

Estimation of Isotacticity in Semicrystalline Polymers

LAWRENCE E. NIELSEN

Plastics Research Laboratory, Monsanto Chemical Company, Springfield, Massachusetts

With the increased interest in stereospecific polymers, it becomes important to know the degree of isotacticity and the distribution in the lengths of stereo blocks making up the polymer molecules. Coleman¹ has suggested a method of measuring the degree of isotacticity based on melting points.

Another method of estimating isotacticity would appear to be possible from measurements of the maximum attainable crystallinity of a given polymer. The greater the isotacticity (or syndiotacticity), the more crystalline a material can be. However, even with molecules containing only a single stereo block, the material will not be 100%

crystalline because of chain entanglements, restrictions imposed on the remaining amorphous parts of a chain by the parts which crystallize first, and cooling at a rate too fast for equilibrium to be attained.

Polyethylene may be used as a model polymer to estimate the maximum crystallinity as a function of isotacticity. Polyethylene is a degenerate case of an isotactic material in which branch points or comonomer units act like atactic links to break up the polymer chain into stereo blocks. Figure 1 gives the degree of crystallinity of polyethylene as a function of isotacticity (mole fraction of linear poly-

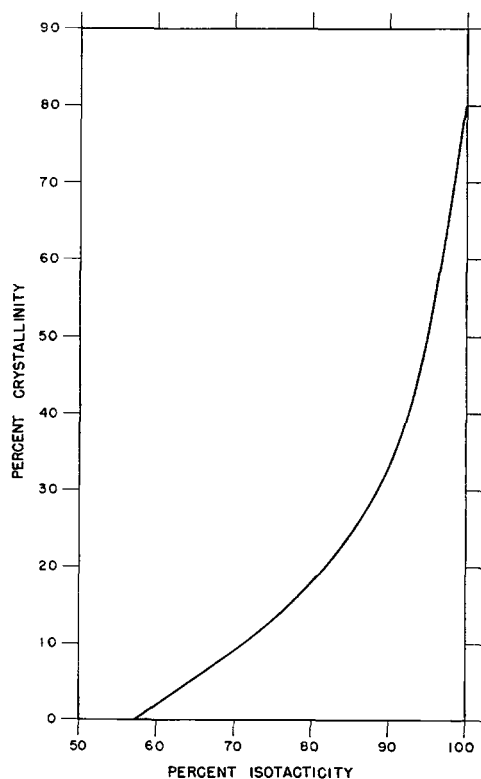


Fig. 1. Degree of crystallinity as a function of isotacticity (or syndiotacticity). Atactic material corresponds to 50% isotacticity.

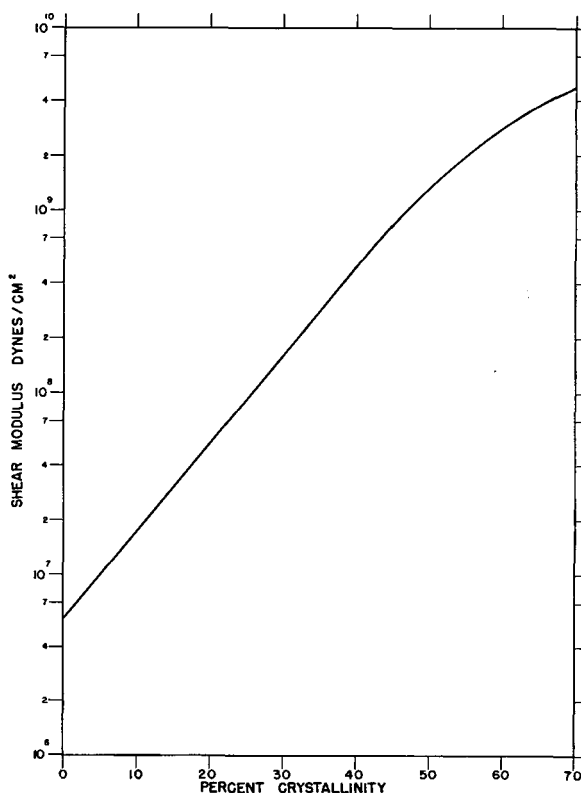


Fig. 2. Dynamic shear modulus as a function of degree of crystallinity for ethylene polymers.

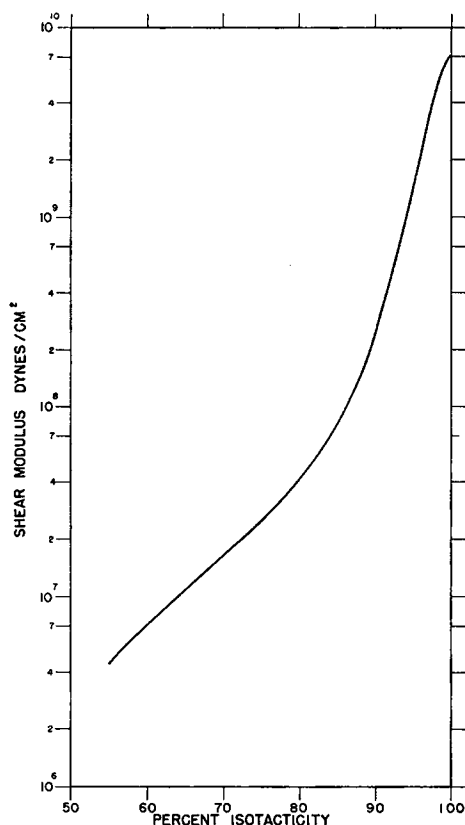


Fig. 3. Dynamic shear modulus as a function of isotacticity.

ethylene). This curve was determined from a series of polyethylenes of different degrees of branching and from a series of ethylene-vinyl acetate copolymers. The crystallinity was determined from density measurements at 0°C.² Unfortunately, this curve does not represent the maximum possible crystallinity; although the samples were cooled slowly, no effort was made to cool so slowly that equilibrium conditions were reached.

Figure 1 may now be used to obtain crude estimates of the isotacticity of any semicrystalline polymer which has been given the proper heat treatment to attain maximum crystallinity.

In many cases the degree of crystallinity is not known. In such cases, the crystallinity (and isotacticity) can be roughly estimated from the dynamic shear modulus. Figure 2 shows the approximate modulus as a function of crystallinity for the same series of ethylene polymers used in Figure 1. Above the glass temperature the modulus is determined primarily by the amorphous rubbery phase, and, according to the theory of rubber elasticity, the modulus should be nearly independent of the chemical structure of the polymer. Thus, it may

be assumed that Figure 2 should hold approximately for any partially crystalline polymer.

By combining Figures 1 and 2, the isotacticity may be estimated from dynamic shear modulus measurements by using Figure 3.

The results given in Figures 1-3 are certainly not exact and need to be refined. However, it is believed that the ideas are correct for the most part, and the results may be used to rank materials of the same type with regard to isotacticity, even though the values of isotacticity are not quantitatively correct.

In the above discussion, the crystallinity (or modulus) should be measured just above the glass temperature. At higher temperatures the smaller crystallites may melt. The temperature dependence of the crystallinity (or modulus) may be used to get some idea of the distribution in the lengths of the stereo blocks. If all the blocks are the same length, the melting point will be fairly sharp, and the modulus will drop only slowly until the neighborhood of the melting point is reached, at which point the modulus will drop very rapidly. If the polymer chains contain both long and short blocks, the short blocks will melt at a lower temperature than the long blocks. In this case, the crystallinity will drop as the temperature increases, and the modulus will drop rapidly with temperature over a wide range.

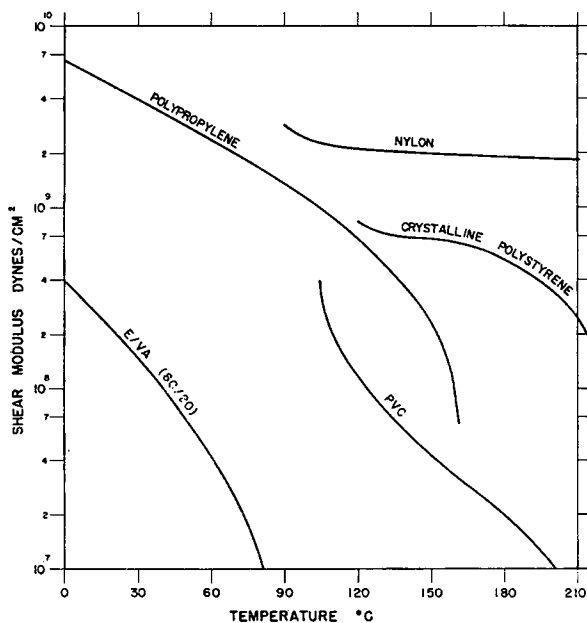


Fig. 4. Temperature dependence of the dynamic shear modulus of polymers of different degrees of crystallinity.

Figure 4 illustrates some of the possible variations in shear modulus with temperature. In a material such as nylon, where the whole chain may be considered as a single long block, the modulus is practically independent of temperature over a large temperature range. In an ethylene-vinyl acetate copolymer there is a very broad distribution in the length of the blocks, and the modulus is very temperature-dependent. Polypropylene is a material which is probably not 100% isotactic and which has stereo blocks which vary somewhat in length. Polyvinyl chloride may be an example where there are a number of very short syndiotactic blocks along with blocks of considerably greater length. This could account for the drop in modulus at the lower temperatures compared with the relatively small temperature dependence at higher temperatures. This interpretation is based on the assumption that the materials are, again, not too far from an equilibrium condition in which maximum crystallinity is attained. Table I lists the degree of isotacticity (or syndiotacticity) and crystallinity as calculated from Figures 2 and 3 for the materials given in Figure 4; the estimated values appear to be reasonable.

TABLE I
Crystallinity and Isotacticity of Polymers

Polymer	Crystallinity, %	Isotacticity, %
Nylon	55	96
Polystyrene (crystalline)	43	93
Polypropylene	65	97
Polyvinyl chloride (polymerized at $-40^{\circ}\text{C}.$)	30	88
Ethylene-vinyl acetate copolymer (80/20)	38	90

The author thanks Dr. Norman Aubrey for the data on polyvinyl chloride and Dr. Seymour Newman for the data on crystalline polystyrene. The ethylene-vinyl acetate copolymers were made and supplied by Dr. O. Deex and Messrs. H. Leeper and W. Bir.

References

1. Coleman, B. D., *J. Polymer Sci.*, **31**, 155 (1958).
2. Nielsen, L. E., unpublished data.

Synopsis

A new method is suggested for estimating the degree of isotacticity and the distribution of block lengths in semi-crystalline polymers. The method is based upon the maximum attainable crystallinity and its dependence upon temperature. An alternate approach is based upon the dynamic shear modulus and its temperature dependence above the glass temperature.

Résumé

On propose une nouvelle méthode d'estimation du degré d'isotacticité et de la distribution de la longueur de blocs dans les polymères semi-cristallins. La méthode se base sur le maximum de cristallinité que l'on peut obtenir et sa dépendance vis-à-vis de la température. Une autre méthode se base sur le module dynamique de cisaillement et sa dépendance en regard de la température au dessus de la température de transition vitreuse.

Zusammenfassung

Ein neue Methode zur Bestimmung des Grades der Isotaktizität und der Verteilung von Blocklängen bei semikristallinen Polymeren wird angegeben. Die Methode beruht auf der Bestimmung der maximal erreichbaren Kristallinität und ihrer Temperaturabhängigkeit. Eine zweite Methode beruht auf der Messung des dynamischen Schermoduls und seiner Temperaturabhängigkeit oberhalb der Glasumwandlungstemperatur.

Received August 27, 1959