



Figure 1.

TABLE I

[Inh], moles/cc. $\times 10^4$	t_i , hr.	$q(t_i)$, moles of cuts	
		$\times 10^4$ cc.	$q(t_i)/$ [Inh]
0	0	0	1
1.52	1.3	1.31	0.86
3.0	1.8	3.5	1.17
7.6	2.4	7.25	0.95

chains. This is not inconsistent with our previous hypothesis that scission occurs in the termination step of the oxidative chain reaction; namely, there is scission at the step at which two RO_2 radicals react with each other.^{3,4}

We have studied $q(t)$ vs. t at various levels of N_0 and conclude that scission is occurring randomly throughout the network with slight preference for the crosslinks. This is very reasonable in terms of the chemical structure. For low values of N_0 , $q(t)$ defined by eq. (1) is essentially independent of N_0 . The value of N_0 discussed in this paper is within this range. This means that the overall scission can be regarded as random on this range.

The partial support of the Office of Ordnance Research (U.S. Army) and the Goodyear Tire and Rubber Company is deeply appreciated.

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Received June 18, 1962

Determination of Isotacticity in Polypropylene

It has been suggested by a number of workers¹⁻⁵ that certain absorption bands in the infrared spectrum of polypropylene are indicative of the helical configuration. The bands in question are at 1167, 997, and 841 cm^{-1} . These absorptions are due to a combination of vibrational modes, one mode being characteristic of the methyl group in the helical chain configuration. With proper annealing, essentially all the isotactic chains can be made to exist in the helical structure. The helical content in an annealed polypropylene sample should then effectively be a measurement of the isotacticity.

Infrared methods of measuring isotacticity in polypropylene have previously been proposed for the 1167 and the 997 cm^{-1} bands.^{3,4} However, with respect to materials of isotactic content of less than 90% there is considerable disagreement between results of the two methods. A third method, based on the 841 cm^{-1} band, was developed. All three methods utilize the 974 cm^{-1} band as an internal thickness measurement. This band is linear, with thickness between 1 and 5 mils, and is essentially independent of isotacticity. In Table I are listed the ratios of the absorbancies of the 1167, 997, and 841 cm^{-1} bands to the 974 cm^{-1} band for the standards chosen as 100% and 0% isotacticity.

The assumption is made, in all three methods, that the change in absorption ratio is linear with the change in isotactic content. Good agreement is obtained among the three methods near the 100% and 0% isotactic levels, indicating little difference in the standards chosen for them. However, considerable disagreement occurs between the extremes, and in order to determine which one, if any, of the three methods gives a valid measure of isotacticity an independent determination was chosen.

According to Flory's theory⁶ the composition of a random copolymer consisting of crystallizable and noncrystallizable units may be calculated from the melting point by means of the following equation:

$$1/T_m - 1/T_m^\circ = (-R/\Delta H_1) \ln N_1$$

In terms of polypropylene the helical segments are the crystallizable units and the atactic segments are the noncrystallizable units. The melting point of the pure crystal-

TABLE I
Absorbance Ratios for 100% and 0% Isotactic Contents in Polypropylene

Standard for 100% isotactic content	Absorbance ratio	Standard for 0% isotactic content	Absorbance ratio
Theoretical 100% crystalline material ³ (sp. vol. = 1.069)	$A_{1167} \text{ cm.}^{-1} / A_{974} \text{ cm.}^{-1} = 1.055$	Ether-soluble extract	$A_{1167} \text{ cm.}^{-1} / A_{974} \text{ cm.}^{-1} = 0.347$
Residue from heptane and ether extracts	$A_{997} \text{ cm.}^{-1} / A_{974} \text{ cm.}^{-1} = 1.00$	Acetone-soluble extract	$A_{997} \text{ cm.}^{-1} / A_{974} \text{ cm.}^{-1} = 0.180$
Highly isotactic experimental polypropylene	$A_{841} \text{ cm.}^{-1} / A_{974} \text{ cm.}^{-1} = 0.960$	Molten polypropylene (180°C.)	$A_{841} \text{ cm.}^{-1} / A_{974} \text{ cm.}^{-1} = 0.000$

TABLE II
Polypropylene Isotacticities Obtained from Flory's Theory and by Infrared Methods

Sample no.	Insoluble in:	Soluble in:	M.p., °C.	Flory's theory	Isotacticities		
					Infrared, cm. ⁻¹ band		
					1167	997	841
I	Diethyl ether	<i>n</i> -Pentane	110-115	62	59	12	28
I	<i>n</i> -Pentane	<i>n</i> -Hexane	122-126	68	68	29	43
I	<i>n</i> -Hexane	<i>n</i> -Heptane	136-140	76	72	28	46
I	2-Ethylhexane	<i>n</i> -Octane	142-145	80	79	52	69
I	<i>n</i> -Octane		155-165	90	93	85	95
II	2-Ethylhexane	<i>n</i> -Octane	173-174	99	97	85	98

line species, T_m° , is taken as 176°C.; ΔH_I is the heat of fusion and has a value of 2600 cal./mole unit.⁷ Therefore, by determining the melting point T_m of a polypropylene sample the mole fraction of isotactic segments, N_I , may be calculated. Since only one molecular species is involved, the mole fraction and the weight fraction are the same. Thus values obtained from the melting point formula can be compared directly with values obtained from infrared data.

A series of extractions was carried out on two experimental polypropylene samples. A melting point was determined for each fraction extracted. Films (ca. 1 mil) of the various fractions were molded and annealed overnight at 105°C.

Per cent isotacticities were determined from Flory's equation and from the three different infrared methods.

The results are listed in Table II. At high isotactic contents all three methods agree fairly well, but at isotactic contents of 80% and less only the method based on the 1167 cm.⁻¹ band is found to give good agreement with values from Flory's theory.

Therefore, it appears that the method suggested by Brader³ gives a good measure of the isotactic content for polypropylene, at least in the 60-100% range.

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Received June 1, 1962

High Molecular Weight Polycationics

Since polyvinylpyridine was quaternized and studied by Fuoss and Strauss,¹ many studies of polyvinylpyridinium systems have been made, by these authors and their co-workers, and by others.^{2,3} Our interest has been directed to a different class of polyquaternaries.

Vinylbenzyl chloride was chosen as a starting monomer, because it can be readily polymerized⁴ and copolymerized,⁵ and its product polymers may then be used to prepare polycationics of widely varying properties and stabilities. The free radical polymerization of vinylbenzyl chloride requires care, because of the reactivity of the chloromethyl group. Mass polymerization at high temperatures results in crosslinking, while emulsion polymerizations at 50°C.