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(Covering the Period from September 1, 1958 to August 31, 1967)

by

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I. INTRODUCTION

This Final Report briefly summarizes the main results of the research supported by the Office of Naval Research at Mellon Institute under Contract Nonr-2693(00) during the period September 1, 1958, to August 31, 1967.

These summaries are grouped into the following categories: synthesis of model polymers, crystalline polymers, rheological studies and chain conformation of polymeric chains.

The first category includes the synthesis of linear polystyrenes and poly(α -methylstyrene) with narrow distribution of molecular weights, of well-characterized branched and comb polystyrenes. [The techniques developed at Mellon Institute for the synthesis of such linear polystyrenes have been adopted by the Pressure Chemical Company of Pittsburgh for the production of standard polymers which are now widely used. Investigations employing these polymers have been reported in increasing numbers in research papers from laboratories throughout the world.] Other incidental results in organic chemistry have also been included.

The section on crystalline polymers includes morphological studies by optical microscopy and light scattering, crystallization kinetics, crystallographic investigations and viscoelastic studies. The investigated polymers include many nylons, poly-(tetramethyl-p-phenylene siloxane), polymethylene, poly(ethylene oxide)- HgCl_2 complex, polyamide-iodine complexes, and polyethylene. The instruments developed include a microbeam light-scattering apparatus, cryogenic torsion pendulum, phase angle and amplitude comparator, and a stabilizing circuit for photomultipliers based on optical feedback.

Under rheological studies we include: a representation for the zero shear viscosity of a wide group of polymers as a function of molecular weight, temperature, and concentration; a corresponding states relation for the temperature dependence of the viscosity of a wide class of materials; the viscoelastic behavior of polystyrene over a wide range of time, temperature, and molecular weights; an analysis of the free vibration method in linear viscoelasticity; viscoelastic, crystal growth rate, and calorimetric studies on 1:3:5 tri- α -naphthyl benzene, a low molecular weight glass-forming compound.

The final section deals with the theoretical calculation of chain dimensions on the basis of a more realistic model.

The appendix lists papers already published or in press.

II. SYNTHESIS OF MODEL POLYMERS

Linear Polymers of Narrow Molecular Weight Distribution
with Selected End Groups

Based on careful consideration of reaction mechanisms and experimental conditions, a number of anionic polymerization techniques were developed for the preparation of polymers of predictable molecular weights with narrow molecular weight distributions. Also characteristic of these investigations has been a thorough characterization of the polymeric products obtained.

In a two-step process, active impurities which would cause deactivation of propagation centers are first rendered inactive prior to anionic polymerization by the gradual addition of initiator (a mixture of butyl-lithium and telomeric styryl-lithium) at a temperature low enough to suppress chain growth. Then additional initiator appropriate for the desired molecular weight is added. The system is then warmed to the temperature where the polymerization is allowed to go to completion [F. Wenger and S.-P. S. Yen, *Makromol. Chem.* 43, 1 (1961)].

In another two-stage process, styrene was polymerized anionically in tetrahydrofuran. In the first stage the initiator (sodium naphthalene) is reacted completely with a small amount of monomer at a relatively high temperature. The rest of the monomer is then added by slow distillation at the polymerization temperature of -78°C . The agreement between measured molecular weights and the ones calculated for the polymerization mechanism is within 10% [F. Wenger, *Makromol. Chem.* 64, 151 (1963)].

Because of the large deleterious effect of impurities on the success of predictable, narrow distribution polymerizations, a theoretical study was made of the relationship of the weight-distribution functions in such systems to (1) the concentration of impurities, (2) the functionality (mono- or bi-) of the initiated species, (3) the kind of polymerization process (batch or continuous monomer addition), and (4) the ratio of rate constants for addition of monomer (k_p) and impurities (k_s) to growing chain ends. In general, the molecular weight distribution is broadened with increasing concentration of impurities. The optimum choice of initiator functionality and polymerization process required to minimize chain length heterogeneity has been determined as a function of the ratio k_p/k_s characteristic of a given system. In batch polymerizations, impurities give rise to unsatisfactory predictability of the molecular weight. [T. A. Orofino and F. Wenger, J. Chem. Phys. 35, 532 (1961) and F. Wenger, J. Polymer Sci. 60, 99 (1962)].

Anionic techniques were modified to allow the synthesis of low molecular weight ($< 10,000$) polystyrene with narrow distribution of chain lengths. The availability of these polymers, together with those of higher molecular weight previously prepared, made possible the formulation of the intrinsic viscosity-molecular weight relation over an exceedingly broad molecular weight range ($500 < M < 1.5 \times 10^6$) [T. Altares, Jr., D. P. Wyman, and V. R. Allen, J. Polymer Sci. A 2, 4533 (1964)]. Especially suitable as initiators for the preparation of low molecular weights, were dilithiocompounds prepared from the products of the reaction between butyllithium and trans-stilbene in benzene solvent

[D. P. Wyman and T. Altares, Jr., Makromol. Chemie 72, 68 (1964)].

The techniques used for the anionic preparation of polymer with narrow chain length distribution make it possible to terminate the polymerization in a way that allows the introduction of desired end groups. Termination by gaseous carbon dioxide was found to yield not only the corresponding polystyrene carboxylic acid but also significant amounts of di-polystyryl ketone and tri-polystyryl carbinol [D. P. Wyman, V. R. Allen, and T. Altares, Jr., J. Polymer Sci. A 2, 4545 (1964)].

On the basis of electrochemical considerations, sodium-biphenyl was successfully employed as an initiator in a one-step low temperature polymerization which yielded a polystyrene with a M_w/M_n rate of 1.03 [F. Wenger, Makromol. Chemie 36, 200 (1960) and 37, 153 (1960)].

To prepare narrow distribution poly-(α -methylstyrene), short chain dianions were formed in the reaction of sodium and monomer in tetrahydrofuran above the ceiling temperature. These were then used for the controlled purging of impurities and as initiator in the subsequent polymerization at -78°C . [F. Wenger, J. Am. Chem. Soc. 82, 4281 (1960) and Makromol. Chem. 37, 143 (1960)].

The Structure and Properties of Branched Polymers

An unequivocal evaluation of the influence of chain branching on the bulk and solution properties of amorphous polymers necessitates studies on a series of well-defined branched polymers varying systematically in structure and molecular weight. As part of an effort to provide a basis for the selection of appropriate materials, theoretical studies

were completed on two types of branched polymers: comb molecules, defined as linear backbone chains to which linear branches are attached by one end at various segments along the main chain; and cruciform molecules, consisting of a number of linear chains connected by one end at a common junction. It was found that the weight-to-number average chain length ratio of comb molecules depends primarily upon the value of the corresponding ratio for the constituent backbone chains. To a lesser extent, branched molecule heterogeneity depends also upon the heterogeneity of the side chains and the average number of these attached. The effects of branching on molecular dimensions should be observable for a large variety of comb and cruciform structures. Heterogeneity in the number of side chains attached, a structural variable difficult to eliminate in the synthesis of these materials, is shown to be of minor consequence in the case of some architectural forms whose molecular dimensions vary significantly with other, more easily controlled, structural parameters. [T. A. Orofino, *Polymer* 2, 295 and 305 (1961)]

Methods of synthesizing well-characterized branched polymers of both the star and comb type were devised and tested. In the former case, polymers with p branches of known uniform length are attached to a common multifunctional center. In the tetrachain-star ($p = 4$) this was achieved by coupling anionically produced low molecular weight polystyrenes of narrow molecular weight distribution to 1,2,4,5-tetra(chloromethyl)benzene. In the comb type, the synthesis is aimed at obtaining a very narrow distribution of backbone lengths and of side chain lengths with the branches attached at random to the backbone.

The backbone was prepared by very low level chloromethylation with very mild conditions of various narrow distribution high molecular weight polystyrenes which were then reacted with the anionically produced polymers needed to give the desired length of side chain. [T. Altares, Jr., D. P. Wyman, V. R. Allen, and K. Meyersen, J. Polymer Sci. A 3, 4131 (1965)].

(In related work not supported by ONR, a tetrafunctional star polystyrene ($M_w/M_n = 1.05$) was prepared by coupling polystyrylpotassium with 1,2,4,5-(tetrachloromethyl)benzene. The narrow distribution of molecular weights was attributed to the use of a novel initiator, α -phenylethylpotassium rather than a lithium compound. This organopotassium compound was chosen as the initiator because its character is more saltlike and therefore would greatly decrease the likelihood of the complicating side reactions which occur with the previously employed organolithium initiator. [S.-P. S. Yen, Makromol. Chem. 81, 152 (1965)])

Other Organic Reactions

Two forms of symmetrical tetraphenylbutane had been known to exist for some time. Evidence was adduced to show which form was meso and which dl [D. P. Wyman, J. Org. Chem. 27, 3712 (1962)].

A study was conducted on the use of phosphorous pentachloride as a chlorinating agent for a variety of alkylated aromatic and aliphatic hydrocarbons in either a thermal or catalyzed (benzoyl peroxide) reaction [D. P. Wyman, J. Y. C. Wang, and W. R. Freeman, J. Org. Chem. 28, 3173 (1963)].

III. CRYSTALLINE POLYMERS

An intensive study was made of the crystallization kinetics and morphology of poly-(tetramethyl-p-phenylene siloxane) a polymer which has approximately the same melting point as polyethylene but which can be readily supercooled to the glass without crystallization. Spherulite growth rates have been measured over a wide molecular weight range (monomer to 1.4×10^6) for fractions, mixtures of fractions, and unfractionated samples over the temperature range $20^\circ - 130^\circ\text{C}$. Rates are markedly dependent on molecular weight as well as molecular weight distribution, but the temperature at the maximum rate of crystallization is unaffected by these variables. For fractions of molecular weight greater than 100,000, however, the spherulitic growth rate is found to be independent of molecular size whereas the viscosity is a sensitive function of chain length. Thus the growth rate is not, as is frequently assumed, simply a function of the macroscopic viscosity. On the basis of current spherulitic models and the growth rate data, the crystallite surface free energy perpendicular to the molecular chain direction was found to increase with chain length and reach a "saturation" level at a molecular weight about 100,000. Molecular weight plays a secondary role in spherulitic morphology, especially at the higher crystallization temperatures. [J. H. Magill, J. Appl. Phys. 35, 3249 (1964) and J. Polymer Sci. A-2, 5, 89 (1967).]

An extensive series of studies was made on the morphology of polyamides. Each of the polymers in this group can occur in many spherulitic forms depending on the crystallization temperature. Different

morphologies within a given spherulite as well as different types of spherulites can co-exist together at a given temperature. Crystallization from the melt at temperatures not too far below the polymer melting point can yield crystal platelets exhibiting properties similar to single crystals. For a number of nylons (56, 96, 6, 66, 210, 610, 106, 1010), the conditions under which various of the morphologies form were determined. The temperature dependence of spherulite growth rate was measured for several of the nylons and interpreted in terms of current theories of crystallization. [J. H. Magill, J. Polymer Sci. A 3, 1195 (1965); Polymer 6, 367 (1965); J. Polymer Sci. A-2, 4, 243 (1966).] Similar studies were performed as d,l- and l-poly(propylene oxide) [J. H. Magill, Makromol. Chem. 86, 283 (1965)].

When a high molecular weight (10^5 to 10^6) linear polymethylene is prepared from diazomethane at dry ice temperatures, it crystallizes in the rarely found triclinic form. At temperatures above -25°C it transforms irreversibly to the more common orthorhombic form. For this low crystallinity ($\sim 50\%$) polymer, a glass temperature of -30°C was found from linear expansion measurements [J. H. Magill, S. S. Pollack, and D. P. Wyman, J. Polymer Sci. A 3, 3781 (1965)].

The interaction of polyamides with iodine in iodine-potassium iodide solution was studied by infra-red spectroscopy. On the basis of data on 31 polyamides, it was shown that the changes in structure which occur on sorption usually conform to a pattern determined by the type of polyamide, i.e. "even-even", "odd-odd", etc. [I. Matsubara and J. H. Magill, Polymer 7, 199 (1966)].

During a crystallographic study on poly(ethylene-oxide), a complex [empirical formula $(\text{CH}_2\text{CH}_2\text{O})_4 \cdot \text{HgCl}_2$] was formed between mercuric chloride and the oriented polymer. In spite of a major change in the unit cell dimensions, the X-ray investigation showed that the fiber orientation is maintained [A. A. Blumberg, S. S. Pollack, C. A. J. Hoeve, J. Polymer Sci. A₂, 2499 (1964)].

As a method of characterizing sub-spherulitic morphology, the light scattering patterns of a number of crystalline polymers were examined. The materials included various nylons, polyethylene oxide, polyethylene, and poly(tetramethyl-p-silphenylene siloxane). This technique may be extended to serve as a method for following local motion during a macroscopic deformation [G. C. Berry, J. H. Magill, and M. H. Birnboim, ONR Technical Report No. 14]. In the instrument used for this technique, a laser beam is employed as the light source and the scattering takes place from a known region in the sample [M. H. Birnboim, J. H. Magill, and G. C. Berry, ONR Technical Report No. 13 and Proceedings of the Interdisciplinary Conference on Electromagnetic Scattering, Amherst, 1965, Pergamon Press, in press].

Viscoelastic studies have been made on a polyethylene fraction (molecular weight 3.09×10^5) which had been crystallized at 131°C over a period of two weeks. By low angle X-ray scattering, a spacing of 926 Å was found. The dynamic elasticity and loss were determined over appreciable frequency and temperature ranges. In addition to the data on the α -(high temperature) loss region, these studies made available a more detailed set of data over the region of the γ -(low temperature)

loss region than heretofore reported for a crystalline polymer. The magnitude of the frequency dispersion in the γ region is very temperature dependent in contrast to the almost temperature-independent magnitude of the α -region. Thus the γ -loss region cannot be due to a single type of mechanism with a simple temperature dependence. This result emphasizes again the necessity of covering broad frequency as well as temperature ranges in viscoelastic measurements. It was also noted that, in some regions of frequency and temperature, non-linear effects occur at amplitudes of strain much lower than previously suspected [M. H. Birnboim and J. S. Burke, ONR Technical Report No. 18].

The above results were obtained with an instrument system designed and built at Mellon Institute. The system consists of a basic processing unit and a specific apparatus, currently the cryogenic torsion pendulum unit. The former, which exploits the instrumental capabilities of a small computer, can automatically determine phase and amplitude from direct current to 500 kHz with high accuracy and noise rejection, measure temperature from 4 to 500°K, generate sinusoidal and other waveforms from 30 to 10^3 Hz, set a frequency synthesizer, provide the experimenter with oscilloscope and other displays as a basis for instant judgment of each measured point, and enormously reduce data handling and processing. The torsion pendulum unit includes the sample, force and response transducers, thermometers, and cryogenic jacket. This system provides the experimenter with a new ability to see, to judge, and to control the details of a measurement [M. H. Birnboim, J. S. Burke, and R. L. Anderson, Instr. Control Systems, in press, and ONR Technical Report No. 17].

Preliminary data on the same sample of polyethylene at a single frequency over a wide temperature range had been obtained on another instrument, a self-excited resonance apparatus, capable of determining the modulus and loss from 4°K to 400°K. Modulus changes could be measured to 1 part in 10^7 [M. H. Birnboim and P. H. Thornton, Bull. Am. Phys. Soc. II, 10, 312 (1965) and ONR Technical Report No. 13]. Data were obtained on single crystals of Cu-Ge and Ag-Zn alloys. Some samples exhibit unusual history-dependent sharp loss peaks of width less than 1°K [M. H. Birnboim and P. H. Thornton, ONR Technical Report No. 13].

As a part of an earlier form of the apparatus, an instrument was developed which could measure the ratio of amplitude of two sine waves and the phase angle between them down to the range of very low frequencies and small phase angles [M. H. Birnboim, Bull. Am. Phys. Soc. II, 8, 270 (1963) and U. S. Patent No. 3,286,176, November 15, 1966, and ONR Technical Report Nos. 7 and 8]. A method was also found for stabilizing photomultipliers by using optical feedback. This technique eliminates difficulties which arise due to the long-time drifting gain exhibited by photomultiplier tubes [M. H. Birnboim, ONR Technical Report No. 13].

IV. RHEOLOGICAL STUDIES

A convenient representation has been found for the dependence of the zero shear viscosity, η , of high polymers on molecular weight, temperature and concentration:

$$\eta = F(X)\zeta(\rho)$$

where

$$X = Z(\langle s^2 \rangle_0/M)\phi_2/v_2$$

and

$$F(X) = (N_0/6)X_c(X/X_c)^a$$

with

$$a = 3.4 \quad \text{for} \quad X > X_c$$

$$a = 1.0 \quad \text{for} \quad X < X_c.$$

Here Z is the chain length, $\langle s^2 \rangle_0$ is the unperturbed radius of gyration, ϕ_2 is the volume fraction of polymer, v_2 is the specific volume of the polymer, and ζ is the density. The above relation holds to a good approximation independent of the degree of branching, and for a wide range of polymers. The value of X_c is approximately the same for all polymers [T. G Fox and V. R. Allen, *J. Chem. Phys.* 41, 344 (1964); T. G Fox, *J.*

Polymer Sci. C 9, 35 (1965)]. A critical listing of values of Z_c and discussion of the various methods for estimating Z_c was published.

[H. Markovitz, T. G. Fox, and J. D. Ferry, J. Phys. Chem. 66, 1567 (1962)].

The whole area was reviewed in a recently completed article [G. C. Berry and T. G. Fox, Advances in Polymer Science, in press].

If viscosity data for a wide variety of materials is plotted as a function of the reduced temperature parameter T_m/T (T_m is the melting point), the data for chemically similar substances fall together. This corresponding-states relation appears to be more useful than many others which have been proposed [R. J. Greet and J. H. Magill, J. Phys. Chem. 71, 1746 (1967)].

The viscoelastic behavior of a variety of polystyrenes was determined over wide ranges of time and temperature by means of the Plazek magnetic bearing torsional creep apparatus. The wide time range (almost 10^5 logarithmic decades) over which data were obtained permitted the conclusion that the simple time-temperature equivalence (usually assumed to be valid for amorphous polymers) does not hold for these materials. The flow part of the deformation has a different temperature dependence from the recoverable part [D. J. Plazek, J. Phys. Chem. 69, 3480 (1965)]. Data obtained over a more limited part of the time scale can readily lead to fallacious temperature reduction and thus to erroneous extrapolated values of the viscosity [D. J. Plazek, J. Polymer Sci. A-2, in press].

The molecular weight dependence of the viscoelastic behavior was determined in a creep-recovery study of a set of polystyrenes with

narrow molecular weight distribution. The molecular weight ranged from 3,400 to 800,000. Particularly surprising results were obtained on the samples with molecular weight less than 20,000. In contrast to the slight temperature dependence found for polystyrenes of higher molecular weight, the steady state recoverable compliance J_e of these samples is very temperature dependent. For a molecular weight of 3400, this temperature dependence is enormous; J_e increases thirty-fold between 70 and 100°C. Perhaps even more significant is the fact that, near the glass temperature of this low molecular weight polymer, the creep behavior loses its macromolecular character and approaches that observed for nonpolymeric materials such as 1,3,5 tri- α -naphthylbenzene or glucose [D. J. Plazek and V. M. O'Rourke, ONR Technical Report No. 18].

In one of the most widely used methods for determining the dynamic mechanical properties of viscoelastic materials, a mechanical system which includes the sample is set in motion by an impulse. From the period of the resulting oscillation and the rate of damping, the dynamic elasticity and loss are usually calculated on the basis of a theory which is, at best, only approximate. On the basis of the theory of infinitesimal linear viscoelasticity, an exact analysis of this experiment was carried out [H. Markovitz, J. Appl. Phys. 34, 21 (1963)].

To test some of the theories and generalizations frequently used in various branches of polymer physics, a number of extensive studies have been made on a low molecular weight material which could be investigated over wider ranges of parameters than polymers could have been. This fruitful investigation was performed on the glass-forming compound,

1:3:5 tri- α -naphthyl benzene (TONB).

The shear viscoelastic behavior was determined over a 10^4 to 10^5 range of the time scale by means of a torsional creep apparatus designed and built by Dr. D. J. Plazek at Mellon Institute. The temperature range extended from 50° above to 20° below the glass transition temperature, a range over which the viscosity varied by a factor of 10^{14} . In contrast to the narrow spectra reported for other liquids of similar molecular weight, the retardation spectrum of TONB extends over nine logarithmic decades of time. Thus a high molecular weight is not a necessary prerequisite for a broad relaxation spectra. By assuming that the occupied volume is independent of temperature, free-volume theory has been successfully adapted to describe the temperature dependence of the viscoelastic behavior over the entire temperature range covered by the data [D. J. Plazek and J. H. Magill, *J. Chem. Phys.* 45, 3038 (1966)].

The kinetics of crystallization of TONB was measured from 69°C (25° above T_g) almost to the melting point (199°C), a temperature range over which the growth rate varies by a factor of more than 10^5 . Contrary to the assumption frequently made in theories of crystallization, the mass transport contribution to crystal growth was experimentally found to have a different temperature dependence than does the viscous flow [J. H. Magill and D. J. Plazek, *Nature* 209, 70 (1966) and *J. Chem. Phys.* 46, 3757 (1967)].

From calorimetric measurements, the specific heat of TONB was determined from 200°K to 560°K in the glassy, liquid, and crystalline states. These data, coupled with the extensive viscosity data mentioned

above, allowed a comparison to be made between the Adam-Gibbs and free volume theories of the temperature dependence of the viscosity. The former appears to represent these data over a somewhat more extended temperature range than the latter [J. H. Magill, submitted to J. Chem. Phys.].

V. CHAIN CONFORMATIONS OF POLYMERIC CHAINS

In a more realistic model of actual polymer chains, the calculation of chain dimensions includes the effect of interactions between substituents attached to neighboring chain atoms on restricted rotation about chain bonds. The theoretical work of Volkenstein and Lifson was extended to include more general types of chains. The mean-square end-to-end distances of the polyisobutylene chain [C. A. J. Hoeve, *J. Chem. Phys.* 32, 888 (1960)] and of the polyethylene chain [C. A. J. Hoeve 35, 1266 (1961)] have been calculated in reasonable agreement with values deduced from viscosity data.

APPENDIX

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Chain Conformations of Polymeric Chains

"Unperturbed Chain Dimensions of Polymer Chains," C. A. J. Hoeve, J. Chem. Phys. 32, 888 (1960)

"Unperturbed Mean Square End-to-End Distance of Polyethylene," C. A. J. Hoeve, J. Chem. Phys. 35, 1266 (1961)

Unclassified

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polystyrene, poly(α -methyl styrene), polymethylene, polyethylene, polyethylene oxide, nylon, polyamide, polyisobutylene. Branched polymers Light scattering, viscosity, viscoelasticity, creep, dynamic mechanical properties, torsion pendulum, photomultipliers (stabilization of), rheology, free volume, 1:3:5 tri- α -naphthylbenzene, anionic polymerization, crystallization rate.						

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