N-63-4-2

OFFICE OF NAVAL RESEARCH

Contract Nonr-2693(00)
Task No. NR356-407

TECHNICAL REPORT NO. 9

Mellon Institute
Pittsburgh, Pennsylvania

Covering period from September 1, 1962 to February 28, 1963

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I. INTRODUCTION

INTRODUCTION

In the preceding technical report (No. 8) Fox and Allen presented several relationships representing correlations between the observed viscosity η and the molecular structure for various polymer systems. Unfortunately they were then unaware of the prior work of Tobolsky who suggested several years ago a relation between η and the mean-square radius of gyration $\overline{s_o^2}$ for amorphous linear polymers. Thus some of the general conclusions of Fox and Allen were found earlier by Professor Tobolsky; further, his equation when applied to branched polystyrenes predicts the relationship, $\eta \sim (gM)^{3.4}$, obtained in this research project. We believe Tobolsky's relationship to be of great importance, and regret that we overlooked it earlier. We are encouraged by its applicability to continue the search for even more comprehensive general relationships for predicting quantitatively the viscosity of macromolecular systems from a minimum number of "molecular" parameters.

In this period methods for making "monodisperse" polystyrenes of molecular weight of 1000 or lower have been developed, thus making possible the synthesis of desired "monodisperse" star-type polystyrenes with very short branches. Methods for introducing a chloromethyl group on the aromatic ring of a predetermined fraction of the styrene units in a polystyrene chain, with negligible crosslinking, have been developed. It is planned to employ this technique for the introducting of eight $-CH_2Cl$ groups on a "monodisperse" polystyrene octamer, and to utilize the resultant compound as an octafunctional terminator for polystyryl lithium to produce star-type polymer molecule with eight branches.

A "monodisperse" polystyrene "backbone" of molecular weight 1.4×10^5 containing on the average one $-CH_2Cl$ group per 400 styrene units, was reacted with an excess of "monodisperse" polystyryl lithium "branches" to yield a product containing a comb-type polymer. This polymer, which was separated from the unattached excess "branches" by fractional precipitation was shown by molecular weight studies to have on the average of three branches per chain, as expected. Its melt viscosity was given approximately by the same equation which applied to high molecular weight star-type polystyrenes.

Calibration of the forced oscillation torsion pendulum has progressed, and a description of the instrument was submitted for the American Physical Society Meeting in March.

Dr. Hoeve accepted a position at the National Bureau of Standards, and terminated his work here on February 1. However, he will keep in close touch with the progress of Dr. Blumberg, who will complete, by September, the x-ray studies on mercuric chloride-poly(ethylene oxide).

II. MOLECULAR STRUCTURE AND THE MELT VISCOSITY OF POLYMERS

(T. G Fox and V. R. Allen)

II. MOLECULAR STRUCTURE AND THE MELT VISCOSITY OF POLYMERS

(T. G Fox and V. R. Allen)

The results of our viscosity studies reported in the preceding progress report (No. 8) indicated the following two conclusions (among others):

1. For star-type branched polymers, the viscosity η is given by the expression

$$\eta \sim (gM)^{3.4} \qquad (1)$$

where g = $[(\overline{s_o^2})_{branched}/(\overline{s_o^2})_{linear}]_{M=constant}$ expresses the decrease in the unperturbed mean-square radius of gyration $\overline{s_o^2}$ resulting from exchanging a branched for a linear polymer of the same molecular weight M.

2. For linear polymers

$$\eta_{c,T_g} = B \cdot f_g \qquad (2)$$

where η_{c,T_g} is the viscosity of the polymer of critical chain length Z_c at the reference temperature T_g, f_g is the molecular friction coefficient (values available from measurements of Ferry and coworkers), and B is essentially the same constant for different polymers.

Recently it came to our attention that in prior work Tobolsky has reported (A. V. Tobolsky, "Properties and Structures of Polymers", John Wiley and Sons, New York, 1960, p. 78) that the viscosities of linear polymers obey the relation

$$\eta = A \, \overline{s_o^2}^{\,3.4} \qquad (3)$$

where A is the same constant for four different polymer series, provided that their viscosities be compared in corresponding states, i.e., at the same value of $T - T_g$.

Tobolsky's finding applied to branched polystyrenes would lead us to expect $\eta \sim (gM)^{3.4}$, as we have observed. Equations (2) and (3), while not identical, both indicate the existence of a general formula for the viscosity of a macromolecular system and chain dimensions. We regret that we were previously unaware of Tobolsky's equation, and believe that it will be of great assistance both in planning and in interpreting the results of the present researches.

III. STAR TYPE POLYSTYRENES

(D. P. Wyman, T. Altares, Jr., V. R. Allen, T. G Fox, W. R. Freeman,
K. Meyersen, and J. Wang)

III. STAR TYPE POLYSTYRENES

(D. P. Wyman, T. Altares, Jr., J. Wang, and W. R. Freeman)

In previous work we found for star type polystyrenes consisting of p branches of equal length united to a common center that for p = 3 or p = 4

$$\eta \sim (Mg)^{3.4} \qquad M \geq M_c$$

$$g = \frac{3}{p} - \frac{2}{p^2}$$

We aim to extend these studies to lower molecular weights and to star type polystyrenes of p = 8. Progress in developing the required synthetic techniques is reported here.

A. The Preparation of Low Molecular Weight Monodisperse Polystyrenes

1. Butyllithium-Tetrahydrofuran (D. P. Wyman and T. Altares, Jr.)

Certain portions of the present program required the use of monodisperse polystyrene polymers of low molecular weights ($M < 30,000$). These are not preparable by use of butyllithium initiation in benzene solvent because $k_p/k_i = 550$, and narrow distributions below M = 30,000 are not obtained. However, in a recent publication* it was pointed out that small amounts of tetrahydrofuran will greatly influence and change the kinetics. Thus, k_i becomes instantaneous whereas k_p is only accelerated by a factor of 4-5. This situation fulfills one of the ideal requirements for preparing monodisperse polymers, i.e., initiation is very rapid compared to propagation. Since transfer and termination steps are negligible, we have taken advantage of this procedure to prepare monodisperse polymers with very low molecular weights. To date polymers with M = 500, 900, 1800, 3200, and 6500 have been prepared. Data now available indicates that they all have narrow molecular weight distributions.

All experiments are done in high vacuum. The styrene is added to benzene and the system is cooled to partially freeze the solution. Butyllithium is added next to the very cold solution and it is thoroughly mixed. Care is taken to work rapidly during these steps. It should be pointed out that while both propagation and initiation are quite slow at low temperatures, some reaction does occur. The addition of tetrahydrofuran (about 2 moles/mole butyllithium) causes the onset of a rather spectacular reaction. The solution which is partially frozen thaws immediately. The color goes from a light yellow or light orange to an intense, dark red, and the polymerization is complete in minutes (for the low molecular weight polymers, $M < 7,000$).

An interesting facet of this work is that we are attempting to evaluate the lower members ($M < 1,000$) via gas chromatography. This arose from observations that these appeared to be capable of being molecularly distilled. Short (6 inch) apiezan columns have been used with some success and glass filled columns will be tried.

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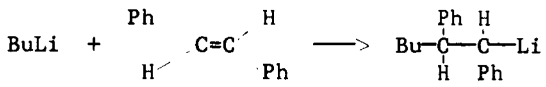
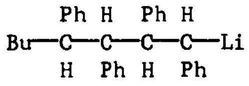
*S. Bywater and D. J. Worsfold, Can. J. Chem., <u>40</u>, 1564 (1962).

2. Reaction of Butyllithium with Trans-Stilbene (D. P. Wyman and T. Altares, Jr.)

In conjunction with the same problem of obtaining low molecular weight monodisperse polymers, a study of the reaction of butyllithium with stilbene in benzene was undertaken. This was based on the expectation that the reaction would predominantly follow equation (1). Compound 1 was expected to behave very similarly to styryllithium and would thus be a good initiator for anionic polymerization. The results of this study indicated that the reaction was considerably more complex than anticipated and these results are summarized in the following scheme:

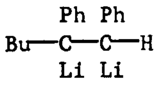
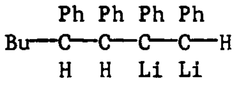
(1)  1

$$\text{BuLi} + \text{Stilbene (excess)} \xrightarrow{60\text{-}70°} 1$$



$$1 + \text{stilbene} \rightleftharpoons \text{Bu}{-}\underset{\text{H}}{\overset{\text{Ph}}{\text{C}}}{-}\underset{\text{Ph}}{\overset{\text{H}}{\text{C}}}{-}\underset{\text{H}}{\overset{\text{Ph}}{\text{C}}}{-}\underset{\text{Ph}}{\overset{\text{H}}{\text{C}}}{-}\text{Li} \quad 2$$

(1+1) + (1+2) + (2+2)

 3 +  4

$$\text{Bu}{-}\underset{\text{Li}}{\overset{\text{Ph}}{\text{C}}}{-}\underset{\text{Li}}{\overset{\text{Ph}}{\text{C}}}{-}\text{H} \quad 3 \quad + \quad \text{Bu}{-}\underset{\text{H}}{\overset{\text{Ph}}{\text{C}}}{-}\underset{\text{H}}{\overset{\text{Ph}}{\text{C}}}{-}\underset{\text{Li}}{\overset{\text{Ph}}{\text{C}}}{-}\underset{\text{Li}}{\overset{\text{Ph}}{\text{C}}}{-}\text{H} \quad 4$$

The disproportionation reaction was virtually quantitative and 3 and 4 and their mixtures indeed behaved as difunctional initiators obeying $M = \frac{\text{g monomer}}{1/2\ \text{moles initiator}}$. Low molecular weights were obtainable and the molecular weight distributions of these polymers were narrow, although most contained a small (< 10%) amount of very low molecular weight material arising from termination and/or small quantities of unconverted butyllithium.

B. The Chlorination of Hydrocarbons with PCl_5 (D. P. Wyman, W. R. Freeman, and J. Wang)

During the course of studies on the preparation of cruciform precursors a brief investigation of hydrocarbon chlorination with PCl_5 was conducted. Aromatic substances readily dissolve PCl_5. Upon heating a reaction occurs which can be described overall as the following:

$$RH + PCl_5 \longrightarrow RCl + PCl_3 + HCl$$

The purpose of the study was to see if selectivity in positions substituted could be found. The results indicated that (1) simple olefins, like cyclohexene, add a molecule of chlorine across the double bond and the addition is trans, (2) aliphatic hydrocarbons and simple alkylaromatics chlorinate by free-radical substitution with about the same positive selectivity as in photochlorination, (3) very active aromatic rings, such as mesitylene, react mainly via an ionic mechanism to give ring rather than side chain substitution. Tentatively the free-radical mechanism suggested by these results is as follows:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$Cl_2 \longrightarrow 2Cl\cdot$$

$$Cl\cdot + RH \longrightarrow R\cdot + HCl$$

$$R\cdot + PCl_5\cdot \longrightarrow RCl + PCl_4\cdot$$

$$\cdot PCl_4 \longrightarrow PCl_3 + Cl\cdot \quad \text{mostly}$$

C. Preparation of Octafunctional Terminator (K. Meyersen, D. P. Wyman, and J. Wang)

A considerable amount of effort was devoted in the past towards the synthesis of a pure, well-characterized compound which possessed 8 reactive aromatic chloromethyl groups. Such compounds are unknown in the literature and a variety of reaction schemes were employed in efforts to prepare them (see previous reports). All of these, for one reason or another, failed.

During studies directed towards the synthesis of chloromethylated polystyrenes to be used for the preparation of comb type polymers, it was found that at least 2/3 of the benzene rings (and perhaps more) in a polystyrene chain could be chloromethylated with only negligible amounts of side reactions (such as coupling via a Friedel-Crafts alkylation of an unsubstituted ring by a chloromethyl group). Having available the means of preparing well defined low molecular weight polymers (see above) then offers the most attractive inroads to the synthesis of these compounds, i.e., the chloromethylation of low molecular weight polystyrenes of narrow molecular weight distributions.

While the chloromethylation reaction does not appear to be subject to serious side reactions it is far from simple and straightforward. A clean-cut variation of percent chloromethylation with time has not been achieved and there is considerable scatter in the experimental points. At best, trends appear to be reproducible. Nevertheless the method is useful and the desired materials can be obtained, although more than one experiment is often necessary.

Basically the system involves the treatment of dilute solutions of polystyrene in CCl_4 solvent with excess $CH_2Cl{-}O{-}CH_3$ and $SnCl_4$ catalyst. After appropriate times, the reaction is quenched with methanol and water The CCl_4 solution of chloromethylated polymer is then washed with H_2O, then dilute $NaHCO_3$ solution, and precipitated in methanol. The final step is to freeze dry the polymer out of benzene.

Two approaches are being pursued. One involves the complete chloromethylation (1 $ClCH_2$ group/benzene ring) and the other involves the lesser chloromethylation of a slightly higher homolog (e.g., DP = 12 with 2 $ClCH_2$ groups/3 rings). Preliminary results indicate that both methods will work.

The overall reaction of $ClCH_2OCH_3$ with aromatic hydrocarbons can be written as

$$Ar{-}H + ClCH_2OCH_3 \longrightarrow ArCH_2Cl + CH_3OH$$

This being the case one might expect reactions such as the following to occur:

$$CH_3OH + SnCl_4 \longrightarrow CH_3{-}O{-}SnCl_3 + HCl$$

The compound $CH_3{-}O{-}SnCl_3$ would be expected to be a catalyst, but with different reactivity than $SnCl_4$. The same can be expected for $(CH_3O)_2SnCl_2$, $(CH_3O)_3SnCl$, etc. Furthermore, HCl itself is probably a catalyst (inasmuch as acids can cleave ethers). These reactions probably explain most of the complexity of the reactions. While outside of the scope of this program, it offers an excellent example of a system which is constantly changing, not only in concentration of various species, but also in the nature of these species. It is then, basically, a fascinating reaction system for further study.

These preparations are being continued by Dr. Meyersen.

D. Preparation of Low Molecular Weight Tetrachain Polystyrene (T. Altares)

The method of making tetrafunctional polystyrenes utilizes a very pure tetrachloromethyl benzene to couple four polystyryl lithium chains together at a common center by splitting out lithium chloride. By necessity monodisperse polystyryl lithium chains must be used if the branched material is to be of narrow molecular weight distribution. A method has been perfected for the preparation of low molecular weight, narrow distribution polystyrenes (Section III, A-1 above) and for the preparation and ultra purification of the tetrafunctional precursor. A method involving a change of solvent (from benzene to 50:50 tetrahydrofuran) has been developed for the coupling of the two reactants to form a tetrachain polystyrene. Synthesis of four low molecular weight tetrachain polystyrenes has been completed (branch $M < 30,000$).

Two of these are very good (TAPS #45-P x 4 and #46-P x 4, $M = 11,000$ and 7,000, respectively), as they were prepared from very pure tetrafunctional precursor (tetrachloromethyl benzene) and polystyryl lithium as per methods in Section III, A-1 above. Another sample (TAPS #42-p x 4) prepared in the same fashion yielded a deep yellow polymer which contained a sizeable quantity of multifunctional components. The cause of this was found to be the tetrafunctional precursor. If the precursor is not extremely pure (six to eight recrystallizations) some degradation reaction takes place, which the solvent exchange technique used for ultra purification (See Section IV-B) cannot rectify, and the multifunctional colored material results.

Prior to the tetrahydrofuran technique (Section III, A-1), a low molecular weight tetrachain was made (TAPS #33-p x 4, branch M = 13,000). The distribution was expected to be broad (M branches range from 2,000 to 15,000) but without a method for making low molecular weight polystyrene of narrow molecular weight distribution there was no recourse. It was planned to fractionate the desirable three molecular weight ranges from this sample. TAPS #45-p x 4 and #46-p x 4 (above) have since been made and replace TAPS #33-p x 4.

E. Characterization of the Tetrachain Polystyrenes (V. R. Allen and T. G Fox)

The two low molecular weight star-type branched polystyrene samples described in the preceding section were fractionated from a 50/50 methanol-water mixture as the precipitant. Each sample was separated into six fractions, corresponding to ca. 90% of the whole polymer. Viscometric and light scattering determination of the fractions is proceeding.

IV. COMB-TYPE BRANCHED POLYSTYRENES

(D. P. Wyman, T. Altares, Jr., V. R. Allen, T. G Fox, K. Meyersen,
J. Wang, and P. R. Kaufman)

IV. COMB-TYPE BRANCHED POLYSTYRENES

A. Chloromethylation of Polystyrene (D. P. Wyman, K. Meyersen, J. Wang, and P. R. Kaufman)

The chloromethylation of various polystyrene polymers with narrow molecular weight distributions is being continued. These compounds which possess one chloromethyl group/30-300 benzene rings are used as precursors for the preparation of comb polymers. The reactions are prone to the same problems discussed in the section on octachain terminators and the experimental procedures are the same. Once again, while there is scatter in the experimental data, the overall procedure is very useful and Dr. Meyersen is continuing the preparations.

B. Preparation of a Comb-Type Polystyrene (T. Altares, Jr.)

(TAPS #37 and 37 Comb)

1. Synthesis of chains for reaction with comb precursor. The reactants used to make active chains for reaction with the comb precursor consisted of 7.6 gms very pure styrene, 2.6×10^{-4} moles butyl styryl lithium containing 7.2×10^{-4} moles tetrahydrofuran, and 100 ml of benzene (distilled from anion solution into the reaction flask). The procedure used was the "one shot technique" for active chains of molecular weight ca. 35,000 (1.0 to 1.5×10^{-4} moles of impurities were estimated; an excess of styryl lithium was added to deactivate them). Predicted molecular weight: 36,200; molecular weight found by $[\eta] = 34{,}800$.

2. Coupling of living chains with comb precursor.

(a) Purification of precursor--1.176 gms of comb precursor was purified by solvent exchange in vacuo between the precursor and an anion solution. The solvent used was tetrahydrofuran and the anion solution was sodium biphenyl. Six exchanges of solvent were used and ultimately the precursor was sealed in a flask with 100 ml of very pure tetrahydrofuran, distilled in from anion solution. The precursor was of M = 140,000, Cl analysis indicated 3.6 chloromethyl groups per polymer molecule.

(b) Preparation of living chains was as per (1) above, with the precursor flask sealed on the polymerization reactor; 2.9 gms of chains were removed for control purposes prior to coupling (all done under vacuum).

(c) Coupling of reactive anion chains with comb precursor--After removal of control chains, the tetrahydrofuran solution of chlorinated precursor was titrated drop by drop into the remaining excess of chains with stirring. Addition took 1-1/2 hours, after which the reaction was terminated with methanol.

(d) Stoichiometry--Chains in excess are necessary during the coupling. A large excess of chains were used in this case. Theoretically there were:

$$\frac{3.6 \times 1.176}{1.4 \times 10^5} = 3.02 \times 10^{-5} \text{ moles of chains needed for a 1:1 reaction}$$

but

$$\frac{4.7}{3.48} \times 10^4 = 13.5 \times 10^{-5} \text{ moles of chains were used}$$

$\therefore$ there was 226% excess of chains.

The above reaction yielded 23.7% comb polymer in the reaction mixture. Recovery of the reaction product was effected by precipitation in a 10-fold excess of methanol; the filtered product was recovered by freeze drying. Recovery was quantitative.

C. Characterization of a "Comb-Type" Polystyrene (V. R. Allen and T. G Fox)

The sample of polystyrene used for the "backbone" was of narrow chain length distribution, $M_w/M_n = 1.05$, with $M_v = 140{,}000$. Based on the chlorine analysis of the chloromethylated sample, the backbone was computed to contain, on the average, 3.6 reactive sites, i.e., one $-CH_2Cl$ group per 400 repeating units in the chain.

The coupling reaction had been carried out in an approximate four-fold excess of active chains (see above); hence it was necessary to separate the coupled "comb-type" polymer from the unreacted (linear) side-chain precursor. The branched species were separated by fractionation from a 0.4% solution in benzene at 30°C with methanol as the precipitant. From data obtained in previous studies on linear polymers, the precipitant concentrations were predetermined to give three fractions of (a) $M_{linear} > 220{,}000$, (b) $M_{linear} > 180{,}000$, and (c) $M_{linear} > 140{,}000$. The remaining polymer was assumed to be uncoupled linear branch precursor, $M_v = 35{,}000$, and was not recovered from solution.

The combined fractions of coupled material recovered was 23.7% of the reaction product, in good agreement with the stoichiometric ratio of 0.23 moles of chloromethyl groups per mole of branch precursor. The ultracentrifugal sedimentation velocity patterns indicated, at least qualitatively, that the separation was clean, i.e., the coupled product, fractions A and B combined, did not contain an appreciable amount of low molecular weight polymer (unreacted linear precursors).

The weight average molecular weight of the coupled product was found to be 242,000 from light scattering. From this, the average number of branch sites per backbone, $\bar{p}_n$, was calculated from

$$\bar{p}_n = \frac{M_{w(\text{branched})} - M_{w(\text{backbone})}}{M_{w(\text{branch precursor})}} = 2.9 \qquad (1)$$

in good agreement with the value of $\bar{p}_n = 3.6$ obtained from chlorine analysis.

Previously it was reported that the theta point intrinsic viscosity of "star-type" branched polystyrene obeyed the relation of Zimm[1]

$$[\eta]_\theta = k(Mg)^{1/2} \qquad (2)$$

where $g = [s^2_{o(\text{branched})}/s^2_{o(\text{linear})}]_M$. The branching coefficient, g, for this comb-type polymer was computed from the theoretical expression of Orofino.[2]

$$g = \frac{Z(xZ+3\bar{p}_n y^2) + \bar{p}_n y^3(1-3\bar{p}_n/x)}{Z^3 + 3Z\bar{p}_n y^2(1-\bar{p}_n/x) + (\bar{p}_n y^3/x^2)(x-\bar{p}_n)(x-2\bar{p}_n)} = 0.65 \qquad (3)$$

where Z, x, and y are the degree of polymerization of the branched molecule, the backbone, and the branch precursor, respectively. Thus, from equations 2 and 3, using $K = 8.5 \times 10^{-4}$,

$$[\eta]_{\theta,\text{calculated}} = 0.334; \qquad [\eta]_{\theta,\text{observed}} = 0.340$$

These results demonstrate that a "comb-type" branched polystyrene of specified structure can be prepared by the procedure described in the previous sections. The applicability of equation 2 to "comb-type" branch molecules is indicated by these results but additional data are required, particularly for structures which are not as similar to the star-type structure, i.e., $\bar{p}_n > 3$ and $x/y > 4$.

References

1. B. H. Zimm, in Rheology, Vol. III, Chapter 1, F. R. Eirich, ed., Academic Press, New York, 1956; ___ and R. W. Kilb, J. Polymer Sci. 37, 19 (1959).

2. T. A. Orofino, Polymer 2, 295 (1961).

D. Melt Viscosity of a "Comb-Type" Branched Polystyrene (V. R. Allen and T. G Fox)

The isothermal viscosity-molecular weight relation for "star-type" branched polystyrene was reported (Technical Report No. 8) as

$$\eta_{217^\circ} = 4.5 \times 10^{-14}(M_g)^{3.4} \qquad 4 \times 10^4 < M_g < 2.5 \times 10^5 \quad (1)$$

for tri- and tetra-branch molecules. Assuming that the comb-type polymers obey the same relation, we may predict for the polymer described in the previous sections

$$\eta_{217^\circ} = 4.5 \times 10^{-14}(242{,}000 \times 0.65)^{3.4} = 22{,}000 \text{ poise}$$

The measured viscosity for this sample was $\eta_{217^\circ} = 29{,}000$, ca. 25% high. Although this discrepancy is quite large and certainly outside of the experimental error in the measurement of viscosity, it corresponds to only 7% error in molecular weight. Since the calculated and observed $[\eta]_\theta$'s were the same (previous section), it would be suspect that this discrepancy is attributable to the errors in the measurement of both molecular weight and melt viscosity. However, it may be that this difference is real and that equation 1 may not be a general expression applicable to all types of branch structures. Planned studies should yield valuable information concerning this particular point.

V. THE FORCED OSCILLATION TORSION PENDULUM

(M. H. Birnboim and H. Markovitz)

V. FORCED OSCILLATION TORSION PENDULUM

(M. H. Birnboim and H. Markovitz)

A forced oscillation torsion pendulum for obtaining the dynamic mechanical and creep properties of a large variety of solids and liquids over a wide time-temperature range has been constructed. Both the mechanical and electronic systems have been completed, and the testing, trouble-shooting, and calibrating of the past few months is continuing.

The following abstract concerning the phase and amplitude comparator part of the instrument was submitted to the American Physical Society Meeting in St. Louis.

> Phase Meter and Amplitude Comparator Extending to Ultralow Frequencies and Small Phase Angles. Meyer H. Birnboim
>
> An instrument has been developed to measure the relative amplitude and phase difference between 2 electrical sinusoidal signals in the range of 10^{-4} to π rad, over a frequency range from 10^{-5} - 10^{3} c.p.s. The signals control tunnel diodes that recycle through their critical point at a 1 x 10^{6}-c.p.s. rate; thereby, a stable triggering level, elimination of hysteresis, and integration over signal and diode noise are achieved. A logic circuit insures that the measured phase angle is independent of the relative amplitude of the 2 signals, of their mean voltages, and of inequality of triggering voltages. The logic eliminates the necessity of any auxiliary phase-delay network sometimes used for small angles. The relative amplitude of the signals is determined in terms of measured time intervals and the sine-wave equation. The instrument has applications in the measurement of viscoelastic and dielectric properties of high polymers.

VI. DIMENSIONS OF POLYMER CHAINS

(A. A. Blumberg)

VI. DIMENSIONS OF POLYMER CHAINS

(A. A. Blumberg)

During this report period the work has been exclusively with the mercuric chloride-poly(ethylene oxide) complex.

The diffraction pattern has been indexed. The unit cell is orthorhombic with a, b, c, dimensions 13.46, 17.11, and 11.59Å.

Assuming seven ethylene oxide units for each mercuric chloride, the calculated density is 1.93 gm/cc. Experimentally, the density of several oriented complex fibers lies in the range 2.08-2.12 gm/cc. Upon long exposure, the x-ray diffraction diagram also shows the features of a mercurous chloride powder pattern.

Diffusion and complex formation studies are in progress.

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University of Pittsburgh
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Pittsburgh 13, Pennsylvania (1)

Dr. P. A. Miller
ONR Branch Office
1000 Geary Street
San Francisco 9, California (1)

Mr. J. P. Reese
Aerospace Industries Association
610 Shoreham Building
Washington 5, D. C. (10)

Dr. W. N. Lipscomb
School of Chemistry
Harvard University
Cambridge 38, Massachusetts (1)

Dr. G. Barth-Wehrenalp
Pennsalt Chemicals Corporation
P. O. Box 4388
Philadelphia 18, Pennsylvania (2)

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Department of Chemistry
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Propellants Synthesis Section
Reaction Motors Division
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Chicago 37, Illinois (1)

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Department of Chemistry
University of Illinois
Urbana, Illinois (1)

Dr. C. Haber
Naval Ordnance Laboratory
Corona, California (1)

Dr. J. H. Faull, Jr.
ONR Branch Office
495 Summer Street
Boston 10, Massachusetts (1)

Dr. J. E. Leffler
Department of Chemistry
Florida State University
Tallahassee, Florida (1)

Dr. A. B. Burg
Department of Chemistry
University of Southern California
Los Angeles 7, California

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Institute of Rubber Research
University of Akron
Akron, Ohio (1)

Monsanto Chemical Company
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Boston 49, Massachusetts
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Chemistry Research Department
Non-Metallic Materials Division Rm 4-171
Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland (1)

Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland
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Plastics Technical Evaluation Center
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Research Center
Painesville, Ohio (1)

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Union Carbide Research Institute
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Tarrytown, New York (1)

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Union Carbide Chemicals Company
Technical Center
South Charleston, West Virginia (1)

Dr. T. P. Wilson
Union Carbide Olefines Company
P. O. Box 8004
South Charleston, West Virginia (1)

Dr. Robert S. Marvin
Rheology Section
National Bureau of Standards
Washington 25, D. C. (1)

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Dr. B. Wunderlich
Department of Chemistry
Cornell University
Ithaca, New York (1)

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Department of Chemistry
University of Arizona
Tucson, Arizona (1)

New York Naval Shipyard
Material Laboratory
ATTN: Mr. B. B. Simms
Brooklyn 1, New York (1)

Dr. Fred Gornick
Macromolecules Section
National Bureau of Standards
Washington 25, D. C. (1)