup>1</sup>H NMR detection (On-Line SEC-NMR). *Polym. J.* 1998, 30, 439
- Reference 4: Tackx, P.; Bremmers, S. Chemical composition distribution of polyolefins by SEC-FTIR. *Polym. Mat. Sci. & Eng.* 1998, 78, 49-50.
- Reference 5: Deshmukh, S., Brüll, R., Macko, T., Arndt, J. H., Bernardo, R., Niessen, S. (2022). Characterization of ethylene-propylene-diene terpolymers using high-temperature size exclusion chromatography coupled with an ultraviolet detector. *Polymer*, 242, 124585.
- Reference 6:  
Reference 7:  
Reference 8:  
Reference 9:  
Reference 10:
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### **Abstract:**

The distribution of the pendant double bond along the molar mass axis impacts the vulcanization behavior of polyolefin elastomers such as ethylene-propylene-diene (EPDM). However, the analysis of this parameter has so far been hindered by the lack of suitable detection techniques. Towards this goal we have investigated the potential of ultraviolet detector (UV) detector for high temperature size exclusion chromatography of EPDM terpolymers containing 5-ethylidene-2-norbornene (ENB), dicyclopentadiene (DCPD), and vinyl norbornene (VNB) as termonomer.

The influence of termonomer structure and experimental parameters such as, mobile phase, analyte concentration and temperature on the spectroscopic response was probed. EPDM containing ENB showed a significantly stronger UV-absorption compared to terpolymers with VNB and DCPD. The absorbance was found to correlate with the sample concentration approaching signal saturation at higher ENB content. Temperature did not have any significant effect on the UV absorbance of EPDM.

Based on the results, a method was developed, which can profile the content of diene along the molar mass axis. An evaporative light scattering detector (ELSD) was employed to monitor the analyte concentration, in combination with the UV detector, to quantitatively measure the distribution of ENB content along the molar mass distribution. This work could be extended for other two termonomers DCPD and VNB and for commercially relevant elastomers such as butyl rubber.