Communications to the Editor

Gas Phase Macroions

In considering how it might be possible to obtain gas phase intact ionized macromolecules for mass analysis in a macromass spectrometer, the idea occurred to one of us[1] to electrospray dilute solutions of macromolecules into air or other suitable gas at atmospheric pressure and to sample the air for macroions by means of a supersonic probe. By allowing a dilute polymer solution containing a volatile solvent to flow out of a tip of a hypodermic needle electrostatically charged to a negative voltage of about 10 kV, a spray of finely divided and electrically charged droplets is produced.[2] On evaporation of the solvent the charged droplets should become electrically unstable and break down into smaller drops,[3,4] provided that the charges remain on the drops. Depending on the polymer concentration and molecular weight, a sufficient dispersion of the drops into smaller drops should result in drops containing only one macromolecule per drop. Finally, on complete evaporation of the solvent from these drops, it was hoped[1] that gas phase macroions would result.

In this note we now give evidence for the production of macroions in the gas phase by the above suggested technique. Experimental details will be published later; the general arrangement consisted of the spray system, an evaporation chamber through which nitrogen gas flowed at atmospheric pressure to provide the necessary heat of evaporation and to carry off the solvent, two plates with circularly shaped apertures at variable distances downstream from the hypodermic needle and charged 3 and 1.4 kV negative, respectively, to help to focus the beam of charged particles, and finally at ground potential a supersonic nozzle and skimmer system of the type described theoretically by Kantrowitz and Grey[5] and first studied experimentally by Kistiakowsky and Slichter[6] with beams of NH_3 gas. In our experiments, the pressures were about 0.15 torr in the region between the nozzle and skimmer and 10^{-4} torr in the region beyond the skimmer. The jet velocity at the skimmer for these pressures was estimated to be about Mach 4. With a similar nozzle and skimmer system Becker and Henkes[7,8] were able to obtain nearly pure argon from a mixture of 80% H_2 and 20% Ar. It was hoped that the much heavier macromolecules would become similarly concentrated during the gas flow through our supersonic probe.

To distinguish the heavy macroions from solvent ions we have measured ion currents to a Faraday cage downstream from the skimmer with a repeller grid between, on which were imposed negative voltages up to 3 kV. From the calculations of Kantrowitz and Grey[5] the molecular velocity held by the greatest number of molecules at Mach 4 is 7×10^4 cm sec^{-1}; if polystyrene molecules of mass 411,000 and 51,000 had this velocity, the repeller voltage requirements to cut out currents due to these molecules assuming a unit charge would be 1200 and 150 V, respectively. In the case of the solvent molecules the voltages required would be only about 0.2 V.

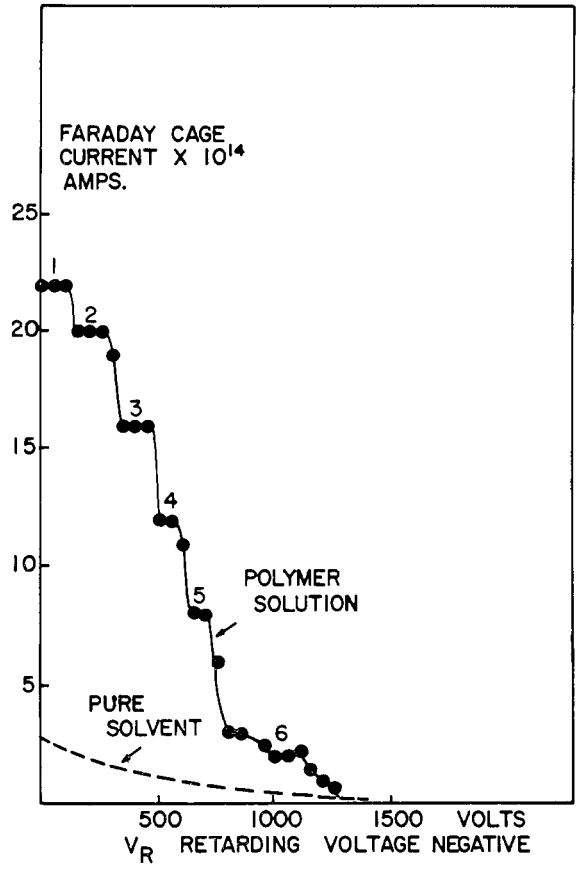

Figure 1. Current to the Faraday cage as a function of the repeller voltage: 0.005 wt % each of polystyrene of mol wt 411,000 and 51,000, respectively; solvent, 3 parts of benzene to 2 parts of acetone by volume; spacings, needle to first aperature 2 in., first aperture to second aperture 3 in., second aperature to nozzle 3 in.

Actually, it was found (Figure 1) that all current to the Faraday cage could be stopped by a repeller voltage of about 1500 V. In this case the solvent was a mixture of three parts of benzene by volume to two of acetone and the solute was 0.005 wt % each of polystyrene of mol wt 411,000 and 51,000. Probably the current both in the case of the pure solvent and polymer solution which persists to such high repeller voltages is due to a small number of droplets which had not completely evaporated.

The order of magnitude difference between the current to the Faraday cage with solvent only being sprayed in one case and the dilute polymer solution in the second indicates definitely, we believe, that gas phase macroions were produced by the electrospray–evaporation technique described above. Furthermore, the interesting breaks and plateaus in the current–voltage curve suggest that ions of different multiple charge as well as of the

(1) M. Dole, Preprints, *Intern. Symp. Macromol. Chem., Tokyo, Japan*, **6**, 132 (1966).
(2) For a discussion of the physics of electrostatic sprays, see R. L. Hines, *J. Appl. Phys.*, **37**, 2730 (1966).
(3) L. Rayleigh, *Phil. Mag.*, **14**, 184 (1882).
(4) J. W. Cahn, *Phys. Fluids*, **5**, 1963 (1962).
(5) A. Kantrowitz and J. Grey, *Rev. Sci. Instr.*, **22**, 328 (1951).
(6) G. B. Kistiakowsky and W. P. Slichter, *ibid.*, **22**, 333 (1951).
(7) E. W. Becker and W. Henkes, *Z. Phys.*, **146**, 320 (1956).
(8) See also R. Klingelhöfer and P. Lohse, *Phys. Fluids*, **7**, 379 (1964).

two different masses existed. For example, numbering the plateaus from 1 to 6 beginning at the top, the voltage of the break between plateaus 4 and 5, 620 V, is almost exactly twice that between plateaus 2 and 3, 317 V, etc. It must be pointed out, however, that this work is just beginning and we have not yet learned how to control the electrospray so as always to obtain plateaus of the type of Figure 1. Nevertheless, the plateaus have been obtained in a number of experiments and we believe them to be real. Incidentally, the existence of the plateaus demonstrates a high degree of velocity monochromatization[5] which should be especially significant in the case of macroions as a component of the gas stream. The possibility that some of the ions consisted of aggregates of macromolecules or of macromolecules with condensed solvent molecules cannot be excluded. Thus, the drop in current from plateau 1 to 2 might be due to repelling ions of mol wt 51,000 with a single unit charge (calculations indicate that this is about the correct repeller voltage) and the drop from 2 to 3 to repelling ions of a double aggregate of molecular weight twice 51,000 with a single unit charge. It is planned to build a time-of-flight mass spectrometer to measure mass-to-charge ratios and so to enable us to make a more quantitative study of the macroions produced by the electrospray technique.

Acknowledgment. This research was supported by a grant to Northwestern University by the National Institute of General Medical Sciencies, Grant No. GM13194. We are indebted to Dr. K. Katsuura for some early studies of our plans for the macromass spectrometer during his tenure of a Postdoctoral Fellowship at Northwestern University during the academic year 1963–1964. The work at Bendix was done under a subcontract with Northwestern University. We are much indebted to C. H. Tosswill, Head of the Advanced Instrumentation Department, Bendix Research Laboratories, for his helpful interest in and support of this research. Subsidiary aid from the Advanced Research Projects Agency through the Northwestern University Materials Research Center is also gratefully acknowledged.

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Received October 13, 1967

Mechanism of Ultraviolet Stabilization of Polymers

The weathering degradation of polymers in outdoor applications can often be attributed to photochemical reactions initiated by the absorption of light by a carbonyl group in the polymer. In the case of polyethylene, for example, such groups have seen shown to be formed by air oxidation during the molding or extrusion process.

To protect polymers from weathering degradation, it has become common practice to compound them with a uv stabilizer such as a substituted hydroxybenzophenone which absorbs most of the ultraviolet radiation and dissipates the energy in a harmless manner. Such a stabilizer behaves essentially as an ultraviolet screen. Recently, it has been suggested[1] that stabilization of polymers is also possible by a mechanism which involves a direct transfer of the electronic energy from the excited state of the polymer molecule to a suitable stabilizer molecule. We wish to report experimental evidence that such a process can indeed take place and may represent an important stabilizing mechanism for polymeric systems.

It has been shown by Hartley and Guillet[2] that ethylene–carbon monoxide copolymers which contain ketone groups in the main chain undergo the same photochemical reactions as simple aliphatic ketones and may be used as model systems for studying photodegradation. The main reactions are the Norrish type I (eq 1) and type II

$$\sim\!CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2\sim \longrightarrow \sim\!CH_2CH_2\overset{\overset{O}{\|}}{C}\cdot + \cdot CH_2CH_2\sim \quad \text{or } \sim\!CH_2CH_2\cdot + \cdot CH_2CH_2\sim + CO \qquad (1)$$

(eq 2). Both these processes break the chain and the

$$\sim\!CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2\sim \longrightarrow \sim\!CH_2COCH_3 + CH_2{=}CH\sim \qquad (2)$$

net effect can be determined by following the rate of change in the molecular weight of the polymer. In the present experiments the quantum yield for the degradation of the polymer was determined in solutions of decahydronaphthalene at 80° in the presence of varying amounts of 1,3-cyclooctadiene (COD). This compound has been shown to be an efficient acceptor of triplet excitation energy from acetophenone[3] which has a triplet energy similar to that of the aliphatic ketones.[4] The irradiations were carried out in a thermostated quartz cell using light of 3130 Å from a medium-pressure mercury arc, isolated by means of a Jena uv P.I.L. interference filter. The light absorbed was monitored by a photomultiplier which was calibrated by uranyl oxalate actinometry. The solutions were degassed by several freeze–thaw cycles under high vacuum and sealed under vacuum. The molecular weights were determined by single-point viscosity measurements in a viscometer sealed to the reaction cell. The limiting viscosity number $[\eta]$ was calculated from the logarithmic viscosity number using the value of k in the equation

$$\frac{\ln \eta_r}{c} = [\eta] - k[\eta]^2 c$$

determined in a separate set of experiments. The relation used for molecular weights was $[\eta] = 3.873 \times 10^{-4} \bar{M}_n^{0.738}$ as determined by Uberreiter, *et al.*[5] The

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(2) G. H. Hartley and J. E. Guillet, *Macromolecules*, in press.
(3) R. S. H. Liu, *J. Amer. Chem. Soc.*, **89**, 112 (1967).
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(5) K. Uberreiter, H-J. Orthman, and S. Sorge, *Makromol. Chem.*, **8**, 21 (1952).