Meetings

High Polymers

The ninth Canadian High Polymer Forum, held at the Guild Inn, Toronto, 26–28 October 1959, was attended by 142 polymer chemists from England, the United States, and Canada. The forum chairman was M. H. Jones (Ontario Research Foundation), and the session chairmen were S. Bywater (National Research Council), H. H. G. Jellinek (Essex College), M. Rinfret (Montreal), and G. Olah (Dow of Canada).

At the business meeting the following officers for the tenth forum were elected: chairman, L. A. McLeod (Polymer Corp.); program chairman, K. E. Russell (Queen's); secretary-treasurer, D. A. I. Goring (Pulp and Paper Research Institute).

At the forum banquet the guest speaker, C. H. Bamford of Courtaulds, Maidenhead, spoke on patterns in reactions and polymers. He said that detailed information is now available concerning transfer reactions of polymer radicals with a variety of substrates. For a hydrocarbon substrate such as ethylbenzene, the rate constants for the hydrogen abstraction process involving a series of polymer radicals are fairly accurately proportional to the rate constants for the corresponding reactions with toluene. In these reactions with hydrocarbon substrates, polar factors are very small. With ferric chloride, butyl mercaptan, or carbon tetrabromide as substrates, a logarithmic plot of rate constants for the transfer reaction against rate constants for the corresponding reaction with toluene gives a number of scattered points. The pattern of points is, however, very much the same in all three cases. With triethylamine as substrate, an "inverse" pattern is obtained. Patterns of the first type are obtained in additional reactions involving the same polymer radicals and a number of vinyl monomers.

The observed patterns can be interpreted in terms of polar effects, the rate constant depending considerably on the extent to which the substituent in the radical is electron-withdrawing or electron-releasing. From a quantitative treatment Bamford concluded that it is possible to express the rate constant for the transfer reaction of a radical with a given substrate in terms of the rate constant for transfer with toluene and the Hammett σ constant for the radical. Predictions based on this quantitative theory are in excellent agreement with experimental results.

The main sessions began with a paper by J. K. N. Jones (Queen's) on problems in polysaccharide chemistry. In pointing out some of the difficulties involved in complete structural determinations of polysaccharides, Jones said that it is not always possible to decide whether traces of sugars occurring with the main hydrolysis products of polysaccharides were part of the original macromolecule. Degrees of branching can be readily obtained with the Haworth methylation technique, but frequently it is almost impossible to achieve 100 percent methylation of a polysaccharide. The major problem in this field is to imitate the action of enzymes on sugars and sugar derivatives to produce polymers similar to those found in plants and animals.

B. L. Funt and F. D. Williams (Manitoba), in their paper on retardation and inhibition of methyl methacrylate polymerization, described investigations of the effect of benzoquinone on methyl methacrylate polymerization in which they used C^{14} -tagged quinone and initiator. They observed a transition from retardation to inhibition at a critical concentration of benzoquinone. The session closed with a short color film on polymer interactions, made available by W. F. Busse (Du Pont Co.).

The first in a series of papers on polymer degradation was presented by H. A. Kraessig and J. Neal (Industrial Cellulose Research), who discussed the degradation of cellulose by megavolt electrons. They showed that at low dose rates the number of chemical bonds broken is a linear function of the dose, and that the sensitive volume corresponding to cleavage of a single bond is close to the volume of a monomer unit. Experiments on wet cellulose indicate that water has a considerable protective action. H. H. G. Jellinek (Essex College) and W. A. Schlueter described work performed at the University of Cincinnati on the photodegradation of polyacrylonitrile in solution, in which light of wavelength 2537 A was used. The rate of degradation *in vacuo* is proportional to the light intensity, and the number of broken bonds is less than 10^{-8} per quantum absorbed. W. C. Schneider (American Cyanamid Co.) spoke on the thermal stability of polyacrylonitrile. He observed that at 240°C in the absence of oxygen the polymer breaks down very rapidly, giving a complex mixture of products, but that in the presence of oxygen a more controlled reaction gives water, ammonia, and hydrogen cyanide as the only volatile products. J. R. Schaefgen (Du Pont) presented a paper on the thermal degradation of poly-*p*-xylylene. The rate of degradation was measured in a chlorinated aromatic solvent in the range 285 to 321°C. Degradation is random, and the activation energy is 58 kcal/mole. Anthracene decreased the rate of degradation, but common transfer agents are inactive.

R. J. Orr (Polymer Corp.) presented a paper on thermochemical aspects of free radical butadiene-styrene copolymerization. A treatment of the thermodynamics of copolymerization has been devised which can be applied to high-conversion material. The sum of the entropy changes for the two heteropolymerization steps was found to be about 50 entropy units per mole, on the assumption that the residual entropy contributed by the glassy state is zero.

C. Booth and L. R. Beason (Shell Chemical Co.) gave a paper on statistical treatment of polymer fractionation data. A styrene-butadiene copolymer was fractionated, and the fractionation data were subjected to a simple binomial analysis. The resulting molecular weight distribution was in good agreement with that calculated from the kinetics of the emulsion system. J. A. Manson, W. W. Graessley, and L. M. Hobbs (Air Reduction Co.) described the determination of the breadth of molecular weight distribution in polyethylene by an irradiation technique. Samples of high-pressure and low-pressure polyethylene were irradiated from a cobalt-60 source and were analyzed for soluble and gel fractions. From the results it is possible to calculate weight and number average molecular weights of the original polyethylene samples.

A. Rezanowich and D. A. I. Goring (Pulp and Paper Research Institute) have investigated the polyelectrolyte properties of a lignin sulfonate microgel. Their measurements of the polyelectrolyte expansion of fractions of sodium lignin sulfonate indicate a microgel structure for the macromolecule. They developed a theory on the assumption that the microgel structure has free charges only on the surface and showed that the theory agreed fairly well with experimental results.

D. J. Worsfold and S. Bywater (National Research Council) spoke on properties of poly-α-methylstyrene produced by anionic polymerization. They have made a thorough molecular-weight analysis of poly-α-methylstyrene samples produced with sodium naphthenide as catalyst. One important result is a determination of the intrinsic viscosity-molecular weight relationship for polymer samples of very sharp distribution.

M. Senez and H. Daoust (Montreal), in their paper on heat parameters for polyisobutylene solutions, compared heat parameters determined for the polyisobutylene-chlorobenzene system by calorimetry and by the viscosity method of Fox and Flory. The data fit the Fox and Flory treatment of viscosity data.

W. Heller and M. Nakagaki (Wayne State), in discussing the exact theory of the scanning method for determining particle sizes from light scattering, gave accurate calculations of the angular positions of maxima and minima for nonabsorbing spheres for the large relative refractive index of 1.20. The results for other relative refractive indices can now be calculated fairly readily.

T. Gillespie (Dow Chemical Co.) presented papers on the limited flocculation of a colloidal system by a water-soluble polymer and the rheology of a polystyrene latex thickened with methylcellulose. His results on the flocculation of styrene-butadiene latex by methylcellulose indicate that the stabilization of a hydrophobic colloid by a hydrophilic colloid is due to changes in the balance of the flocculation and deflocculation processes. Methylcellulose thickens a polystyrene latex by causing a reversible partial flocculation.

A. Novak and E. Whalley (National Research Council) presented data on the infrared spectrum of polyformaldehyde and showed that these data could be interpreted on the assumption of a helical model for the polymer.

E. H. Immergut, G. Kollmann, and A. Malatesta (Dunlop Research Centre) reported results on the cationic copolymerization of propylene and isoprene. They prepared soluble copolymers under carefully controlled conditions, using aluminum chloride as catalyst at −78°C (molecular weight range, 4000 to 10,000). Reactivity ratios for propylene and isoprene are approximately 0.23 and 0.5. M. H. Jones, U. Martius, and M. P. Thorne (Ontario Research Foundation) discussed the polymerization of 1-butene by metal alkyl-titanium halide catalysts. They reported the results of chemical and x-ray analyses of the complex catalysts produced by the interaction of aluminum triisobutyl or lithium *n*-butyl with titanium trichloride or tetrachloride. Kinetic results for the polymerization of butene-1 with aluminum triisobutyl-titanium trichloride were given; the products were of very high molecular weight (intrinsic viscosity between 5 and 6).

C. H. Bamford, in a paper on termination by primary radicals in vinyl polymerization, said that when the initiator concentration is high, a plot of rate of polymerization of styrene versus monomer concentration is curved. This can be quantitatively accounted for by assuming termination of some growing polymer radicals by primary radicals from the initiator. The velocity constant for primary radical termination is about 60 times that for mutual termination. The interaction of unlike radicals was discussed by C. Sivertz and Y. Ebisuzaki (Western Ontario) in a paper on the measurement of the cross-termination velocity constants for picrylhydrazyl and alkyl radicals. They studied the thermal decomposition of azobisisobutyronitrile at such low concentrations that the combination of free cyano-alkyl radicals competed with the reaction with diphenylpicrylhydrazyl. The relationship between the two velocity constants was derived.

L. E. Coleman and J. F. Bork (Lubrizol Corp.) spoke on the reactivity ratios of N-vinyl oxazolidone and N-vinyl pyrrolidone with vinyl monomers. N-vinyl oxazolidone copolymerizes well with vinyl chloride and vinyl acetate but not with styrene and methyl methacrylate; N-vinyl pyrrolidone is more reactive than N-vinyl oxazolidone. W. E. Walles, W. F. Tousignant, and T. Houtman (Dow Chemical) have studied poly-N-vinyl, 5-methyl, 2-oxazolidone, a new complexing polymer, of molecular weight 150,000. It is soluble in water below 40°C and insoluble at higher temperatures. This behavior is explained in terms of a change from a structure which presents largely hydrophilic groups to the solvent to one which is almost entirely hydrophobic.

R. J. Ceresa and F. H. Cotton (National College of Rubber Technology, London), in presenting a paper on the mechanicochemical modification of high polymers, said that cold mastication of elastomers in the presence of 0.1 percent aluminum isopropoxide eventually leads to gels; under similar conditions a mixture of polyvinyl acetate and polyethylene may give a fair yield of block copolymer.

R. J. Richardson (Atomic Energy of Canada) spoke on radiation grafting of high polymers. Nylon tenting fabric was irradiated with gamma rays in the presence of styrene to give polystyrene grafts largely on the surface of the nylon, with a resultant improvement in the weathering properties of the fabric. Irradiation of nylon and terylene in the presence of acrylonitrile and vinyl pyrrolidone gave a slight improvement in dyeing response.

J. R. Tichy (Maine Medical Center), in his paper on the polymerization of phosphorous pentachloride and urea, presented analytical data on the products of this complex polymerization. In the last paper presented, R. W. Lenz and W. K. Carrington (Dow Chemical) discussed the preparation of phenylene sulfide polymers by the Macallum polymerization. The reaction of *p*-dichlorbenzene with sulfur and sodium carbonate at 300° to 350°C to give a phenylene sulfide polymer of high molecular weight probably proceeds partly by a direct attack of sulfur diradicals on the dihalide and partly by attack of sodium sulfide formed by reaction of sulfur with sodium carbonate.

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Forthcoming Events

March

13–14. American Otological Soc., Miami Beach, Fla. (L. R. Boies, University Hospital, Minneapolis 14.)

14–16. American Railway Engineering Assoc., annual conv., Chicago, Ill. (N. D. Howard, AREA, 59 E. Van Buren St., Chicago 5.)

14–17. Positive Health of Older People, forum, Miami Beach, Fla. (A. Mallach, National Health Council, 1790 Broadway, New York 19.)

14–18. National Assoc. of Corrosion Engineers, 16th annual, Dallas, Tex. (W. A. Mapler, NACE, 18263 W. McNichols Rd., Detroit 19, Mich.)

15–16. American Broncho-Esophangological Assoc., Miami Beach, Fla. (F. J. Putney, 1712 Locust St., Philadelphia 3.)

15–21. Nondestructive Testing, 3rd intern. conf., Tokyo and Osaka, Japan. (S. Ishizaka, Scientific Attaché, Embassy of Japan, 2514 Massachusetts Ave., NW, Washington 8.)

16–18. Genetics Soc. of Canada, 5th annual, Vancouver, B.C. (Miss K. Cole, Dept. of Biology and Botany, Univ. of British Columbia, Vancouver 8.)

17. Congress for Pharmacists, 2nd annual, Jamaica, N.Y. (Congress for Pharmacists, Public Relations Office, St. John's Univ., Jamaica 32.)

17–19. American Radium Soc., conf., San Juan, Puerto Rico. (ARS, 635 East Union, Pasadena, Calif.)

17–19. Blood Platelets, intern. symp. (by invitation only), Detroit, Mich. (Miss S. A. Johnson, Henry Ford Hospital, Detroit 2.)

17–19. National Federation of Science Abstracting and Indexing Services, annual, Washington, D.C. (R. A. Jensen, 301 E. Capitol St., Washington 3.)

17–20. International Assoc. for Dental Research, Chicago, Ill. (D. Y. Burrill, Northwestern Univ. Dental School, 311 E. Chicago Ave., Chicago 11.)

18–19. American Laryngological Assoc., Miami Beach, Fla. (L. Richards, Massachusetts Institute of Technology, Cambridge.)

20–23. American Assoc. of Dental Schools, Chicago, Ill. (R. Sullen, 840 N. Lake Shore Drive, Chicago 11.)

20–26. American Cong. on Surveying and Mapping, Washington, D.C. (C. E. Palmer, American Soc. of Photogrammetry, 1515 Massachusetts Ave., NW, Washington 5.)

20–26. American Soc. of Photogrammetry, Washington, D.C. (C. E. Palmer, ASP, 1515 Massachusetts Ave., NW, Washington 5.)

21–24. American Acad. of General Practice, 12th annual, Philadelphia, Pa. (AAGP, Volker Blvd. at Brookside, Kansas City 12, Mo.)

21–24. Institute of Radio Engineers, natl. conv., New York, N.Y. (L. G. Cumming, IRE, 1 E. 79 St., New York 21.)

22–24. High-Polymer Physics, 20th, Detroit, Mich. (T. L. Smith, American Physical Soc., Stanford Research Inst., Menlo Park, Calif.)

23–25. National Council on Alcoholism, annual, New York, N.Y. (M. Ross, American Psychiatric Assoc., 1700 18 St., NW, Washington 9.)

23–25. Optical Spectrometric Measure-