The Density Determination of rf Plasma Polymers

INTRODUCTION

The densities of nine rf plasma-produced polymers were determined in a gradient column. These polymers were found to be more dense than the conventional polymers produced from the same monomer species via free-radical, ionic, or condensation polymerizations.

EXPERIMENTAL

Polymer Samples. The nine polymer samples used were prepared in an rf plasma as given by Thompson and Mayhan.[1,2]

Apparatus. The gradient density column used was 107 cm in length, 5.7 cm in diameter, and surrounded by a circulating constant-temperature water jacket maintained at 30.0°C. The density gradient media was established using carbon tetrachloride (ρ = 1.595 g/cm², bp = 76.8°C) and n-heptane (ρ = 0.684 g/cm³, bp = 98.4°C). The solvents were distilled directly into the column to establish the gradient. By changing the solvent ratio and the separation obtained during distillation, both the density mode and range were tailored to the polymer samples.

Calibration. Aqueous zinc chloride standards were prepared and their densities measured to ±0.0002 g/cm³ at 30.0°C. A reference scale was attached behind the water jacket to magnify and establish the position of both the standards and polymers within the gradient density column. A calibration curve was constructed by plotting (position)$^{1/2}$ of the standard drops versus their densities. A nearly linear curve resulted which served as the calibration for the polymer samples within the column.

Polymer Densities. The density of each polymer was determined by adding several fragments of the polymer to the columns. Since the density of more than one polymer was determined simultaneously, the individual polymer particles were tracked through the column by recording their (x,y,z) coordinate within the column at various time intervals. The samples were observed up to 24 hr or more before a final reading was taken. It is pertinent to note that the samples studied had approximate dimensions of 1–2 mm × 1–2 mm × 1–3 microns. Also, a density gradient of 0.100 was typically encompassed by 25–30 cm of column length. As a result of these conditions, the establishment of an equilibrium density level required considerably longer than is normally expected by the gradient density technique. It has been assumed that the solvent system had no effect on the polymers since experiments in which bulk amounts of the polymers were subjected to refluxing conditions showed a maximum of 1% weight loss in 16 hr. No dimensional changes were observed on specific polymer particles. A typical record of column position (expressed as density) versus time is shown in Figure 1.

RESULTS AND DISCUSSION

The results of the density determinations are given in Table I. The density range for each polymer is given because the density was found to vary with the monomer concentration, the power level, and the position within the reactor. Also reported are the densities of a single crystal and of the amorphous linear polymer for comparison.

Preliminary evidence based upon elemental analysis indicates that these polymers have vastly different structures than were anticipated for the crosslinked variety of a given monomer. As an example, the plasma polyethylene was found to contain 20–30 wt-% oxygen. Oxygen and sometimes nitrogen have also been found in other polymers. Investigations are underway to determine the source of these elements and how they are combined in the polymer molecule. The densities of the plasma polystyrene and
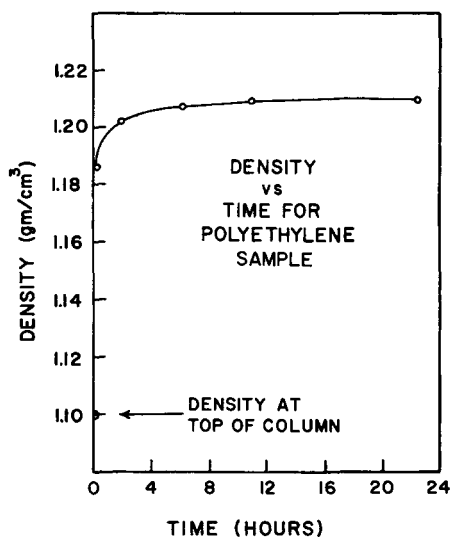
Fig. 1.

polyethylene exceeded those of the linear crystalline polymers. Low-angle x-ray diffraction patterns indicate that these polymers are amorphous. This indicates that substantial changes in structure and/or morphology have occurred. The chemical composition, density, and refractive index have been found to vary as a function of the operating parameters of a particular experiment as well as the reactor and coil or plate design. These observations are reported so as not to mislead the reader in interpreting the density data. The utility of these data at present is to call to the attention of other investigators the density ranges to be expected for plasma formed polymers and to

TABLE I
Polymer Densities

Starting monomer	Density range of plasma polymer, g/cm^3	Crystal density of linear polymer,[a] g/cm^3	Amorphous density of linear polymer,[a] g/cm^3
Styrene	1.332–1.408	1.126	1.04
Ethylene	1.141–1.231	1.014	0.852
Vinyl chloride	1.463–1.499	1.44–1.522	1.39
Vinyl fluoride	1.341–1.395	1.44	—
Benzene	1.331–1.364	—	—
Acrylonitrile	1.402–1.436	1.11 syndiotactic	—
		1.54 isotactic	
Allene	1.195–1.203	—	—
Methylvinyl- dichlorosilane	1.435–1.454	—	—
Allylamine[b]	1.212	—	—

[a] From Geil.[3]

[b] Sample supplied by Drs. T. Wydeven and J. Hollandan, NASA-Ames, Moffett Field, California.

NOTES

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supplement data previously reported.[1,2] Anyone interested in having densities of a limited number of plasma polymers determined should contact K. G. Mayhan.

Acknowledgment

References

1. L. F. Thompson and K. G. Mayhan, *J. Appl. Polym. Sci.*, **16**, 2291 (1972).
2. L. F. Thompson and K. G. Mayhan, *J. Appl. Polym. Sci.*, **16**, 2317 (1972).
3. P. H. Geil, *Polymer Single Crystal*, Wiley, New York, 1963.

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