JOURNAL OF APPLIED POLYMER SCIENCE VOL. 14, PP. 383-391 (1970)

Automatic Recording Capillary Viscosimeter with Dilution

PH. GRAMAIN AND R. LIBEYRE, *C.N.R.S. Centre de Recherches sur les Macromolécules, 6, Rue Boussingault, Strasbourg, France*

Synopsis

A capillary viscosimeter with automatic determination and recording of flow times of liquids up to 200°C is described. This viscosimeter, which is specially suited for studies of polymeric solutions, includes an automatic dilution system and determines intrinsic viscosity with a precision better than 0.01%.

INTRODUCTION

Viscosity measurements are currently carried out in industrial and research laboratories for the characterization of samples. Valuable data concerning the size and shape of molecules may be obtained from measurements of the viscosities of their solutions. The capillary viscosimeter has been widely used owing to its sensitivity, accuracy, and simplicity; it has furthermore the advantage of a sound theoretical basis.

In order to improve the precision of the results and to eliminate tedious and time-consuming routine, a great number of technical devices have been described previously.[1-9] It appears that most of them operate on the same basic principle: the downward passage of the meniscus is timed by a photoelectric device. A beam of light is transmitted through a glass tube containing the liquid and reaches a photosensitive element. The intensity of the transmitted beam is reduced when the tube is empty. This variation starts or stops an electronic timer.

All the devices thus far described have many disadvantages. They require a complicated system which involves tedious adjustments and assemblage. Two independent photosensitive elements are generally needed and their stability is of major importance to obtain good reliability. Moreover, all the detectors are immersed in a thermostated bath; this gives rise to problems involving water tightness and anticorrosion, and therefore limits the applicability of the technique to relatively low temperatures. The reliability and proper working of the photosensitive elements are not guaranteed for temperatures exceeding 80°-100°C.

The apparatus described here, which still retains a photoelectric detection, eliminates the disadvantages previously cited. It automatically determines and records efflux times and assures reproducibility of the mea-

surements. Moreover, particularly for studies of polymeric solutions, it includes an automatic dilution system to determine quickly the intrinsic viscosity.

PRINCIPLE OF OPERATION

The entire apparatus is shown in Figure 1. The viscosimeter tube (Ubbelohde type in the figure) is surrounded by a cylindrical glass jacket; this setup allows temperature control with a circulating thermostated liquid. The detector is clamped on the outside in front of the viscometer bulb. The passage of the meniscus in front of the upper lamp starts the counter which has a quartz crystal oscillator. The meniscus stops the counter as it passes the lower lamp and the efflux time is registered and printed. A few seconds later, a small air pump coupled with a pneumatic valve forces the sample into the bulb. Once the ascending fluid passes the upper lamp, the pump is automatically turned off, the counter sets to zero, a second run starts, and so on.

For the automatic dilution procedure a calibrated piston buret is connected to the viscosimeter. After some runs (the number of runs is selected

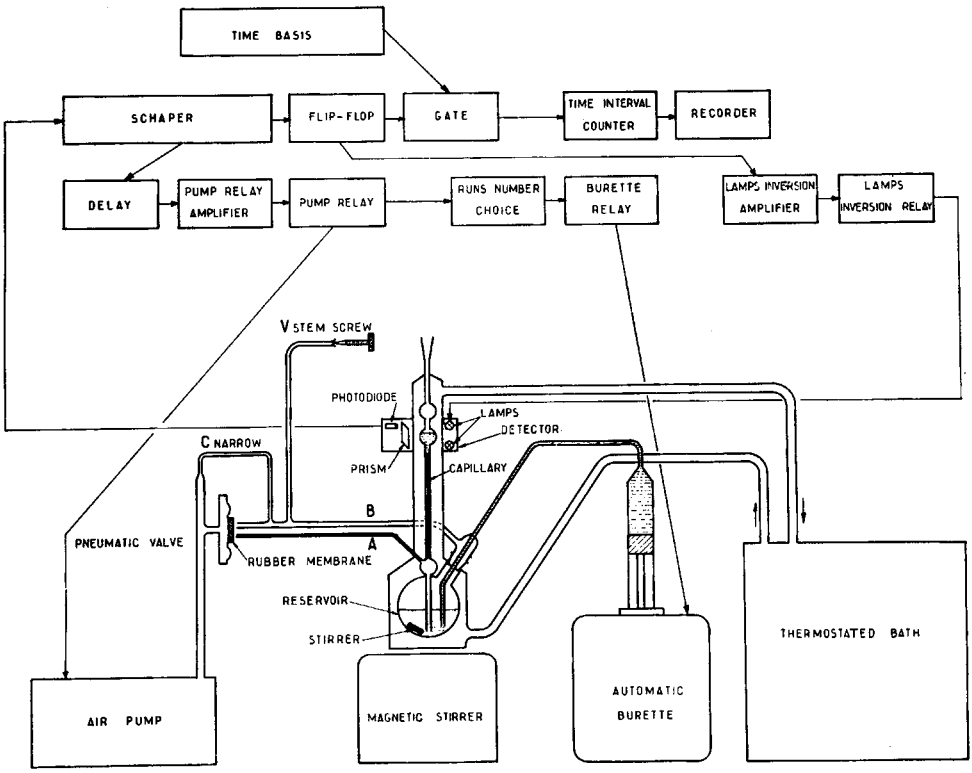

Fig. 1 Working diagram of automatic viscosimeter.

by the operator) the buret adds diluent. A magnetic stirrer homogenizes the solution. The printer checks the dilution process and another run proceeds.

DETAILS OF CONSTRUCTION

Viscometer. The two types of viscosimeter employed are shown in Figure 2. One of them is the Ostwald-type viscosimeter, the second is the Ubbelohde dilution type. The setup allows easy temperature control. This design enables suitable observations and occasional manipulations by the operator without disturbing the thermal stability.

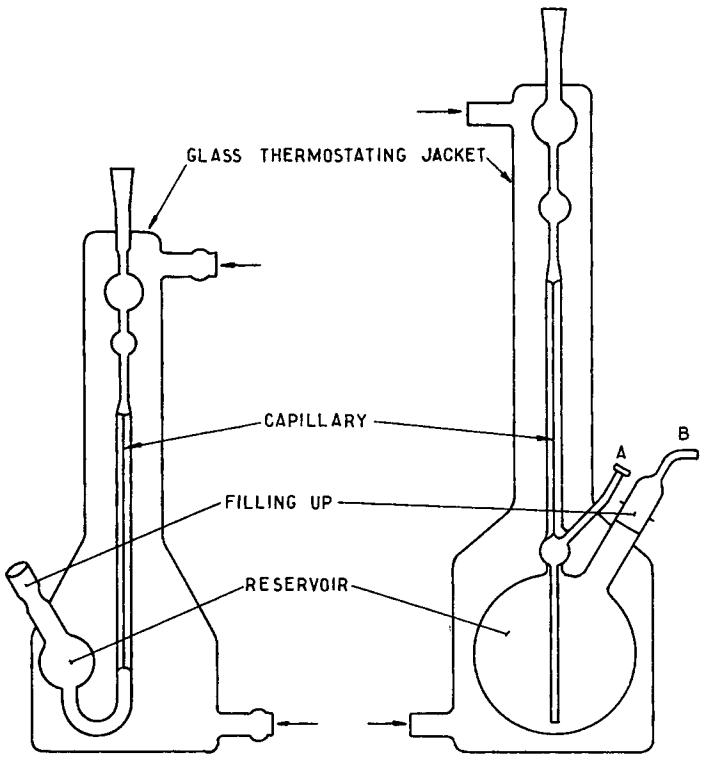

Fig. 2. Diagram of Ubbelohde dilution viscosimeter (right) and Ostwald viscosimeter (left).

The Ubbelohde-type viscosimeter requires only a small amount of solution ($\simeq$3 cc). Furthermore, the easy access to the solution reservoir facilitates cleaning, stirring, and the dilutions. The length of the capillary tube is 10 cm and the internal diameter of the tube at the point of detection is 2 mm.

Detector. The photoelectric detection system is shown in Figure 3, A removable metallic frame block is held on the jacket by means of a

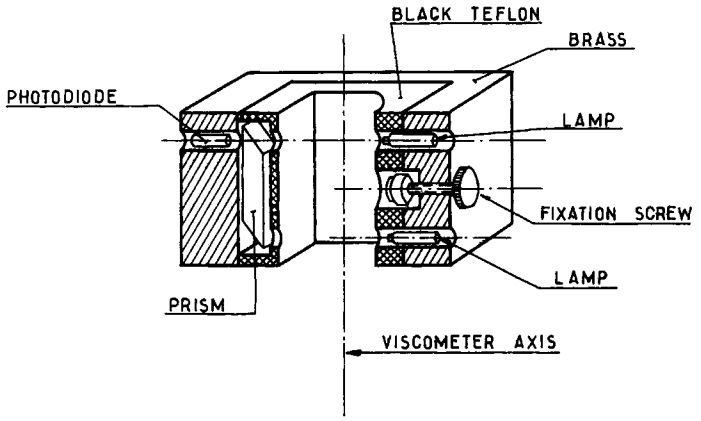

Fig. 3. Drawing of detector.

screw. In order to avoid thermal conduction and to operate at higher temperatures, the inside of the block is composed of black Teflon.

The detector includes: two miniature lamps with soldered contacts which are undervolted to ensure long lifetime; a small rhombohedral glass or plexiglass prism; one silicon photodiode.

Pump and Valve. The air pump is switched on by means of a relay when the ascending meniscus passes the upper lamp. The signal which starts or stops the pump is electronically delayed for a few seconds to permit the meniscus of the ascending fluid to cross completely the point of detection. In the case of downward flow, the same delay is necessary to completely drain the capillary and therefore avoid subsequent bubble formation when the liquid flows upward again.

A schematic diagram of the pneumatic valve is depicted in Figure 1. As the pump works, a rubber membrane obstructs A and B, and the viscosimeter reservoir, connected by the narrow C, is put under pressure. The pressure may be regulated with a stem screw V. If the tube A, which brings the capillary base into contact with the atmosphere, is closed, the liquid rises in the capillary. Inversely, when the pump is turned off and the membrane deflates and opens A and B, the liquid flows down. As A is slightly closer to the membrane than B, the reservoir is first connected with atmosphere and the backflow of the liquid in A is avoided. When the Ostwald viscometer is used, A is connected to B. Air may be easily replaced by an inert gas.

Register and Printer. A low-frequency quartz crystal oscillator was chosen for the timing. The decades are digit-illuminated tubes with a resolution of 0.001 sec. An Addo X printer gives a permanent record of the results.

Automatic Dilution. The automatic dilution system includes a calibrated piston buret (Metrohm) and a control device. The contact of the relay, when the pump is turned off, acts on an electromechanical counter, unit

by unit. When this counter reaches the chosen number of runs, the buret operates and the piston moves to a predetermined position. Injection proceeds as the liquid moves down. The buret has a total capacity of 20 cc and the initial volume of the solution in the viscosimeter is 4 cc. Each step of the piston screw thread corresponds to 0.2 cc, and a program with successive dilution of 2–2–4–12 cc was chosen to give the following concentrations: 2C/3, C/2, C/3, C/6. It is also possible to put the first 4 cc of solvent into the viscosimeter and the solution in the buret. In this case, concentrations would be: C/3, C/2, 2C/3, 5C/6.

DISCUSSION

Thermal stability and proper operation of the detector are of major importance to obtain high precision and reliability.

Temperature

The temperature of a liquid has a marked effect on its viscosity; usually the effect is more pronounced at lower temperatures. For instance, at 20°C the viscosity of water changes 2.4% per degrees. Assuming a precision of 1/10,000 for the efflux times, a thermal stability better than 0.003°C is needed. Using a constant temperature bath built in our laboratory, the following thermal fluctuations inside the jacket were recorded with the Hewlett Packard quartz thermometer:

$$\Delta t = \mp 0.002°C \text{ for } 20°C < t < 50°C,$$
$$\Delta t = \mp 0.005°C \text{ for } t\ 70°C.$$

Obviously, temperature stabilization with a circulating liquid yields good precision. The influence of the surrounding room temperature was also taken into account. Around 25°C, the temperature recorded at the outlet of the jacket increased by 0.005°C for 1° increase of the ambient temperature. This effect is less marked for higher temperatures.

Detection

Consider a simplified setup consisting of a photodiode and a lamp located on both sides of the viscosimeter tube. Figure 4a shows the ideal signal shape as the liquid meniscus descends. Suppose the value I = i starts the recording process the instant t_1 is perfectly determined, whatever the variation of levels 1 and 2 may be. However, in practice, the signal has rather the form shown in Figure 4b. The time to pass from level 1 to level 2 depends on the meniscus velocity, the optical device, etc.; it may take several tenths of a second. If there should be a variation in the positions of 1 and 2 (broken line), the timing starts at a different time t_2. This means that the precision and reliability of the detection system depends strongly on the stability of both lamps and photodiodes and also on the electrical setting.

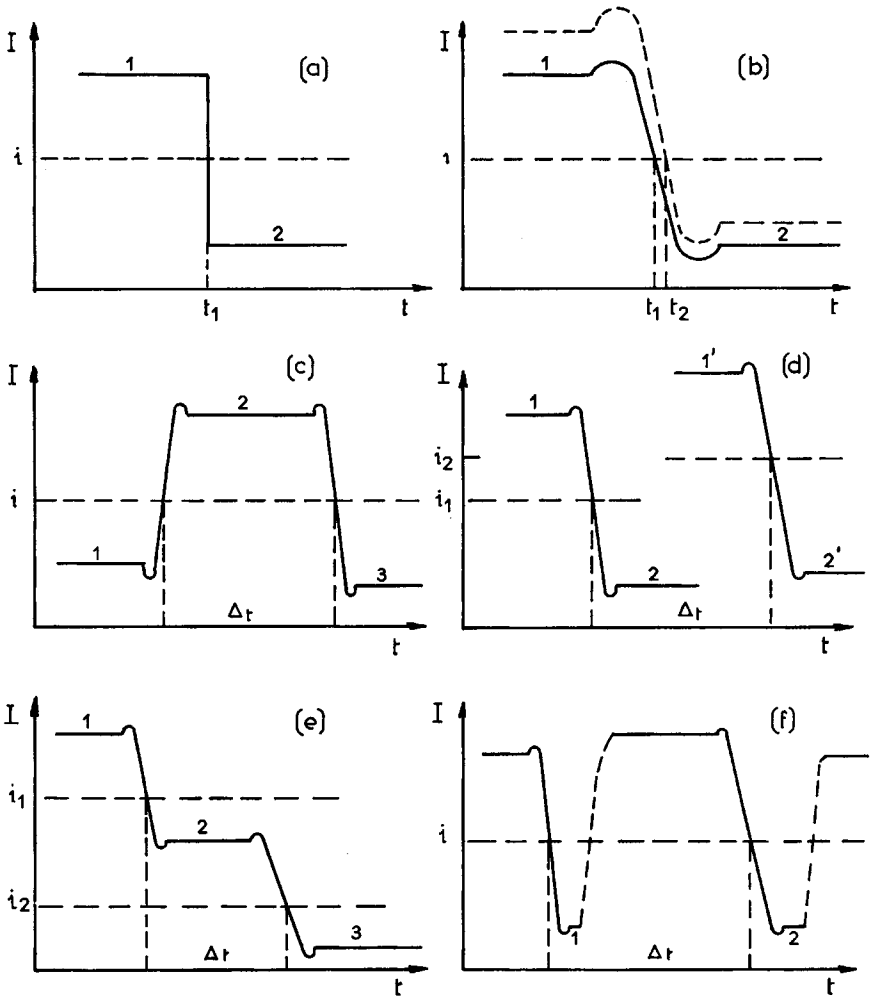

Fig. 4. Response of detector to movement of meniscus for different setting: (a) one photodiode: ideal signal shape; (b) one photodiode: experimental signal shape; (c) two photodiodes: differential setting; (d) two photodiodes: two separate trigger circuits; (e) two photodiodes: two triggers with only one amplifier; (f) only one photodiode: our setting.

Stability of Lamps

The stability of the miniature lamps are generally good, provided a few elementary precautions are taken: contacts should be soldered, a regulated power supply must be set in, and the voltage should be chosen to keep the filament at a suitable temperature. Although the light intensity decreases slowly with time, nevertheless it is possible, as will be shown later, to correct this effect by slightly increasing the voltage.

Stability of Photodiodes

The operating photodiodes are subject to fatigue and their sensitivity undergoes variation with time. This phenomenon is typical for each photodiode and cannot be easily avoided.

Electrical Setting

The different points previously discussed may be corrected by improving the electrical setting. Two main schemes were proposed:

Differential Setting. The photodiodes are connected in a differential setting. A unique voltage amplifier with one trigger is used. The signal is given in Figure 4c. If the intensity bases 1, 2, or 3 are not stable, the measured efflux time fluctuates. Initially, we observed with this technique[6] a slight and constant decrease of the efflux time (about 0.01 sec for 1 hr).

Utilization of Two Amplifiers.[8] The signal is given in Figure 4d. Here, the difference in the recorded efflux time will be minimized. As the two signals have the same slope, the differences in the efflux times will be small if there should be an instability of one of the sensitive elements. However, this technique needs two strictly stable triggers and amplifiers.

It should be possible to make use of only one amplifier with two triggers (Fig. 4e). This method supposes that the triggers are perfectly stable. Moreover, the width between levels 1 and 2 and levels 2 and 3 are closely related to the geometrical shape of the viscosimeter tube and to the refractive index of the liquid, and a suitable adjustment of the assembly would become exceedingly difficult.

The apparatus described in the present paper makes use of only one photodiode. The sensitivity change of the photodiode (which in practice is always a slow process) has no effect on the measured efflux time. The optical system is shown in Figure 3 and the corresponding signal that would be expected is depicted in Figure 4e. In order to avoid the two threshold levels, a relay is used which operates only one lamp at a given moment. After the meniscus has passed the upper lamp, the relay switches on the lower lamp, and vice versa. It is possible to adjust separately the light intensity of the two lamps in such a manner that the intensity transmitted to the photodiode is the same in either case. The equipment needs no further adjustment.

The signal is shown in Figure 4f. The broken lines correspond to the time periods necessary to load the two lamps. Levels 1 and 2 are adjusted to the same value (empty tubes). The error which results from fluctuations in the diode characteristics is insignificant compared to the error which arises using the preceding techniques. To avoid the successive switching off and on of the lamps, one could possibly use a chopper system or use only one lamp with a tipping optical device. However, as indicated by our measurements, the successive switching on and off of the lamps does not affect the reliability and precision of the measurements.

RESULTS

To demonstrate the precision of the apparatus, some typical experiments performed with an Ubbelohde viscosimeter of 0.4 mm capillary diameter are reproduced:

Figure 5a gives viscosity data for methyl ethyl ketone at 30°C. During a 5-hr run, the precision is about 0.005%.

Figure 5b gives data for *n*-dodecane at 29°C. The precision is better than 0.002%.

Figure 5c reproduces measurements for *n*-dodecane at 140°C using a commercial temperature bath (Type F Haake). The dispersion caused by temperature fluctuations is more pronounced in this case.

Figure 6 reproduces an automatic dilution run on a solution of poly-(vinyl acetate) in methyl ethyl ketone at 25°C. The viscosity data were

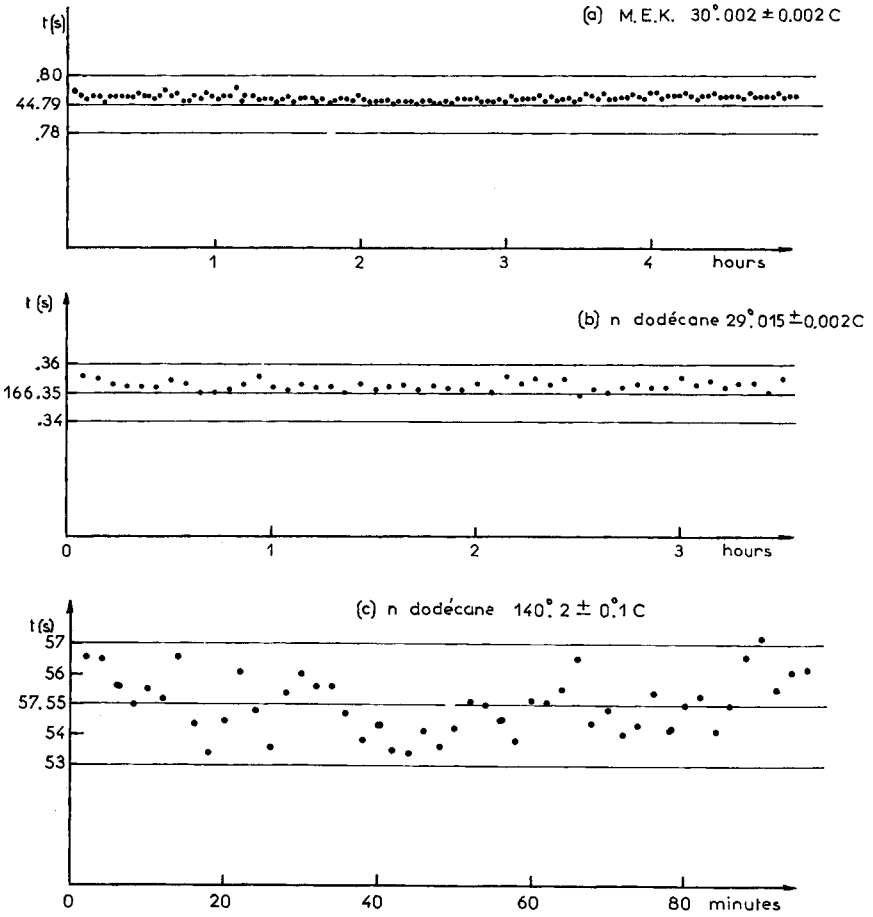

Fig. 5. Flow time variations with time: (a and b) with our temperature bath; (c) with a commercial temperature bath (Type F Haacke).

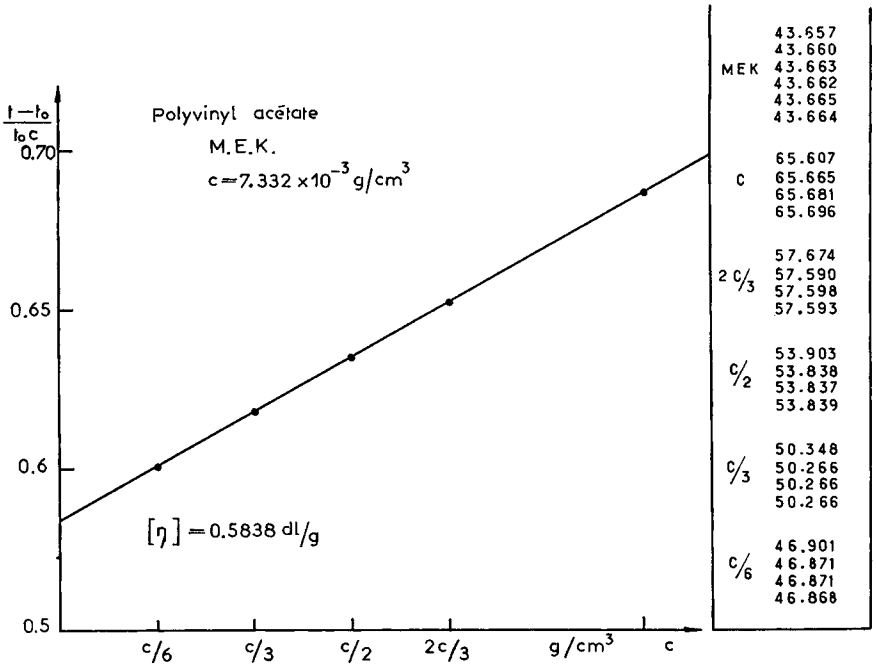

Fig. 6. Example of an automatic dilution experiment: intrinsic viscosity determination.

extrapolated to infinite dilution with the help of an Olivetti Programma 101 desk calculator. The value of 0.583847 (100 dl/g) is given to the last significant figure. It is obvious that this precision is meaningless if one considers the other independent errors.

References

1. G. Jones and S. K. Talley, *J. Amer. Chem. Soc.*, **55**, 624 (1933).
2. G. Jones and S. M. Christian, *J. Amer. Chem. Soc.*, **61**, 82 (1939).
3. G. Goldfinger and W. Greatbatch, *Instrum. Automation*, **30**, 88 (1957).
4. M. Krishevskij and B. Palchinskij, *Vysokomol. Soedin.*, **3**, 936 (1961).
5. T. Erdey-Gruz, D. Berky, O. Kaposi, and B. Rozsondai, *Acta Chim. Hung.*, **31**, 385 (1962).
6. J. Leray and Ph. Gramain, *J. Chim. Phys.*, **62**, 976 (1965).
7. B. J. Steel, *J. Sci. Instrumen.*, **42**, 751 (1965).
8. J. H. Larkins, J. D. Perrings, G. R. Shepherd, and B. J. Noland, *J. Chem. Educ.*, **42**, 555 (1965).
9. K. G. Lawrence, *Chem. Ind.*, 1338 (1966).

Received July 28, 1969