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A New Automatic Dilution Viscometer and its Use for the Determination of Intrinsic Viscosities of Polymer Solutions

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A detailed description is given of an automatic capillary viscometer, which performs the following operations automatically: intake of a measured amount of polymer solution; measurement of the efflux time, repeated up to seven times; dilution to six different concentrations, the lowest concentration being 1/5 of the original concentration; measurement on solvent; emptying, rinsing, and drying; all operations are performed on pure solvent and on six polymer solutions. All measurements are recorded on punch-tape.

The performance of the viscometer is illustrated by measurements and calculations of the intrinsic viscosity of aqueous solutions of a poly(ethylene glycol).

I. INTRODUCTION

Determination of the intrinsic viscosity of polymer solutions is one of the most commonly performed measurements in polymer chemistry, although it is generally a very time-consuming and tedious operation. Several automatic viscometers are now commercially available;[1,2] however, none of these dilute automatically. As a result, dilutions as well as emptying, rinsing, and drying still must be performed manually. Therefore we have developed a new viscometer, which automatically performs all these operations in addition to measuring the efflux times of the various solutions.

The apparatus consists of a capillary viscometer, a series of containers for polymer solutions and for solvent, all immersed in a thermostat, a piston-burette, and containers for rinsing liquids. The viscometer, the piston-burette, and the containers are all connected to each other and to various pumps through a series of tubes and valves. The passage of the meniscus between two lines of the viscometer is read by two photo-diodes, and the time difference is recorded on punch-tape, ready for computer processing.

II. DESCRIPTION OF THE VISCOMETER FUNCTIONS

A flow-sheet of the viscometer is shown in Fig. 1.

The viscometer itself is of the Ubbelohde suspended-level type,[3] constructed according to the specifications given by the British Standards Institution.[4]

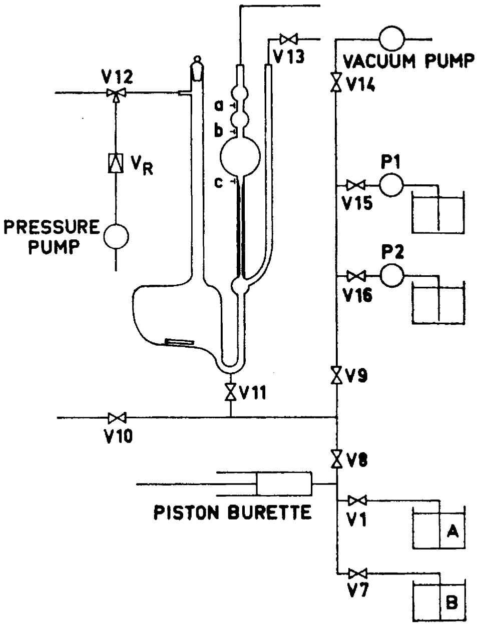

Fig. 1. Flow-sheet of the viscometer. The capillary viscometer is shown with a stirring-magnet in the mixing-chamber. At *a*, *b*, and *c* the viscometer-diodes are situated. The container *A* indicates the polymer solutions. For further explanations, see the text.

The capillary with its bulbs is interchangeable with others of different specifications, which makes it possible to measure liquids of quite different viscosities. The tube connecting the dilution chamber with the atmosphere is narrow, so that the pressure drop through this tube is of the same order of magnitude as that through the capillary.

In the dilution chamber mixing is carried out by means of a magnetic stirrer. The bottom of the dilution chamber slopes towards the bottom valve V 11, which is placed just outside the thermostat.

The performance of the viscometer can be divided into the following unit operations:

1. Intake of a measured amount of polymer solution.
2. Measurement.
3. Dilution.
4. Emptying, rinsing, and drying.

The position of the valves, the pumps, and the burette during the four unit operations is shown in Fig. 2.

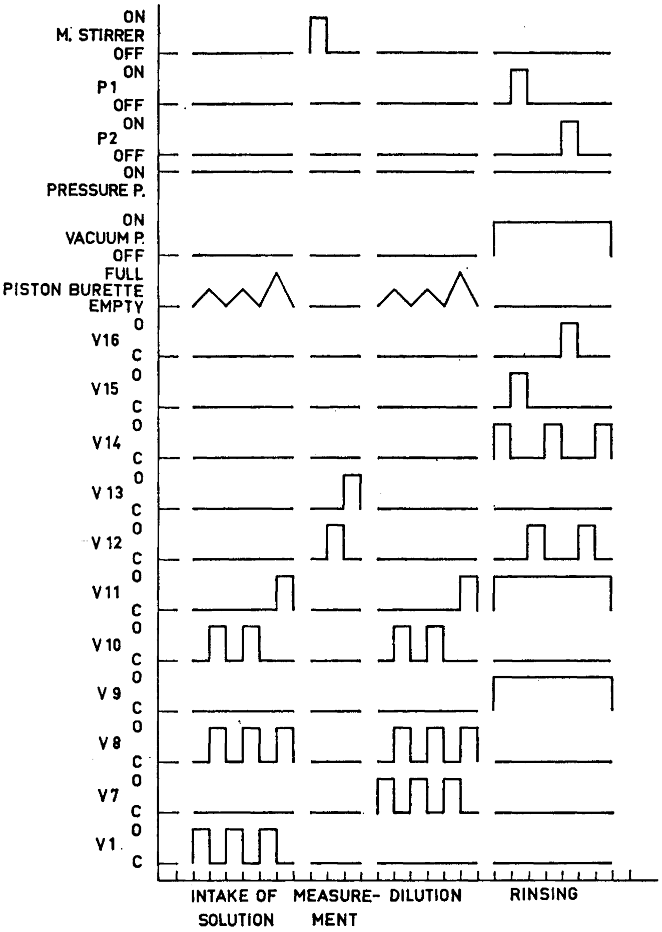

Fig. 2. The state of the magnetic stirrer, the pumps, the burette, and the valves during the four unit operations. The state of the valves is either open (O) or closed (C).

1. *Intake of a measured amount of polymer solution.* The amount of polymer solution which is to be measured is determined by means of the piston-burette. The solution is drawn into the piston-burette from the container A through the open valve V 1. Thereupon V1 closes, V 8 and V 10 open, and the piston-burette is emptied; this operation is repeated; hereby the tubings 1, 8, and 10 have been rinsed twice and are then filled with solution.

Again polymer solution is passed from the container A through V 1 into the piston-burette, V 1 closes while V 8 and V 11 open, and the piston-burette is emptied. When the piston is in the top-position the valves V 8 and V 11 close.

The desired amount of polymer solution has hereby been introduced into the dilution chamber, which completes the first unit operation.

2. *Measurement*. The first step in the process of measurement is start of the magnetic stirrer for a certain time which we denote t_1,* thereupon the three-way valve V 12 opens to the pressure from the pressure pump, the pressure of which is regulated by means of the reduction valve V_R. Hereby the liquid is pressed up through the capillary, V 13 being closed. When the meniscus passes a photodiode at *a*, V 12 opens to the atmosphere, and 1.0 sec later V 13 opens; this ensures that the excess pressure in the mixing chamber has disappeared before V 13 opens. The liquid now flows down through the capillary; when the meniscus passes a photodiode at *b*, the pulses from a crystal-controlled oscillator go to a 6-digit counter; the pulses stop, when the meniscus passes the photo-diode at *c*. The number thus obtained on the counter is the efflux time for the liquid, which is recorded on the punch-tape.

The measurement is performed $2-8$ times, depending on the program chosen, before the solution is further diluted.

3. *Dilution*. Dilution of the polymer solution is carried out analogously to the introduction of the polymer solution. The solvent is taken from container B through the valve V 7. In each run six dilutions are carried out, and after each dilution the measuring sequence is started. After the measuring sequence the fourth unit operation, that of rinsing the viscometer, is started.

4. *Emptying, rinsing, and drying*. This unit operation is started by opening V 11, V 9, and V 14 simultaneously with starting the vacuum pump. In this way the solution is pumped out of the viscometer. After a time t_2* V 14 closes, V 15 opens, and the peristaltic pump P 1 runs for a time t_3*. The empty viscometer is filled with rinsing liquid 1, which can dissolve the polymer and is completely miscible (or identical) with the solvent. When the pump P 1 stops, V 15 closes, and V 12 opens for a time t_4* to admit a pressure which presses a sufficient amount of rinsing liquid 1 up through the capillary and out of the system. When V 12 is again opened to the atmosphere, V 14 is open for a time t_2*, and thereby the remaining rinsing liquid 1 is pumped out. When V 14 is again closed, V 16 is opened, and the peristaltic pump P 2 starts repeating the process with rinsing liquid 2, which is completely miscible with liquid 1 and more volatile. After the second rinsing liquid has been pumped out, suction is continued for a time t_5* in order to dry out the viscometer.

The thermostat will accomodate six containers with polymer solutions, so that the intrinsic viscosity can be determined for six polymer solutions without any manual operations.

It is possible to choose several automatic programs:

i. the rinsing process (unit operation 4)
ii. measurement on a solution initially in the viscometer without change of concentration (unit operation 2)
iii. measurement on solvent (unit operations 1 and 2)
iv. measurement on polymer solution 1 at the initial concentration (unit operations 1 and 2)
v. dilution series on polymer solution 1 without discarding the dilute solution (unit operations 1, 2, and 3)

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* The following times have been found adequate: $t_1=15$ sec, $t_2=2.5$ min, $t_3=1.0$ min, $t_4=0.5$ min, $t_5=5.0$ min.

vi. dilutions series on 1 – 6 polymer solutions with a common solvent (unit operations 1, 2, 3, and 4, repeated)
vii. as program vi, but with measurement on solvent after each polymer solution (unit operations 1, 2, 3, and 4, repeated)

There is a choice, whether 2, 4, 6, 7, or 8 measurements of the efflux time should be performed at each concentration. Also it is possible to repeat the measurements on the polymer solutions, so that a dilution series of polymer solution No. 1 is started as soon as the measurements on polymer solution No. 6 are completed.

For particular use in kinetic investigations, any chosen program of measurements may be repeated at desired intervals of time, since the start function can be externally controlled (*e.g.*, by an electric clock).

Each measurement is characterized by three numbers i, j, k, which show on a 3-digit display during the measurement, and which are recorded on punch-tape along with the efflux time:

i, a number showing which polymer solution ($i = 1, 2, ..., 6$) is being measured. For measurement on solvent the number of the polymer solution immediately preceding it is used, except when the program chosen is that of measurement on the solvent alone. In that case $i = 0$.

j, a number indicating the dilution of the solution being measured, $j = 2c_0/c - 1$, c_0 denoting the undiluted concentration and c the concentration being measured. The dilution program is chosen such that j takes on the values 1, 2, 3, 5, 7, and 9 during a dilution series; this program offers a wide enough concentration-range to permit a reasonable extrapolation of the reduced viscosity to zero concentration. For the solvent $j = 0$.

k indicates the efflux number being performed at the specified concentration, ($k = 1, 2, ..., 8$), according to the program chosen.

III. DESCRIPTION OF THE MECHANICAL COMPONENTS

The photodiodes a, b, and c and their corresponding light-emitting diodes are each encapsulated in hard PVC and packed in a transparent silicone-resin.

The valves V 12, V 13, V 15, and V 16 are 1/8″, normally closed magnetic piston valves of stainless steel, ASCO type 8262B15 and 832087. The dead volume of these valves is immaterial, since they are only used for air and cleaning fluids.

All other valves are specially constructed pinch valves, as shown in Fig. 3. The metal bar C is in its normal position being pressed by the spring F against the tube S, which is placed on the bar B. When the solenoide M is energized, the armature A is drawn into the coil, and as C is lifted 1.0 mm, the pressure on the tube S is removed, thereby rendering free passage to the liquid.

The magnetic system is manufactured by KÜHNKE, type H 4405-25 for 24 V DC.

When M is magnetized, a force of 1.0 kp is transmitted to F with a motion of 1.0 mm of the armature.

The force of the spring *F* is regulated by vertically moving the bar *D*. A spring force of 0.7 kp has been found suitable. The advantage of using these pinch valves is that the dead volume is negligible.

The piston burette is driven by a commercially available synchronous AC-stepping motor, Berger type RSM-48 with gear type A to 120 rpm, the motor turns the spindel *S* (pitch = 0.5 mm per rotation), which drives the piston. The burette itself is a SUMMIT 20 cm^3 glass syringe.

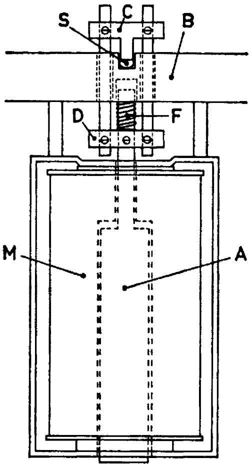

Fig. 3. A diagram of a pinch valve. Inside the solenoide M the armature A is situated. F is the spring, B, C, and D are metal bars, and S is the tubing. The armature is shown in its lowest position with S closed.

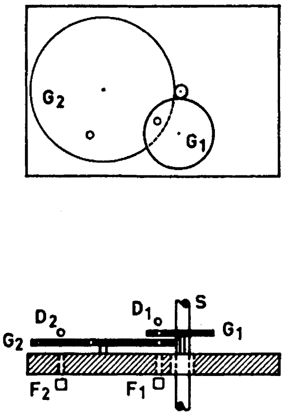

Fig. 4. The arrangement of the gear-wheels for driving the piston-burette. S is the spindel, G_1 and G_2 are gear-wheels, D_1 and D_2 light-emitting diodes, and F_1 and F_2 are photodiodes.

The motor also drives the gear-wheels G_1 and G_2 (Fig. 4), which have ratios with the motor gear-wheel of 4:19 and 1:10, respectively. Each of the gear-wheels G_1 and G_2 contains a bore, and these bores are directly above one another, when the piston is in its topmost position; hereby the light-emitting diode D_1 illuminates the photodiode F_1.

The larger gear-wheel G_2 further contains another bore, which makes it possible for the light-emitting diode D_2 to illuminate the photodiode F_2 14 times from the topmost to the lowest position of the piston.

The magnetic stirrer is driven by an AC stepping motor (Berger, type RSM 36). The magnet is mounted directly on the motor-axle, which rotates with 300 rpm. The motor and the magnet are encased in poly(methylmethacrylate). The power supply for the motor goes through two stainless steel tubes in which the casing is fastened.

The pressure-pump and the vacuum pump are membrane pumps. (Charles Austin, type Dymax MK II).

The reduction valve V_R is manufactured by CONOFLOW, type H-10 for a down-stream pressure of 0 – 5 psi.

The peristaltic pumps, which are specially made for this purpose, are driven by AC stepping motors, Berger type RSM 64, gear B to 120 rpm for P 1, and 60 rpm for P 2.

The valves V 1 – V 7 and the piston burette are connected to a glass manifold with an inner diameter of 1 mm. The connection to V 8 is a teflon tube, similarly with an internal diameter of 1 mm. The valves V 8, V 9, V 10, and V 11 are likewise connected to a glass manifold of the above-mentioned type.

Air and cleaning liquids are passed through Viton tubing with an inner diameter of 2.5 mm.

The tubing for the valves is made of chemically stable Tygon tubing which is mechanically and elastically sufficiently stable to prevent the tubing from remaining closed, even after the valves have been constantly closed for a long time.

The thermostat bath which contains 45 l water, is heated by two heating elements of 500 and 1000 W. Stirring is performed by means of a Heidolph circulation pump type P V, which has a pump-speed of 40 l/min. The temperature is sensed by a 100 Ω platinum resistance thermometer connected to an EUROTHERM thermoregulator. The temperature is adjusted digitally from 0 to 100°C in steps of 0.1°C. The regulator works with PID-control.*

The heating elements are controlled by tyristors switched on and off in the zero crossing point, such that electromagnetic interference is avoided.

IV. DESCRIPTION OF THE ELECTRONIC SYSTEM

The electronic part of the viscometer is contained in two standard 19″ rack units. One contains the thermoregulator for the thermostat, relays for motors and pumps, and power supplies. These are 24 V DC for valves, relays, lamps, and tape-punch, 300 V DC for digit-tubes, 10 V DC for the 5 V voltage regulator, and 24 V DC for the -6 V and $+12$ V voltage regulators. The front panel of this rack unit displays the controls of the thermoregulator, control lamps of valves, piston burette and peristaltic pumps, push-button switches for manual control of magnetic stirrer, peristaltic pumps and valves, and main switches for thermostat and power supplies. The other rack unit contains the electronic control and measuring systems, mounted on 30 printed circuit boards. On the front panel are nine digit tubes, which give the digits i, j, and k, and the efflux time. The front panel also contains control lamps for the various processes as well as switches for choice of program and start of the processes.

The electronic system is shown schematically in Fig. 5. Logically it falls into two parts, a controlling part and a part for measurement and punch-control; in addition to this the electronic system contains the voltage regulators, $+5$ V for the logical circuits and -6 V and $+12$ V for amplifiers and timing-circuits.

The controlling part. The control part is based upon 5 counters, the position of which determine at which point in the processes the viscometer operates.

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* Proportional-Integral Derivative Control.

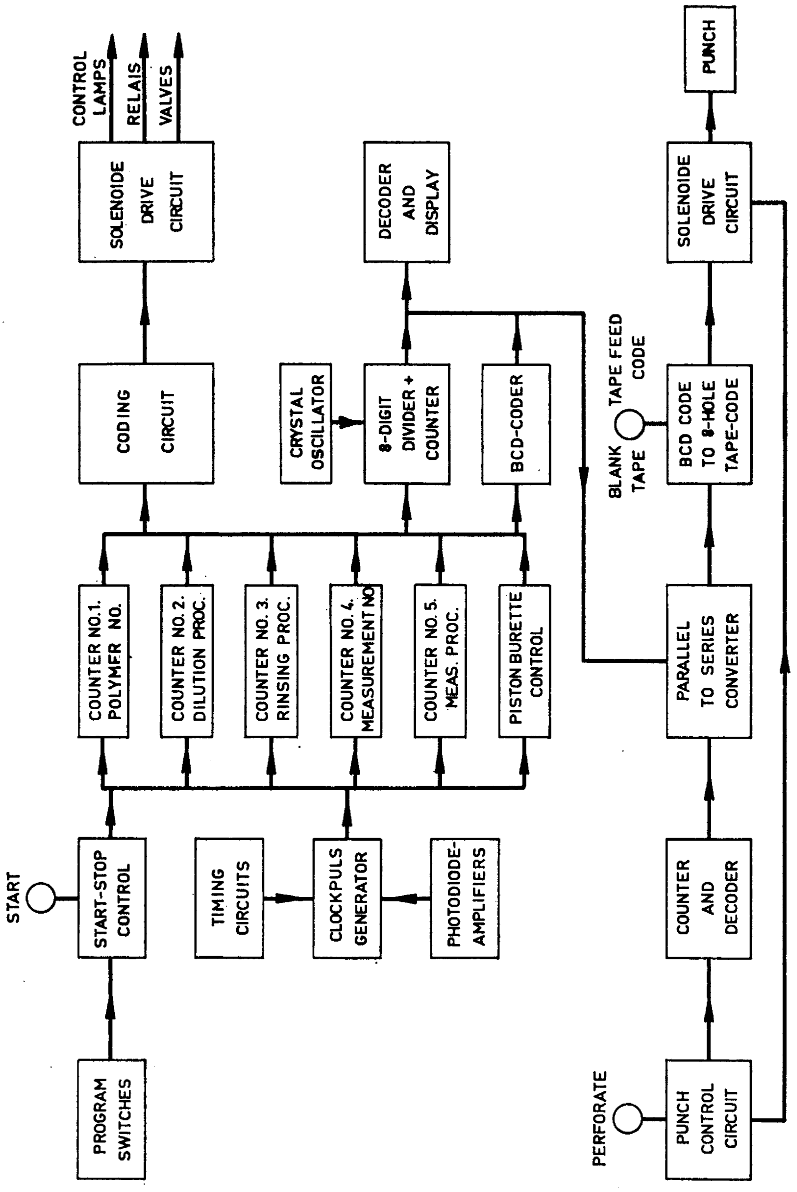

Fig. 5. Functional diagram of the electronic system.

The Start-Stop control controls the start and reset functions of the counter according to the position of the program-switches; its main part is the start-stop flip-flop, which is put in the start position by the start-button, in the stop position by the last step in the program chosen. The counters are built as shift registers where a single 0 goes from one step to the next. Counter No. 1 indicates polymer No. i ($i=1, 2,...,6$). Counter No. 2 controls the dilution process, steps 1 and 2 are rinsing of the tubing with polymer solution, step 3 is solution intake, steps 4 and 5 are rinsing of the tubing with solvent, steps 6, 7, 8, 9, and 10 are dilution steps, 11 is the rinsing process, step 12 is rinsing of tubing with solvent, step 13 measurement of solvent, and step 14 is the rinsing process. Counter No. 3 indicates the 8 steps in the rinsing process. Counter No. 4 indicates the number of efflux at the same concentration. Counter No. 5 controls the six steps in the measuring process. The pulses from the clock-pulse-generator shift the counters from one step to the next. The polymer counter is controlled by the rinsing process in the dilution series; counter No. 2 is controlled by the piston-burette, the last step in the rinsing process, and the last efflux; counter No. 3 is controlled by pulses from the timing circuits, the efflux counter is controlled by the last step in the measuring process; and the counter No. 5 is controlled by pulses from the timing circuits and by pulses from the viscometer-photodiodes.

In the coding circuit the signals for the different valves, pumps, and motors are generated by the immediate position of the counters. The signals from the coding circuits go to the solenoide-drive-circuits, which are transistor switches, conducting 24 V DC to the various valves, relays, and lamps.

The measuring part. The measuring system consists of a 100 kHz crystal-controlled oscillator which is equipped with a comparator type 710 as its amplifying element, and an 8-decade-bcd-counter. The first two decades function as frequency-dividers down to 1 kHz, and the last six decades function as the actual counter, *i.e.* this latter has a resolving power of 1 msec. The reset function for the two parts of the counter is controlled by the measuring-process-counter.

The numbers from the polymer counter, dilution counter, and efflux counter (i, j, k) are translated into bcd-code and are, along with the six digits from the above-mentioned decimal counter, transmitted to decoders and driving circuit for the nine digit-tubes.

The paper-tape-punch is controlled by a control circuit and a 0-11-counter, which is constructed as a binary counter with decoding gates. The control circuit consists of a control flip-flop with trigger circuit, an astable multivibrator for generating driving pulses for the punch, and gate circuits for punch-motor and control lamp. The punch-cycle is triggered by the last step in the measuring process; the pulses from the astable multivibrator are transmitted to the driving circuit, and after each pulse the counter goes one step forward. When the last digit has been punched, the control flip-flop resets, and the cycle is finished. By means of a push-button it is possible to open for the pulses to the driving circuit in order to generate blank tape and tape with tape-feed-code, without triggering the control flip-flop or the counter.

The numbers from the counter are transmitted to the parallel-to-series-converter (a gate circuit where the various digits from the bcd-coder and the six-digit counter are chosen one by one). The bcd-code is translated into 8-hole tape-code by introducing 0 and parity bit, the codes for various other characters are introduced, and the signal is transmitted to the solenoide-drive-circuit, which supplies the pulses for the punch-solenoides.

The paper-tape-punch is manufactured by G.N.T. Automatic A/S, model 34.

Description of circuit elements. The control for the piston burette consists of the following parts: 1. the amplifiers for the signals from the two photodiodes F_1 and F_2; 2. two flip-flops controlling flow into and out of the burette; 3. a binary counter $(0-15)$ which counts the number of signals from F_2 during the influx; 4. a selection circuit. The influx is started by the clock- and start-pulses for the dilution-process-counter. The selection circuit stops the flow into the burette, when the binary counter has reached one of three numbers determined by the dilution process counter; the three numbers, and thereby the volume of liquid admitted to the burette, can be changed by moving wires on the printed circuit board. The emptying of the burette starts when the influx stops, and it is stopped by the signal from the photodiode F_1.

The viscometer-photodiodes work in the photovoltaic mode, hereby their output voltage increases with the logarithm of the intensity of light.[5] Therefore the signal from the photodiodes becomes independent of the absolute intensity of light. After passage through a coupling condenser the signal is amplified in a source follower with matched field effect transistors; the gate voltage of the other FET can be adjusted by means of a trimming potentiometer, and hereby the threshold of the signal can be controlled. The signals from the source followers are amplified in a comparator type 710. A gate circuit, controlled by the measuring-process-counter, determines which photodiode signal is to be transmitted to the clock-pulse-generator.

The timing signals for the rinsing process and the measuring process are generated by 6 unijunction transistor-circuits. During the counter-steps in question a polycarbonate condenser is being charged through a large resistor (10-100 MΩ). The voltage across the condenser is passed through an emitter-follower to the emitter of the unijunction transistor, and, when a certain voltage has been reached, the condenser discharges through the unijunction transistor; the signal generated in this manner is transmitted to the clock-pulse-generator. When the timing-circuit is not in operation, the condenser is kept short-circuited by a transistor.

The matched field effect transistors are Texas Instruments type TIS 69, all other transistors are plastic cased silicium planar types manufactured by Motorola. The logic circuitry is made with Motorola, series MC 830 DTL-logic. All counters are made with Texas Instruments series SN 74N TTL-logic; the shift register counters with type 7473 and 7496 and the decimal counters with type 7490, the decoders and display drivers are type 7441. The comparators are Texas Instruments type SN 72710. All integrated circuits are in plastic dual-in-line case. The light emitting diodes are Texas Instruments type TIL-01 and TIL-09, GaAs-diodes, the sensors are Fairchild type BPY 67 diodes.

EXAMPLE OF THE FUNCTION OF THE VISCOMETER

In order to demonstrate the accuracy of the viscometer and the reproducibility of the data for the reduced viscosity we give a series of measurements on aqueous solutions of poly(ethylene glycol).

The capillary used had the following specifications:

$A = 3.600 \times 10^{-4}$ cm^2/sec^2; $B = 3.850 \times 10^{-2}$ cm^2

(determined by measurements on water at different temperatures as recommended by Bingham and Jackson 6) where A and B are constants in the expression for the kinematic viscosity,

$$\nu = \eta/\varrho = At - B/t$$

Table 1. Efflux times (in msec) from the punch-tape. For explanation of i, j, and k, see the text.

ijk	*t*	*ijk*	*t*	*ijk*	*t*	*ijk*	*t*	*ijk*	*t*	*ijk*	*t*	*ijk*	*t*
111	055399,	112	055396,	113	055398,	114	055395,	115	055395,	116	055397,	117	055397
121	043727,	122	043782,	123	043784,	124	043784,	125	043788,	126	043787,	127	043785
131	038665,	132	038682,	133	038683,	134	038684,	135	038681,	136	038683,	137	038681
151	034031,	152	034059,	153	034056,	154	034054,	155	034055,	156	034052,	157	034050
171	031878,	172	031923,	173	031925,	174	031922,	175	031917,	176	031921,	177	031918
191	030643,	192	030700,	193	030704,	194	030701,	195	030702,	196	030701,	197	030701
101	026417,	102	026415,	103	026411,	104	026411,	105	026414,	106	026412,	107	026415
211	046407,	212	046404,	213	046407,	214	046406,	215	046406,	216	046406,	217	046404
221	038627,	222	038687,	223	038687,	224	038688,	225	038689,	226	038690,	227	038689
231	035172,	232	035175,	233	035177,	234	035177,	235	035176,	236	035176,	237	035177
251	031942,	252	031934,	253	031927,	254	031924,	255	031926,	256	031926,	257	031925
271	030403,	272	030399,	273	030397,	274	030397,	275	030398,	276	030396,	277	300398
291	029469,	292	029515,	293	029518,	294	029517,	295	029516,	296	029515,	297	029514
201	026412,	202	026417,	203	026412,	204	026406,	205	026415,	206	026412,	207	026411
311	038679,	312	038682,	313	038684,	314	038684,	315	038683,	316	038684,	317	038684
321	034039,	322	034048,	323	034051,	324	034051,	325	034054,	326	034052,	327	034052
331	031915,	332	031918,	333	031919,	334	031921,	335	031920,	336	031920,	337	031921
351	029947,	352	029928,	353	029917,	354	029917,	355	029917,	356	029916,	357	029917
371	029003,	372	028987,	373	028984,	374	028984,	375	028985,	376	028986,	377	028985
391	028481,	392	028474,	393	028469,	394	028468,	395	028467,	396	028465,	397	028467
301	026409,	302	026413,	303	026411,	304	026409,	305	026409,	306	026406,	307	026407
411	055388,	412	055387,	413	055387,	414	055387,	415	055389,	416	055391,	417	055390
421	043742,	422	043778,	423	043776,	424	043775,	425	043775,	426	043777,	427	043775
431	038670,	432	038672,	433	038674,	434	038677,	435	038678,	436	038678,	437	038677
451	034022,	452	034050,	453	034053,	454	034059,	455	034051,	456	034051,	457	034051
471	031871,	472	031919,	473	031921,	474	031922,	475	031922,	476	031922,	477	031927
491	030634,	492	030667,	493	030690,	494	030694,	495	030694,	496	030696,	497	030697
401	026404,	402	026407,	403	026409,	404	026408,	405	026408,	406	026412,	407	026403
511	046392,	512	046395,	513	046396,	514	046394,	515	046397,	516	046398,	517	046398
521	038619,	522	038672,	523	038677,	524	038678,	525	038677,	526	038678,	527	038677
531	035168,	532	035163,	533	035171,	534	035173,	535	035172,	536	035172,	537	035174
551	031930,	552	031937,	553	031939,	554	031939,	555	031941,	556	031941,	557	031948
571	030410,	572	030411,	573	030409,	574	030409,	575	030407,	576	030419,	577	030406
591	029485,	592	029511,	593	029518,	594	029517,	595	029518,	596	029518,	597	029518
501	026412,	502	026383,	503	026411,	504	026409,	505	026409,	506	026411,	507	026404
611	038675,	612	038677,	613	038677,	614	038680,	615	038678,	616	038678,	617	038679
621	034036,	622	034050,	623	034049,	624	034048,	625	034051,	626	034052,	627	034000
631	031907,	632	031913,	633	031916,	634	031916,	635	031917,	636	031919,	637	031918
651	029953,	652	029932,	653	029914,	654	029914,	655	029915,	656	029914,	657	029914
671	028998,	672	028990,	673	028989,	674	028989,	675	028988,	676	028988,	677	028987
691	028478,	692	028469,	693	028465,	694	028465,	695	028464,	696	028464,	697	028463
601	026411,	602	026408,	603	026408,	604	026409,	605	026401,	606	026408,	607	026408

and t is the flow time. The flow-time of water at 30°C is 26 sec in this capillary. This time is shorter than that recommended by British Standards Institution by a factor of 10; the reason we use it here is that we want to test the viscometer under the most unfavourable conditions.

The measurements were carried out at 30.00 ± 0.02°C on poly(ethylene glycol), (Hoechst, type 10.000, $\overline{M}_n = 8500$ g/mol, $\overline{M}_w = 11500$ g/mol). Three aqueous solutions with the following concentrations were made: 0.038275 g/cm^3, 0.028706 g/cm^3, and 0.019137 g/cm^3. These solutions were placed in the viscometer as polymer 1 and 4, 2 and 5, and 3 and 6, respectively.

The program chosen was dilution series on all six polymer solutions, measurement on solvent after each dilution series, and with seven measurements at each concentration.

Table 1 shows the raw data from the tape. It is seen that the first determination at each concentration differs from the remaining 6 determinations, because of insufficient mixing, whereas the remaining six determination all have a standard deviation of about 2 msec. Therefore the first determination has been discarded in the calculations.

In the regression analysis on the reduced viscosities (calculated as usual, and corrected for kinetic energy and density) as a function of the concentration [7] the weight-factor used for each average value of the reduced viscosity is the reciprocal value of the variance at each concentration. The values obtained in this way for the intrinsic viscosity, together with their standard deviation, are listed in Table 2.

Table 2. Intrinsic viscosities (cm^3/g) and their standard deviations for the six dilution series.

Polymer solution	Intrinsic viscosity	s.d.
1	19.75	0.14
2	19.73	0.23
3	19.19	0.25
4	19.84	0.14
5	19.74	0.23
6	19.09	0.26

It is seen from the table that there is good agreement between the intrinsic viscosities from the six solutions. The values also agree with data from the literature.[8-12]

Fig. 6 shows a plot of the reduced viscosity *versus* concentration for the six solutions, together with the extrapolated values from the regression analysis.

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* *Note added in proof.* The instrument is now commercially available from UNIVEL, Frydenlund, DK-2950 Vedbæk, Denmark.

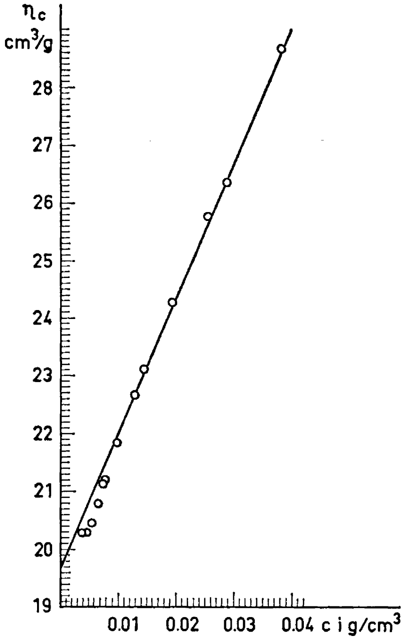

Fig. 6. Reduced viscosity *versus* concentration for the dilution series of the six polymer solutions. The intrinsic viscosity shown is calculated using weighted values of the reduced viscosity.

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REFERENCES

1. Auto-Viscometer, Model 5901A, Hewlett-Packard/F & M Scientific Division, Avondale, Pennsylvania, U.S.A.
2. Viscometer Reader, Rehovoth Instruments Ltd., Rehovoth, Israel.
3. Ubbelohde, L. *Ind. Eng. Chem. Anal. Ed.* **9** (1937) 85.
4. British Standard Specification No. 188—1957, British Standards Institution, London 1957, p. 38.
   See for instance:
5. Millman, J. and Halkiar, C. C. *Electronic Devices and Circuits*, McGraw, New York 1969, pp. 587—591.
6. Bingham, E. C. and Jackson, R. F. *Bull. Bur. Stds.* **14** (1918) 75.
7. Hald, A. *Statistical Theory with Engineering Applications*, Wiley, New York 1955, Chap. 18.
8. Bailey, F. E., Jr. and Callard, R. W. *J. Appl. Polymer Sci.* **1** (1959) 56.
9. Bailey, F. E., Jr., Kocera, J. L. and Imhoff, L. G. *J. Polymer Sci.* **32** (1958) 517 (L).
10. Rempp, P. *J. Chim. Phys.* **54** (1957) 432.
11. Ring, W., Cantow, H.-J. and Holtrup, W. *European Polymer J.* **2** (1966) 151.
12. Müh, G. *Kolloid-Z.* **196** (1964) 140.
13. Added in proof. Hughes, J. and Rhoden, F. (*J. Sci. Instr.* **2** (1969) 1134) have a description of another viscometer with interchangeable capillaries.

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