

Ethylene-Propylene Copolymers: Crystallinity, Infrared, and Creep Studies

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Synopsis

Density, infrared, and creep studies have been made of ethylene-propylene copolymers containing up to about 50 mole-% propylene and their homopolymers. The degree of crystallinity (volume fraction of polyethylene crystals), as measured by density and x-ray studies, decreases with increased propylene content. This change is also reflected in the intensity of the 13.7 μ band in the infrared spectra of the polymers. The measured amount of unsaturation (0.1-0.2%) in the copolymers is too small to account for the presence of several infrared bands which are often attributed to unsaturation. An unsaturation of 0.90% was obtained for a terpolymer where the third component was unsaturated. Indentation-creep studies showed the creep to be nearly proportional to the logarithm of time with a slope of 10% creep per decade for 0.1-10 min. Compliance-temperature graphs were found to be quite similar to those for the styrene-butadiene rubber SBR 1500.

Ethylene-propylene copolymers, first prepared in Italy about 1956, are now being actively developed by a number of American firms. They present considerable economic promise because of the low cost of the raw materials. Outstanding qualities include resistance to ozone (O₃) and molecular oxygen (O₂), as well as good electrical properties.

The determination of the degree of crystallinity is of importance in characterizing ethylene-propylene copolymers, since the high extensibility characteristic of a rubber is obtained only when the degree of crystallization is low. The linear polyethylene and isotactic polypropylene homopolymers are each highly crystalline and lack high extensibility. However, a sufficiently low degree of crystallization can be obtained by copolymerizing ethylene with at least 20-30% propylene; similarly the degree of crystallization is sufficiently reduced by copolymerizing propylene with ethylene.

Samples of the copolymers were obtained from five different sources—four in the United States and one in Italy. One set of five samples represented pilot-plant or production samples and had propylene contents in the range of 30-50 mole-%. In addition a set of five experimental copolymers was studied in which the propylene content as reported by the supplier had been systematically varied from 10 to 50 mole-%. These two sets, designated respectively as PP and E, are listed in Table I together with a number of the properties determined in the present investigation.

TABLE I
Crystallinity and Unsaturation of Some Experimental and
Commercial Ethylene-Propylene Copolymers

Sample	Propylene content, mole-%		Unsaturation by ICl method, %	Density d_{25} , g./cc.	Specific volume V_{25} , cc./g.	Degree of crystallinity	Degree of crystallinity
	Nominal	NBS method				X_v , %	X_x , %
E-1	10	9		0.9122	1.0963	44	25
E-2	20	20		.8758	1.1418	18	11
E-3	31	32		.8592	1.1639	5	1.0
E-4	40	39		.8523	1.1733	0	0.6
E-5	50	53		.8524	1.1732	0	0
PP-1	22-31	35	0.15	.8583	1.1651	5	1.4
PP-2	—	33	0.90	.8566	1.1674	3	0
PP-3	42-45	34	0.11	.8568	1.1672	3	0.4
PP-4	50	37	0.21	.8575	1.1663	4	0
PP-5	50	48	0.12	.8543	1.1706	1	0.8

Sample PP-2 was reported to be a terpolymer where the unsaturation in the third constituent is not in the main chain. Additional samples utilized in the course of the work included a sample of commercial linear polyethylene (Marlex 50) and a sample of polypropylene (crystalline; \bar{M}_n 59,200, \bar{M}_v 213,000).

Values for the degree of crystallinity X_v (volume fraction of polyethylene crystals as calculated from specific volumes) for polyethylene and the copolymers were calculated from the experimentally determined specific volume V by using the usual relation based on the additivity of partial volumes:

$$X_v = \frac{V_a - V}{V_a - V_c}$$

where V_a is the specific volume of the amorphous copolymer and V_c is the specific volume of completely crystalline polyethylene. In the present work the propylene contents of the copolymers were never greater than about 50 mole-% and so the only crystals assumed to be present would be those of polyethylene. This assumption is verified by the infrared and x-ray studies discussed below.

A critical survey of the literature showed that the specific volume of amorphous polypropylene is about 1.176 cc./g. at 25°C., that of amorphous polyethylene is about 1.170 cc./g., and that of completely crystalline polyethylene is about 1.001 cc./g. The value of V_a was therefore obtained as the weighted mean of the values for the amorphous homopolymers. The densities determined by the hydrostatic-weighing method,¹ the corresponding specific volumes, and the calculated degrees of crystallinity of the ethylene-propylene copolymers are given in Table I. In this table are also listed nominal values for the propylene content of each sample,

as well as values obtained by a method developed by Brown, Tryon, and Mandel² in this laboratory. The method involves infrared examination of a pyrolyzate of the polymer.

Observations of x-ray diffraction patterns were made on a recording x-ray diffractometer with the use of $\text{CuK}\alpha$ radiation. The samples were about 2.8 mm. thick. The graph of intensity against double Bragg angle 2θ showed the expected maximum for the amorphous halo at about $2\theta = 18.7^\circ$. When crystals of polyethylene were present, superposed sharp peaks appeared at about 21.2° , representing the 110 reflection, and at about 23° , representing the 200 reflection. On the assumption that these graphs can be interpreted as resulting from amorphous and crystalline regions only, area measurements were made to obtain estimates of X_x , crystallinity as determined by x-ray diffraction. Each number in the last column of Table I represents the ratio of the area under the sharp peaks corresponding to the 110 and 200 reflections (when both are present) and above the broad halo, to the sum of this area and that below the halo multiplied by 1.235. This method of calculating the degree of crystallinity is due to Hendus and Schnell.³ The values of X_x are seen to be considerably less than those given for X_v , the crystallinity as determined from volume measurements. However, the relative order of values is essentially the same. Values less than a few per cent are of doubtful significance in both cases.

Jackson⁴ has recently shown that for a given propylene content the degree of crystallinity depends also to a certain extent on r_1r_2 , the product

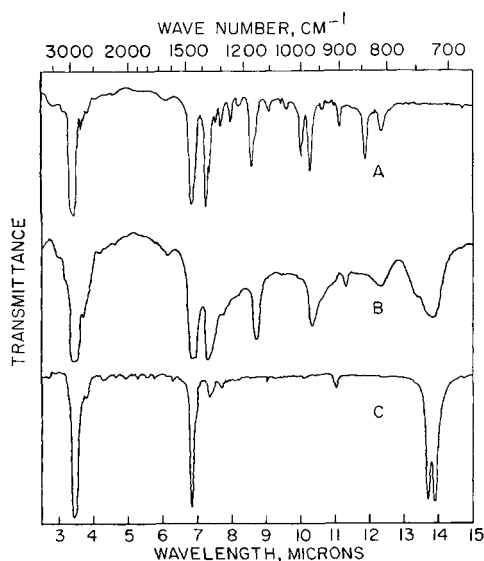


Fig. 1. Infrared spectra: (A) isotactic polypropylene ($\bar{M}_n = 59,200$, $\bar{M}_r = 213,000$); (B) ethylene-propylene copolymer, sample PP-5; (C) linear polyethylene (Marlex 50).

of the reactivity ratios of the monomers in the particular polymerization system. The value of r_1r_2 is a factor determining the randomness of the sequences of ethylene and propylene units. A "random" copolymer is usually defined as one in which the product $r_1r_2 = 1$. For each value of propylene content, the degree of crystallinity X_v , as obtained from the specific volume measurements and given in Table I is in very good agreement with the value X_x calculated by Jackson for a random copolymer ($r_1r_2 = 1$), and observed by him for a copolymer with r_1r_2 near unity. Jackson's observed values were based on the ratio of the area under the x-ray diffraction peaks to that under the portion of the pattern arising from the amorphous region. No values of r_1 and r_2 were available for the polymers in the present study.

Copolymers prepared from diazomethane and diazoethane have been studied by Richardson, Flory, and Jackson.⁵ The products should be the equivalent of random copolymers of ethylene and propylene containing up to about 12 mole-% propylene. They report values of crystallinity, as determined from specific volumes, appreciably less than those found by Jackson. For example, at 10 mole-% propylene their value of X_v would be about 28% as compared with Jackson's value of X_x of about 47%. The reasons for the discrepancy are not clear, but it should be remembered that the polymers were prepared by very different methods.

A study of the infrared spectra of films (0.05–0.12 mm. thick) of the ethylene-propylene copolymer samples was made with a Perkin-Elmer Infracord spectrometer. Figure 1 shows an example of such a spectrum, together with those of the crystalline homopolymers for comparison. Curve *A* is the spectrum of isotactic polypropylene; curve *B* is that for sample PP-5, a copolymer containing about 50 mole-% propylene; curve *C* is the spectrum of a commercial linear polyethylene.

Bands in spectrum *A* of isotactic polypropylene near 7.34, 7.50, 7.66, 7.95, 8.18, 9.05, 9.58, 10.00, 10.60, 11.10, 11.86, and 12.35 μ either become weak or are eliminated at 180°C. (above the melting point) and are therefore considered as being characteristic of crystalline polypropylene.⁶ They are also essentially absent from the copolymer in *B*, for which the specific volume and x-ray studies show negligible crystallinity. The band near 13.7 μ in the doublet in spectrum *C* of linear polyethylene, on the other hand, is related to the crystallinity of polyethylene⁷ and is absent in the copolymer spectrum *B*. It is also absent from the spectra of the samples studied here containing more than 20 mole-% propylene. These results are in accordance with the degree of crystallinity in these samples indicated from the density and x-ray measurements.

The peak near 13.9 μ in both *B* and *C* is related to sequences of approximately six or more CH₂ groups.⁸ The shoulders on the side of the 13.9 μ band between 12.7 and 13.9 μ in *B* and other copolymers are related to sequences of fewer than six consecutive CH₂ groups,⁸ and of course increase in intensity with increased propylene content. At a given propylene content, the number and intensity of these methylene bands should bear

a relationship to the randomness of the sequence of ethylene and propylene in the material, and to the mode of addition of one mer to another. Several authors⁹⁻¹³ have discussed some details of this relationship. The article by van Schooten and Mostert¹⁰ is of special interest because it covers the region between 70 and 85% propylene not previously treated. The combined papers are useful in presenting the variations of the number and intensity of bands between 12.7 and 13.9 μ resulting from wide changes in composition and structural features.

The bands near 8.7 and 10.3 μ in *B* are probably related to the absorptions at 8.55 and 10.25 μ in *A*. The band at 8.7 μ has been attributed to methyl wagging¹⁴ and the band at 10.3 μ to methyl rocking.⁹ The latter band has also been related to internal *trans* unsaturation.¹⁵ It is present in both isotactic and atactic polypropylene.⁶

Films of all the samples listed in Table I were used in these studies of infrared absorption. Bands near 6.05, 10.3, 10.9, and 11.25 μ in nearly all the samples are in regions where unsaturated compounds are known to absorb. Unsaturation was therefore determined on the commercial samples by an iodine monochloride method especially adapted to the determination of unsaturation in highly branched olefins and polymers such as those presumably present here.¹⁶ The results (Table I) indicate that, with the exception of sample PP-2 (a terpolymer containing unsaturation in the third constituent), the degree of unsaturation is appreciably less than that of butyl rubber. The chemical unsaturation values in Table I are in mole % based on the molecular weight of the average mer taken from the composition of the polymer. They represent the per cent of mers or polymer units containing one double bond each. These values are thus about one-half as large as they would be if calculated on the basis of an isoprene unit. Even if doubled, the values are considerably smaller than those for typical butyl rubber; the latter can range from 0.8 to 3.0 wt.-% isoprene. These data suggest that not all the absorption in the four bands mentioned above is due to unsaturation. The unsaturation data are also consistent with the superior ozone resistance of the ethylene-propylene rubbers in comparison with butyl rubber.

It was desired to determine whether any of the absorption near 6.05, 10.3, 10.9, or 11.25 μ which might be attributed to unsaturation could result from additives and thus be removed by extraction of the copolymers. All of the commercial samples were extracted with anhydrous ethanol-toluene azeotrope for 2-hr. periods and films prepared and dried under a vacuum at room temperature. The amount extracted, which may be additives or low molecular weight polymer, was in the range of 4-14%. In each case, the main change in the infrared spectrum was a reduction in the intensity of the band at 11.25 μ . This band may thus be ascribed to impurities or low polymer fractions.

Some information regarding the viscoelastic properties of an ethylene-propylene vulcanizate similar to those which might be used commercially was obtained from indentation-creep studies. For this purpose sample

PP-5 was compounded with 50 parts of HAF black and cured 30 min. at 165°C. with 4 parts of 40% dicumyl peroxide and 0.3 part of sulfur. The International Rubber Hardness Tester was used to measure the indentation, following a procedure recently developed in the NBS laboratories.¹⁷

Studies at room temperature showed the creep to be nearly proportional to the logarithm of the time, with a slope of about 10% per decade from 0.1 to 10 min. Observations made at temperatures of -50, -36, -30, and 25°C. yielded data for a plot of JT (product of compliance and temperature on the Kelvin scale) against the logarithm of the time. The graphs for different temperatures could be shifted along the axis of the logarithm of the time to yield a single master curve describing the viscoelastic behavior of the polymer. The behavior was found to be very similar, qualitatively and quantitatively, to that of the styrene-butadiene rubber SBR-1500 when compounded and cured according to ASTM Formulation 2B (Designation D15-59T).

The length-temperature relation of sample PP-1 containing about 35 mole-% propylene was measured by the use of a photoelectric recording interferometer.¹⁸ From this relation a single glass transition was observed at about -60°C., in general agreement with values reported in the literature.

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Résumé

Des études de densité, d'infrarouge, et de rétrait ont été faites sur des copolymères éthylène-propylène, qui contiennent plus que 50 mole-% de propylène et de leurs homopolymères. Le degré de cristallinité (la fraction de volume des cristaux de polyéthylène) mesuré par des études de densité et de rayons X, diminue avec une augmentation de la teneur en polypropylène. Ce changement se montre aussi dans l'intensité de la bande de 13.7 μ du spectre infra-rouge de ces polymères. La quantité d'insaturation mesurée (0.1-0.2%) dans les copolymères est trop faible pour expliquer la présence des plusieurs bandes infra-rouges généralement attribuées à l'insaturation. Une insaturation de 0.90% a été obtenue pour un terpolymère dans lequel le troisième composant était insaturé. Des études de rétrait à la coupure montrent un rétrécissement environ proportionnel au logarithme du temps avec une tangente de 10% de rétrécissement par décade entre 0.1 à 10 minutes. Les graphiques souplesse-température étaient très semblables à ceux des caoutchoucs SBR 1500 de styrène et butadiène.

Zusammenfassung

Dichte-, Infrarot- und Kriechuntersuchungen wurden an Äthylen-Propylenkopolymeren mit einem Gehalt von bis zu 50 Molprozent Propylen und Homopolymeren angestellt. Der Kristallinitätsgrad (Volumbruch von Polyäthylenkristallen) nimmt nach Dichte- und Röntgenuntersuchungen mit zunehmendem Propylengehalt ab. Diese Änderung zeichnet sich auch in der Intensität der 13,7 μ Bande in den Infrarotspektren der Polymeren ab. Der gemessene Gehalt an Ungesättigkeit (0,1-0,2%) in den Kopolymeren ist zu gering, um die Anwesenheit mehrerer Infrarotbanden, die oft der Ungesättigkeit zugeschrieben werden, zu erklären. Bei einem Terpolymeren mit einer ungesättigten dritten Komponente wurde eine Ungesättigkeit von 0,90% erhalten. Kriechuntersuchungen zeigten, dass das Kriechen dem Zeitlogarithmus mit einer Neigung von 10% Kriechen pro Dekade für 0,1 bis 10 Minuten fast proportional ist. Nachgiebigkeit-Temperaturkurven erwiesen sich denen von Styrol-Butadienkauschuk SBR 1500 recht ähnlich.

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