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LETTERS TO THE EDITORS

Molecular Weight of Polytrifluorochloroethylene by Light Scattering

Solubility studies have shown that the range of solubility parameters covered by solvents for polytrifluorochloroethylene is narrow. Since the same intermolecular forces that are responsible for the solubility parameter of a liquid also determine the index of refraction, substances with about the same solubility parameter also have about the same index of refraction. Consequently, the difference between the index of refraction of this polymer and any known solvent is very small. This, together with the fact that the polymer is soluble only above 115ºC.[i] (some supercooled solutions are stable near 90ºC.), makes the light scattering approach to a study of this polymer difficult.

Mesitylene was chosen as the solvent for this work because it has the most favorable index of refraction and the solution temperature (140ºC.) is far enough below the normal boiling point (165ºC.) that the solutions can be carried through the required manipulations at atmospheric pressure. The index of refraction of the polymer at 25ºC. is 1.43. For the amorphous polymer the coefficient of cubical expansion is 7.43×10^{-4}.[ii] The index of refraction of mesitylene at 25ºC. is 1.497 and its coefficient of cubical expansion is 0.90×10^{-3}. Using the Gladstone-Dale relation to obtain indices of refraction for these materials at 145ºC., the difference in index of refraction is found to be 0.050. This value when divided by the polymer density (1.92 at 145ºC.) gives 0.026 for *dn/dc*, the change in difference of index of refraction with temperature. Dr. A. M. Bueche of this laboratory measured *dn/dc* in a high temperature differential refractometer and obtained *dn/dc* = 0.027.

The light scattering instrument used in this work was built along the lines of those used by previous workers. The filtered light from an A-H4 mercury arc was focused in the center of the light scattering cell. The aperture was limited by two slits just in front of the cell. The aperture of the second slit was slightly larger than the first so that it intercepted light reflected from the edges of the first slit.

Scattered light was measured with a1P21 photo tube whose output was fed to a Ballantine electronic a.c. voltmeter via a 1-megohm load resistor. The light scattering cells were made from 1-inch diameter Pyrex test tubes. The cells were marked so they could be removed and accurately replaced in their former position. Surrounding the cell was an air thermostat. This thermostat was kept at a temperature of 145ºC. Scattered light from the cell passed through a window in the thermostat to reach the phototube which was outside the thermostat.

Weighed amounts of polymer were added to known volumes of solvent at 25ºC. in stoppered flasks. The flasks were placed in a 150ºC. oven until solution took place. The light scattering cell and microporous porcelain "candle"[iii] filtering equipment were also kept in the oven. When everything was up to temperature, the oven door was opened and the solution filtered into the cell in as short a time as possible to prevent cooling and consequent precipitation of polymer. Heavy gloves were used to handle the equipment and the filtration was carried out right in the oven. It should be mentioned that the cells had previously been thoroughly cleaned, rinsed out several times with "candle" filtered benzene, and dried. The cells were then cooled in liquid nitrogen and sealed off. Many measurements could now be made on the solutions sealed up in these cells without losing solvent. After a sufficient number of

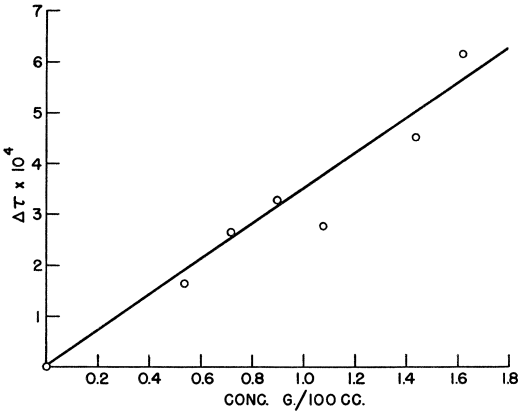

Figure 1

measurements had been made on the solutions, the seal off tips were cut off, the contents of the cells emptied, and any remaining polymer dissolved by soaking in o-chlorobenzotrifluoride at 135ºC. Following this, the cells were rinsed with "candle" filtered benzene and dried. The cells were then filled with mesitylene and the light scattered by the mesitylene in each cell measured. In this manner the effects of

differences in scattering due to cell wall thickness, etc. was eliminated.

The light scattering instrument was calibrated at 25ºC. with 0.75% Dow Styron in butanone and 1.00% Dow Styron in dichloroethane.[iv] The wave length of light was 5461 A. and only 90º measurements were made.

The turbidities as a function of concentration in mesitylene for a sample of polytrifluorochloroethylene made by Kellogg Corporation and designated Kel-F 240 were measured. A plot of turbidity *vs*. concentration is given in Figure 1. It is evident from the figure that the precision of the measurements is rather low. This is due to the extreme difficulties encountered in carrying out the required manipulations at the high temperature and by the very small *dn/dc*. The slope of the line in Figure 1 gives a molecular weight of 3.6×10^5. The osmotic molecular weight of Kel-F 240 has been reported by H. S. Kaufman and M. S. Muthana to be 56,000.[v] Several reasons might be advanced to explain the large difference in molecular weight as determined by the two methods. Perhaps this polymer has a very broad molecular weight distribution or a two-humped distribution. Or, perhaps here is a case of high degree of association of polymer molecules in solution.

It was not possible to determine molecular weights by light scattering for Kel-F 270 or Kel-F 300 because these higher molecular weight materials are not sufficiently soluble in mesitylene.

The intrinsic viscosity of the Kel-F 240 used in the light scattering measurements was 0.59 and the slope of the reduced viscosity vs. concentration plot was 0.21. The viscosities were determined in mesitylene at 145ºC.

H. Tracy Hall

Research Laboratory
General Electric Company
Schenectady, New York

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References

[i] H. T. Hall, to be published.
[ii] Unpublished data, F. P. Price, this laboratory.
[iii] F. P. type #015 porosity, made by the Selas Corporation of America, Scientific Equipment Division, Philadelphia, Pa.
[iv] See C. I. Carr, Jr., and B. H. Zimm, J. Chem. Phys., 18, 1616-1626 (1950), for the absolute scattering power of these materials.
[v] J. Polymer Sci., 6, 251 (1951).