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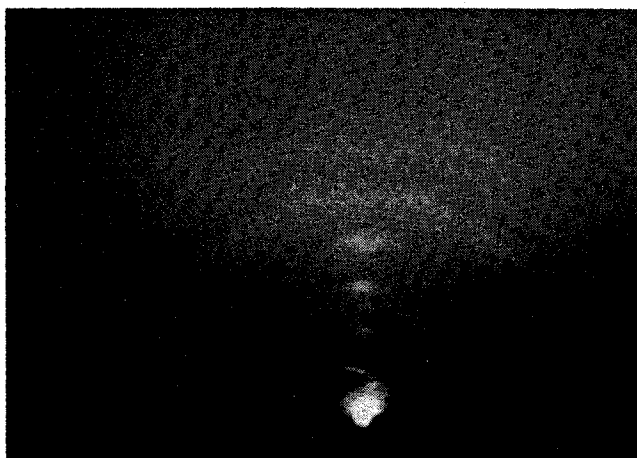


Fig. 1. Diffraction pattern from a surface of stainless steel smeared with resin. Epitaxy is seen here. Periodical spacing parallel to the surface is 7.14 Å. Wave length of electrons, 0.0306 Å. Camera length, 495 mm. Positive enlarged about 2 times.

stainless steel was recognized by electron diffraction. As a matter of fact, this resin does not show adhesiveness here. Separate forms of epitaxy of adhesives are observable from various substrates (glass, light and heavy metals) by electron diffraction. This informs us of the physical and chemical properties of adhesives.

The author wishes to express here his gratitude for Drs. Z. Tuzi and K. Kawata who have kindly encouraged this work.

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Isophasic Dilatometric Transitions of Some Poly(Normal Alpha Olefins)

In a previous communication¹ we showed that it is possible to attribute to the polyethylene a dilatometrically determined (apparent) second-order transition temperature around -21°C . Different transition data for other polyolefins have been recently published.^{2,3} Since our data under reference (2) were given as approximate, we wish to report herewith more consistent values we have obtained for the isophasic volume break temperature of polymers of the first normal alpha-olefins.

The transition temperatures were determined with capillary dilatometers and a procedure as previously described.¹ The isophasic transition temperature was always taken as that corresponding to the intersection

TABLE I

Sample	$[\eta]$ (100 cm. ³ g. ⁻¹)	Crystallinity, % ^a	Transition temperature, °C.	
			Experimental ^b	Mean value
Polypropylene				
A	0.11 ^c	amorphous	-34.5 -35	-35
B	0.28 ^c	80	-35.5 -34.5 -36 -34 -34.5 -35	
C	0.43 ^c	65	-37 -37	
D	0.65 ^c	50	-34 -39 -35	
E	0.78 ^c	45	-35.5 -33.5	
F	0.86 ^c	amorphous	-35 -36.5	
G	0.96 ^c	35	-37 -35	
H	2.82 ^c	85	-34.5	
I	3.47 ^c	75	-36 -35	
Polybutylene				
J	0.76 ^c	amorphous	-48 -43	-45
K	2.00 ^c	60	-45 -44	
Polypentene				
L	—	amorphous	-53 -51.5	-53
M	2.65 ^d	crystalline	-53 -52.5 -53	
N	2.96 ^d	crystalline	-52 -53.5	
Polyhexene				
O	1.99 ^d	amorphous ^e	-49 -51	-50
P	1.99 ^d	amorphous ^e	-51 -50	

^a X-ray determinations, approximate values.

^b Independent determinations with constant rate of heating or cooling (5°/10 min.).

^c In tetraline at 135°C., after conditioning by fusion *in vacuo*.

^d In toluene at 30°C., after conditioning to a moderate temperature.

^e At room temperature.

obtained by prolonging the two straight parts of the $V_{sp}-T$ curve. The temperature range explored was in each case about -70 to 0°C . The samples were prepared by melting *in vacuo* and then slow cooling as in the case of polyethylene.¹

The values of the transition temperatures are listed in Table I. Essentially the same results are given by both completely amorphous and highly crystalline samples, as well as samples of high and low molecular weight. This is in agreement with the fact that, as already noted,^{4,5} in the molten or dilute solution state the properties of isotactic and non-isotactic polymers are the same or differ very little.

In Figure 1 the average values of the transition temperatures of the different polymers studied are plotted against the number of carbon atoms of the lateral chain. The transition temperature decreases from polyethylene to a minimum value for polypropylene and then increases again for polybutene. Therefore, in the amorphous part of the polymer, short side-chains cause a plasticizing effect with regard to the structure corresponding to polyethylene.

The lowering of the dilatometric transition from polyethylene to polypropylene is appreciable, considering that crystal melting temperature of the latter is considerably higher than that of the former. Determinations carried out by us on polypropylenes of high crystallinity (about 85%) have in fact given a crystal melting temperature up to 176°C ., while polyethylene samples prepared by us, having a very linear structure without methyl groups detectable by infrared analysis, have given a melting temperature up to $138-139^{\circ}\text{C}$. This statement evidently does not support the belief that the ratio of the values of the crystal melting temperature and the glass transition temperature should be constant.

The high crystal melting temperature of polypropylene with regard to polyethylene is not surprising, considering the different arrangement of the chains in the crystal lattice (planar zig-zag for polyethylene and helical

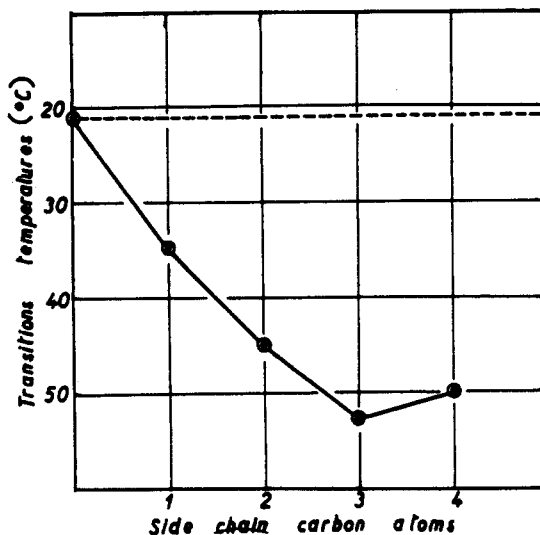


Figure 1.

for polypropylene). On the other hand, the isophasic volume transition considered here is known to be typical of the amorphous (disordered) phase.

The effect of internal plasticizing of the short side-chains is most marked in the case of polypentene, while in polyhexene the cumulative structural effect of the linear lateral chains begins to prevail. In Figure 1 a horizontal dashed line is drawn corresponding to the value of polyethylene, which also must represent the asymptotic value of the isophasic volume transition temperatures of polyolefins having very long lateral chains.

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- (5) See, *e.g.*, G. Natta *et al.*, *J. Am. Chem. Soc.*, **77**, 1708 (1955).

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Light Scattering Measurements on Polyvinyl Chloride Solutions in Tetrahydrofuran

Since Doty, Wagner, and Singer¹ reported light scattering measurements on polyvinyl chloride in dioxane, in connection with work on association of polymers in solution, little or no reference has been made in the literature to the measurement of the weight average molecular weight (\bar{M}_w) of polyvinyl chloride by light scattering. The object of this letter is primarily to publicize a suitable system for the measurement of \bar{M}_w of polyvinyl chloride rather than to present an accurate value of \bar{M}_w for a particular polymer. In this laboratory it has been found that carefully dried tetrahydrofuran is a suitable solvent for light scattering measurements on polyvinyl chloride.

The following were the methods used to prepare polymer, solvent and solutions.

Polyvinyl chloride. Commercial Geon 121 was precipitated from tetrahydrofuran solution by ethanol which was both cooled and stirred by the addition of powdered solid carbon dioxide.

Tetrahydrofuran. Commercial tetrahydrofuran was distilled through a 100 plate column and taken off at a reflux ratio of 49 to 1. Distilled tetrahydrofuran was stored over calcium hydride.

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