Spectroscopic Examination of
Ethylene–Propylene–Norbornenic Diene Terpolymers

C. TOSI, F. CIAMPELLI, and N. CAMELI, *Centro Ricerche di Milano,*
Montecatini Edison S.p.A., I-20133 Milan, Italy

Synopsis

Infrared methods for the analysis of the third monomer in ethylene–propylene–norbornenic diene terpolymers were developed.   They are based either on the C=C stretching vibration near 6 μ or on the =CH— out-of-plane deformation vibration between 11 and 12 μ.   Calibration was made by NMR on selected samples with high unsaturation content.   Particular emphasis was laid on terpolymers with ethylidene norbornene, for which the reliability of the analysis for the third monomer was checked by several techniques, and the transferability to the determination of propylene of the calibration curves set up for the analysis of composition in ethylene–propylene copolymers was studied.
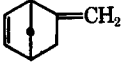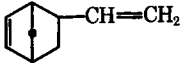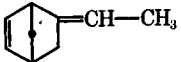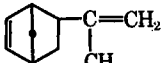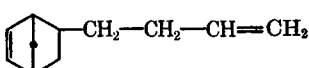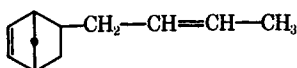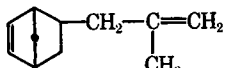
INTRODUCTION

In recent years considerable success has been achieved in producing terpolymers of ethylene (C_2) and propylene (C_3) with nonconjugated diolefins in which one of the two double bonds is present in a norbornenic ring.[1-7]

It is known that the two double bonds employed for preparing an elastomer vulcanizable with sulfur and accelerators should have very different reactivities: one should be most reactive with Ziegler-Natta catalysts, so as to be easily incorporated into the polymer;   the other should be inert in polymerization but react with the vulcanizing agent.   Both these requirements are excellently met by derivatives of norbornene with alkene substituents: the former, by the double bond in the bridged ring;   the latter, by the double bond outside the ring.   The resulting terpolymer is thus formed by flexible polymethylene chains having methyl groups (arising from C_3 units) attached at frequent intervals and, much less frequently, pendant unsaturated groups with norbornane rings (arising from the third monomer).

The production of terpolymers with the norbornadiene types of monomer makes necessary both the development of analytic methods for the evaluation of the third monomer content and a careful control of the transferability of analytic methods worked out for the analysis of composition in C_2–C_3 copolymers to the determination of the amount of the two main components.

In this paper we report on the results obtained for C_2–C_3 terpolymers containing norbornenic units derived from the seven monomers shown in Table I.

TABLE I
Monomers From Which Norbornenic Units Were Derived

Compound	Name	Abbreviation
=CH₂	5-methylene-2-norbornene	MNB
—CH=CH₂	5-vinyl-2-norbornene	VNB
=CH—CH₃	5-ethylidene-2-norbornene	ENB
—C=CH₂ / CH₃	5-isopropenyl-2-norbornene	IPNB
—CH₂—CH₂—CH=CH₂	5-(3-butenyl)-2-norbornene	3-BNB
—CH₂—CH=CH—CH₃	5-(cis-2-butenyl)-2-norbornene	cis-2-BNB
—CH₂—C=CH₂ / CH₃	5-methyl allyl-2-norbornene	MANB

DETERMINATION OF THE UNSATURATION IN STANDARD TERPOLYMERS

A number of chemical and physicochemical techniques (such as iodine monochloride method, gas-chromatographic analysis of the pyrolysis products, IR, NMR) have been used for determining double bonds in C_2-C_3 terpolymers.[8-11]

In our case, after examination of results obtained by the various techniques, we have reached the conclusion that IR spectroscopy is the most suitable method for routine determination of the amount of unsaturation in C_2-C_3 terpolymers. For all termonomers taken into account, two bands can be utilized: either the band around 6 μ characteristic of C=C stretching vibration, or the band, lying somewhere between 11 and 14 μ depending on the kind of unsaturation, due to out-of-plane deformation of the hydrogens on the double bond.

Preliminary evaluation of the absorptivity of these bands requires the availability of some standard terpolymers, with known unsaturation content; in fact, it is not conceivable to adopt the absorptivities deduced from the spectra of monomers, as in the polymers the band intensities could change (and in some instances they actually do, as will be shown later) because of release of the ring strain. As standard terpolymers we used a

number of samples with high termonomer content, in which double bonds were determined by NMR spectroscopy.

The instrument was a 100-MHz Varian spectrometer. Terpolymers were dissolved in tetrachloroethylene at about 10% concentration (w/v), and the examination was carried out at 70°C. The ratio R between the signal from all saturated protons (having chemical shifts of 1–2 δ) and the signal from olefinic protons (having chemical shift of 4.5–5.5 δ) was measured. Particular care was taken in the evaluation of R, for this quantity is very large (and hence badly measurable) even in high unsaturation terpolymers.

Knowledge of R for a given terpolymer allows us to immediately find the weight fraction w of the termonomer in the terpolymer. If M stands for the molecular weight of the termonomer and s and u are the numbers of saturated and unsaturated protons it contains, the weight fraction of its protons is $w(u + s)/M$, and the weight fraction of all (saturated) protons of C_2 and C_3 is $(1 - w)/7$, so that

$$R = \frac{\dfrac{ws}{M} + \dfrac{1 - w}{7}}{\dfrac{wu}{M}}$$

whence

$$w = \frac{M}{7(Ru - s) + M}.$$

It is worth remarking that this NMR examination does not provide the mole fraction of the termonomer, unless the amount of C_2 or of C_3 is independently known. If we indicate by m the mole fraction of the termonomer and by p the mole fraction of C_3, we find

$$R = \frac{m(s - 4) + 2(p + 2)}{mu}$$

and this formula, containing two unknowns (m and p), requires, to be solved, two independent experiments on the same sample.

IR METHODS FOR DETERMINING UNSATURATION

Once the composition of a high unsaturation terpolymer has been established, it becomes possible to determine the molar absorptivity of the characteristic IR bands to be employed for all subsequent samples. For practical purposes, this evaluation is best done by means of calibration curves, giving the weight percentage of the termonomer against the absorbance per unit thickness of the relevant IR bands. Using two or three samples with high, but somewhat different, unsaturation content for each type of terpolymer, we found that for all termonomers taken into account, calibration curves are straight lines through the origin.

IR spectra were recorded on a Perkin Elmer-221 spectrophotometer, on sheets about 0.2 mm thick prepared in a laboratory press at 150°C. The conditions for the analyses were: suppression, 6.0; gain, 2.5; slit program, 9.27; speed, 0.5 μ/min.

No problems arose for drawing baselines, except for the ENB band at 5.93 μ. Our choice is shown in Figure 1. We did not believe it necessary to use a compensating wedge of C_2–C_3 copolymer in the reference beam of the instrument, as proposed by Levine and Haines,[10] not only because of the energy loss that such a wedge would involve, but also because of the difficulties found in compensating in a region where many absorptions are often present. It must be remembered that carbonyl bands of most common antioxidants are observed between 5.7 and 6 μ. Particular care therefore should be devoted to ENB analysis, and in many instances terpolymers need purification before their spectrum is recorded.

As an internal standard of thickness, the band at 2.32 μ was chosen. This band arises from a combination of C—H stretching and C—H bending fundamental vibrations, lying at ca. 3.4 and 6.9 μ. The respective baseline (see Fig. 1) is traced horizontally at 2.1–2.2 μ, as was done also by Takeuchi et al.[12] For C_2–C_3 copolymers, it was assumed[13] that the absorbance of the 2.32-μ band is proportional to the entire number of C–H bonds present, and hence to copolymer thickness. This assumption has been checked for the present terpolymers by plotting absorbance at 2.32 μ versus thickness of the terpolymer sheets, measured with a Stickney gauge, and is fully fulfilled.

The absorptivities of the IR bands characteristic of the termonomers, deduced from NMR calibration, are reported in Table II. Results listed in this table need some comments.
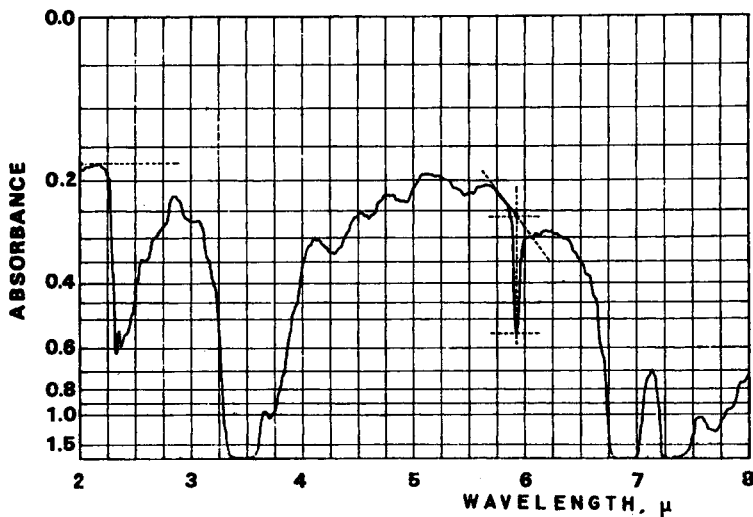

Fig. 1. IR spectrum between 2 and 8 μ of a C_2–C_3–ENB terpolymer containing 18.7 wt-% ENB, showing baselines for ENB band at 5.93 μ and for reference band at 2.32 μ. Sample thickness 0.22 mm.

TABLE II

Wavelength λ, Molar Absorptivity ε, and Coefficient K for IR Bands of Norbornenic Dienes in C_2-C_3 Terpolymers[a]

Monomer	Kind of double bond	C=C stretching band			=C—H out-of-plane deformation band		
		λ	$\epsilon \times 10^{-4}$	K	λ	$\epsilon \times 10^{-4}$	K
MNB	vinylidene	6.02	4.9 / 4.5	0.215	11.47	19.6	0.054
VNB	vinyl	6.10	4.8 / 3.35	0.250	11.03	22.6	0.053
ENB	trisubstituted	5.93	0.85 / 0.54	1.415			
IPNB	vinylidene	6.08	5.8 / 4.0	0.231	11.32	24.4	0.055
3-BNB	vinyl	6.09	4.9 / 4.65	0.330	11.01	18.3	0.081
cis-2-BNB	cis	6.05	1.2 / 1.02	1.22			
MANB	vinylidene	6.06	4.3 / 4.3	0.347	11.28	22.4	0.066

[a] λ in microns, ε in mole⁻¹ cm², K = reciprocal of $A_{1\%, 1cm}$ (see text).

a. The two columns named *K* contain the coefficients (easily calculated from the molar absorptivities) by which the ratios of absorbance/thickness (cm) found in individual spectra of terpolymers should be multiplied to obtain the weight per cent of the termonomer.
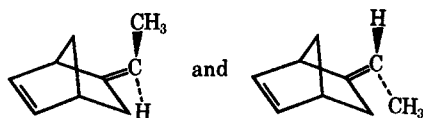
b. In the cited work by Levine and Haines[10] on the IR analysis for ENB in C_2–C_3 terpolymers, the wavelength of the $\nu(C{=}C)$ band is systematically indicated as 5.88 μ. We believe it is only a trivial typographical error. The molar absorptivity deduced from the calibration curve reported in Figure 1 of ref. 10 (0.70 $\times$ 10^4 mole^{-1} cm^2) is somewhat smaller than that found by us, but the discrepancy might be due, at least in part, to the different choice of the baseline.

c. The $\delta({=}CH{-})$ band cannot be used for the analysis of ENB in C_2–C_3 terpolymers, for its wavelength (ca. 12.4 μ) is almost coincident with the wavelength of the rocking vibration of isolated —CH_2— units contained in C_3 sequences. It should be remembered that a correction for the contribution of these units is practically impossible, because their amount depends, for a given terpolymer composition, on the "blockiness" of the polymer, i.e., on the catalyst employed in polymerization. For this reason, the statement by Altenau et al.[11] that the former wavelength is the most useful for identification of ENB in C_2–C_3 terpolymers seems to us rather surprising.

d. The numbers in italics in the column of absorptivity of the $\nu(C{=}C)$ band refer to molar absorptivity found in the respective monomers. With the exception of MANB, these values are less than in the polymers, the minimum ratio being observed in ENB.
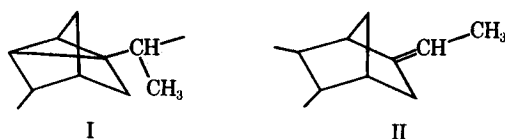
As will be shown in the next paragraph, particular emphasis was laid on terpolymers with ENB, so that more elements are available to explain their behavior than for terpolymers with the other six monomers.

To begin with, ENB monomer is a mixture of two steric isomers:

These two isomers can be separated by preparative gas chromatography (column packed with 25% β,β'-oxydipropionitrile on Chromosorb P, temperature ca. 50°C) and are equally reactive in terpolymerization, but the molar absorptivities of the $\nu(C{=}C)$ band in their IR spectra are very different: ca. 0.28$\times$10^4 and 0.66$\times$10^4 mole^{-1} cm^2, respectively.[14] However, this isomerism cannot be responsible for the difference of absorptivity between ENB monomer and combined ENB in C_2–C_3 terpolymers, as the value observed in the terpolymers is bigger than that for both isomers of the monomer.

One could also think of the possibility that ENB be incorporated into the polymer in a nortricyclene structure (I) as opposed to the more usual polymerization through the norbornene double bond (II):

I   II

This hypothesis has been excluded after examination of a number of ter-polymers with ^{14}C-labeled ENB (see later); however, it could not be used to explain the different absorptivities of ENB, as in such case the absorptivity in the polymer should be less than in the monomer.

The reason for this difference should then be sought in the release of the strain of the norbornenic ring which takes place in polymerization. This statement was confirmed by IR examination of the compound obtained by selective hydrogenation of ENB at the active double bond, viz., 5-ethyl-idenenorbornane (HENB). Hydrogen uptake analysis indicated that HENB had more than 99% of the theoretical unsaturation. The condi-tions in the immediate vicinity of the double bond are very similar for this monomer and combined ENB in the polymer, and the molar absorptivity of the $\nu(C{=}C)$ band should be very close to the same value. For the HENB band at 5.94 μ, we found $\epsilon = 0.80 \times 10^4$ mole^{-1} cm^2, and the agree-ment with the value for combined ENB is good, particularly if one con-siders that NMR analysis of HENB based on integration of the peak due to olefinic proton indicated the presence of a few per cent of structures either completely saturated or containing wholly substituted double bonds.

DETAILED STUDY OF TERPOLYMERS WITH ENB

Among the monomers considered in the preceding paragraphs, ENB is the most reactive in terpolymerization[6] and has by far the greatest practical interest. It therefore seemed advisable to carefully check both the reli-ability of ENB determination and the influence exerted by ENB on the C_3 analysis, when this latter is carried out by means of calibrations set up for C_2-C_3 copolymers.

To make the former check, three different ways were followed: (a) preparation of C_2-ENB copolymers with ^{14}C-labeled C_2; (b) preparation of C_2-C_3-ENB terpolymers with ^{14}C-labeled ENB; (c) material balance determination by vapor-phase chromatography.

In case (a), the ENB content was determined from the radiochemical analysis for C_2, which is very accurate, and the result compared with that obtained on the basis of the 5.93-μ band with the absorptivity used for ter-polymer analysis. Two copolymers were prepared and very good agree-ment was found:

Sample	ENB, wt-%	
	Hundred minus C_2 (radiochemical)	IR
1	53.5	55.8
2	39.5	39.2

In case (b), ^{14}C-labeled ENB was prepared by reaction of cyclopentadiene with ^{14}C-labeled butadiene and subsequent isomerization. Also in this case, good agreement was found:

	ENB, wt-%	
Sample	Radiochemical	IR
1	2.6	3.1
2	3.6	3.5
3	6.5	6.9
4	10.6	10.0

This agreement had a very important consequence, in that it permitted us to rule out the presence of appreciable amounts of ENB incorporated in the nortricyclene structure (I).

Case (c) involved analysis, by vapor phase chromatography, of the gross polymerization mixture before and after polymerization, as described by Levine and Haines.[10] Since by this method ENB in the terpolymer is evaluated as the difference between that initially added to the reactor and that recovered from the polymerization solvent, high ENB conversion (at least 30%) is necessary. Obviously, the method is valid only if the assumption is made that all of the missing ENB is in the polymer. The results of four polymerization runs, listed below, also in this case were quite satisfactory:

		ENB, wt-%	
Run	ENB conversion	VPC	IR
1	48%	17.4	18.7
2	73%	7.2	6.6
3	36%	5.3	6.0
4	72%	4.3	4.3

The second analytic check concerning C_2–C_3–ENB terpolymers aimed at detecting the influence exerted by ENB upon the C_3 determination. The method used for the C_3 determination, first proposed by Bucci and Simonazzi,[15] is based on the near-infrared bands at 1.69 and 1.76 μ that are first overtones of the ν(C—H) fundamental vibrations. We prefer this method to other methods based on bending vibrations[13,16-18] as it has a better reproducibility and is less sensitive to the conditions of polymerization.[19] This method is calibrated for binary C_2–C_3 copolymers, so its utilization for the analysis of terpolymers needs the influence of the third monomer to be carefully taken into account.

In principle, a spectroscopic calibration curve relevant to a two-component system still may be used when a third component is present if, and only if, this component does not contribute to the bands employed for determining the other two nor exert any indirect influence (such as enhancement or suppression) upon these bands. This is not the case for the system

C_2–C_3–ENB; ENB has indeed non-negligible absorptions in all spectral regions utilized for the C_3 determination. An accurate evaluation of these absorptions is practically impossible, as it would demand availability of a homopolymer of ENB with the same repeating units that are present in terpolymers, and such a homopolymer cannot be obtained under the catalytic conditions used in terpolymerization.

An empirical correction therefore should be sought. The simplest empirical correction consists in analyzing a set of terpolymers with ^{14}C-labeled C_2 and subtracting from (or adding to) the measured C_3 content an amount proportional to ENB concentration, the proportionality coefficient k being evaluated in such a way as to minimize the sum of the squares of the differences (total found − 100), where "total found" stands for the sum C_2 (determined by radiochemical counting) + ENB (determined by IR spectroscopy*) + C_3 (determined by NIR (near-infrared) spectroscopy, suitably corrected for ENB influence).

Here a remark appears in order. When the C_3 content in a terpolymer is measured by a method calibrated for C_2–C_3 copolymers, the percentage read on the working curve clearly refers only to the (C_2 + C_3) portion of the terpolymer, and the actual percentage referred to the whole terpolymer will be obtained by multiplying it by (100 − ENB%)/100. These considerations, however, apply only as long as the third monomer does not contribute to one or both of the bands employed to evaluate C_3. ENB, however, absorbs both at 1.69 and 1.76 μ.

In a recent study on the NIR spectroscopy of hydrocarbon functional groups,[20] we have noticed that the former band arises only from methyl groups, whereas the latter results from superposition of methyl and methylene vibrations, the absorptivities of both groups being of the same order of magnitude. As a consequence, the absorbance of the 1.76-μ band in C_2–C_3 copolymers should be roughly proportional to the sample thickness, and the situation should not markedly change in C_2–C_3–ENB terpolymers, owing to the presence of both methyl and methylene groups in ENB. Therefore, the C_3 percentage read on the copolymer calibration curve was referred, in the "total found," to the whole terpolymer. The above-mentioned minimization procedure could then be applied in the following way.

For the check with the ith terpolymer, the total found is given by C_{2i} (radiochemical) + C_{3i} (actual) + ENB$_i$. If we assume the actual C_3 content to be given by the difference between that found and the ENB content times the coefficient k, C_3(actual) = C_3(found) − kENB, the expression to minimize is

$$\sum_{i=1}^{N} \left\{ [C_{2i}(\text{rad.}) + C_{3i}(\text{found}) - k\text{ENB}_i + \text{ENB}_i] - 100 \right\}^2,$$

where N is the number of calibration points, so that k will be the solution of the equation $\partial\Sigma/\partial k = 0$, i.e.,

---

* The IR determination of ENB is influenced very little by C_3 content.

$$k = \frac{\sum\limits_{i=1}^{N} [C_{2i}(\text{rad.}) + C_{3i}(\text{found}) + ENB_i - 100]ENB_i}{\sum (ENB_i)^2}.$$

Having found $k = 0.5$, the C_3 percentage in terpolymers will thus be obtained by subtracting one half of the ENB amount from the percentage deduced from the copolymer calibration curve.

References

1. E. K. Gladding, B. S. Fisher, and J. W. Collette, *Ind. Eng. Chem., Prod. Res. Develop.*, 1, 65 (1962).

2. W. Cooper, D. E. Eaves, M. E. Tunnicliffe, and G. Vaughan, *Eur. Polym. J.*, 1, 121 (1965).

3. G. Natta, G. Crespi, A. Valvassori, G. Sartori, N. Cameli, and V. Turba, *Rubber Plast. Age*, 46, 683 (1965).

4. R. German, R. Hank, and G. Vaughan, *Kaut. Gummi, Kunstst.*, 19, 67 (1966).

5. R. J. de Kock and A. Veermans, *Makromol. Chem.*, 95, 179 (1966).

6. D. L. Christman and G. I. Keim, *Macromolecules*, 1, 358 (1968).

7. N. Cameli, A. Valvassori, and C. Tosi, *Mater. Plast. Elast.*, 34, 1433 (1968).

8. R. Hank, *Rubber Chem. Technol.*, 40, 936 (1967).

9. P. R. Sewell and D. W. Skidmore, *J. Polym. Sci. A-1*, 6, 2425 (1968).

10. I. J. Levine and R. G. Haines, *Rubber Chem. Technol.*, 43, 445 (1970).

11. A. G. Altenau, L. M. Headley, C. O. Jones, and H. C. Ransaw, *Anal. Chem.*, 42, 1280 (1970).

12. T. Takeuchi, S. Tsuge, and Y. Sugimura, *Anal. Chem.*, 41, 184 (1969).

13. F. Ciampelli, G. Bucci, T. Simonazzi, and A. Santambrogio, *Chim. Ind.* (Milan), 44, 489 (1962).

14. T. Simonazzi, private communication.

15. G. Bucci and T. Simonazzi, *Chim. Ind.* (Milan), 44, 262 (1962).

16. Th. Gössl, *Makromol. Chem.*, 42, 1 (1960).

17. P. E. Wey, *Anal. Chem.*, 33, 215 (1961).

18. H. V. Drushel and F. A. Iddings, *Anal. Chem.*, 35, 28 (1963).

19. C. Tosi, M. P. Lachi, and A. Pinto, *Makromol. Chem.*, 120, 225 (1968).

20. C. Tosi and A. Pinto, *Spectrochim. Acta, A*, in press.