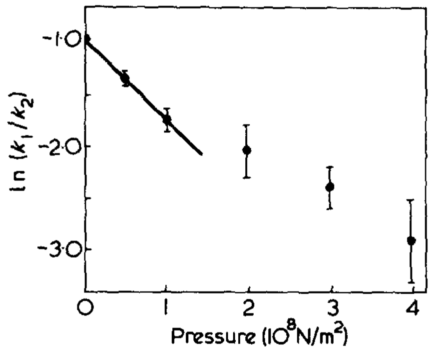

Figure 2 Plot of $\ln(k_1/k_2)$ vs. pressure for polymerization of styrene in toluene at 60°C; k_1/k_2 in dm^3/mol

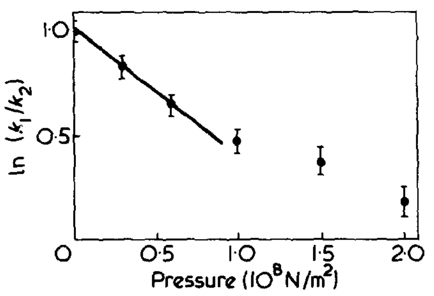

Figure 3 As for *Figure 2*, but with methyl methacrylate as monomer

Neuman[9] has pointed out that, although observed values of $\Delta V^{\ddagger}$ for homolytic scission reactions range from about +1 to +13 cm^3/mol, the true value for the actual scission process is +4 to +5 cm^3/mol; the lower values can be attributed to solvation effects where the transition state is polar and the larger values arise in systems where the observed rates are complicated by cage effects and there are contributions to $\Delta V^{\ddagger}$ from recombination and separative diffusion terms. If $\Delta V_1^{\ddagger}$ (for dissociation of $C_6H_5.CO.O.$) is taken as 4 cm^3/mol then the present results lead to values of -17 ± 3 and -11 ± 2 cm^3/mol for $\Delta V_2^{\ddagger}$ for additions of the radical to styrene and methyl methacrylate respectively. $\Delta V^{\ddagger}$ for the growth reaction in the radical polymerization of a vinyl monomer is thought not to be very sensitive to the nature of the monomer; values of about -18 and about -19 cm^3/mol have been given for styrene[10] and methyl methacrylate[11] respectively. The values of $\Delta V_2^{\ddagger}$ suggested now for addition of the benzoyloxy radical to monomers are generally similar to those found for the growth reactions in the polymerizations. It is known[4] that polar effects are important in the reactions of the benzoyloxy radical and this fact may be significant in connections with values of $\Delta V^{\ddagger}$ for reactions involving the radical; this possibility is being tested by examination of effects of the nature of the diluent upon values of $(\Delta V_1^{\ddagger}-\Delta V_2^{\ddagger})$.

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Correlations in the molecular weight distribution of polymers

It is a well-known fact that the molecular weight distribution (*MWD*) has a preponderant influence on the mechanical and rheological properties of polymers.

Widely used parameters to characterize the *MWD* are $\bar{M}_w$ and $Q = \bar{M}_w/\bar{M}_n$, i.e. the ratio between the weight-average and the number-average molecular weights. It has been shown that the influence of the shear rate on the apparent viscosity of a polymer melt or concentrated solution at a given $\bar{M}_w$ is very much dependent on the value of Q[1].

An important question is whether the parameter Q gives a sufficient description of the *MWD*, in other words, whether there exists a sufficiently universal relationship between the ratios $\bar{M}_w/\bar{M}_n, \bar{M}_z/\bar{M}_w, \bar{M}_{z+1}/\bar{M}_z$ etc. If this question can be answered in the affirmative, dimensionless η–$\dot{\gamma}$ relationships (master curves) may be reliable; if not, one can hardly expect a universal set of η–$\dot{\gamma}$ master curves even for one single polymer.

Theoretical *MWD*s of the Schulz–Flory type give a partial answer only, viz. for those polymers whose mechanism of formation is rather clear-cut and leads to Q values between 1 and 2. In practice, however, most polymers (unblended!) show Q values between 1.05 and 20 or even higher[1].

Calculations by Graessley[2] on the influence of molecular weight distributions on the η–$\dot{\gamma}$ relationship start from an arbitrary *MWD*. Using his formulae, Cote and Shida[3] demonstrated that parameter Q is insufficient to describe the effect, since blends with identical Q values but different *MWD*s were calculated to show a very

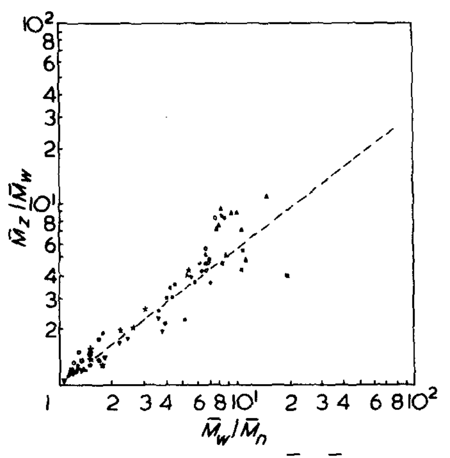

Figure 1 Relation between $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$, literature data. PE: ●, Mendelson *et al.* (ref 4); □, Mills (ref 5); ■, Saeda *et al.* (ref 6); △, Shah and Darby (ref 7); ▲, Wales (ref 8). PS: ▽, Cotton *et al.* (ref 9); ▼, Chee and Rudin (ref 10); ◇, Mills (ref 5). *PP*: ◆, Thomas (ref 11). PMMA: ⊕, Mills (ref 5). PDMS: ○, Mills (ref 5). BR: ☆, Dunlop and Williams (ref 13)

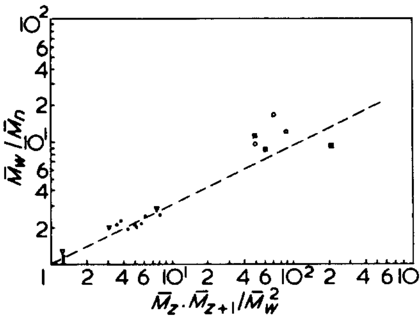

Figure 2 Relation between $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z\bar{M}_{z+1}/\bar{M}_w^2$, literature data. PE: ○, Graessley and Segal (ref 2); ■, Shah and Darby (ref 7). PS: ▽, Graessley and Segal (ref 2). PVC: ●, Collins and Metzger (ref 12).

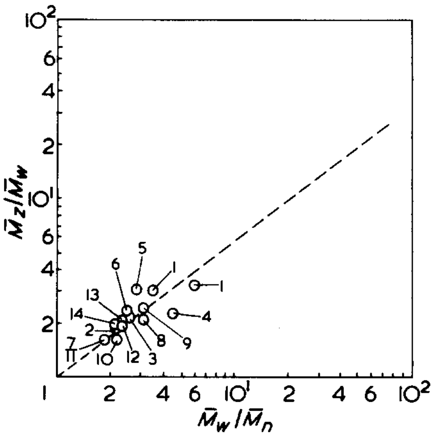

Figure 3 Relation between $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$, experimental results. For meaning of numbers, see *Table 1*

different rheological behaviour. The *MWDs* used by Cote and Shida, however, were artificial distributions markedly deviating from *natural* distributions. Therefore, it has not been proved that the parameter Q is insufficient to describe the behaviour of the polymers with a natural distribution.

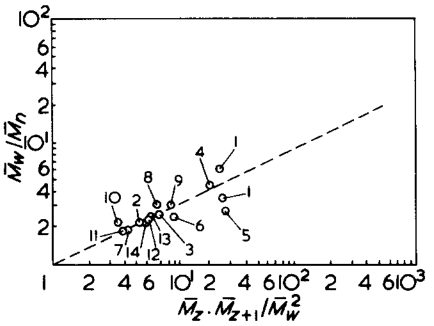

Figure 4 Relation between $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z\bar{M}_{z+1}/\bar{M}_w^2$, experimental results. For meaning of numbers, see *Table 1*

The only way to solve our basic question seems to be an assessment of reliable experimental data. Especially since gel permeation chromatography (g.p.c.) became available, we can rely much more than before on the results of experimental distribution curves.

From the literature we gathered the most important sets of data on the different molecular weight ratios. They are shown in *Figures 1* and *2*.

Our own laboratories provided data for a variety of polymers. These data are reproduced in *Figures 3* and *4*.

All available data indicate the following approximate relationships:

$$\frac{\bar{M}_w}{\bar{M}_n} = Q$$

$$\frac{\bar{M}_z}{\bar{M}_w} \approx Q^{0.75} \qquad \frac{\bar{M}_z}{\bar{M}_n} \approx Q^{1.75}$$

$$\frac{\bar{M}_{z+1}}{\bar{M}_z} \approx Q^{0.56} \qquad \frac{\bar{M}_{z+1}}{\bar{M}_n} \approx Q^{2.31}$$

$$\frac{\bar{M}_z\bar{M}_{z+1}}{\bar{M}_w^2} \approx Q^{2.06} \qquad \frac{\bar{M}_z\bar{M}_{z+1}}{\bar{M}_n^2} \approx Q^{4.06}$$

Although there is a considerable spread in the data of *Figures 1–4, it can be proved that this spread is within the experimental accuracy of experimental* MWD *determination.* From reports by Wales[8] and Meissner[14] one may easily derive the amount of inaccuracy, viz.:

$$|\Delta(\log \bar{M}_w/\bar{M}_n)| \approx 0.12$$

$$|\Delta(\log \bar{M}_z/\bar{M}_w)| \approx 0.18$$

where $\Delta(x)$ is the spread of x in determinations by different investigators and $|\Delta(x)|$ the average absolute value.

So, within the range of experimental accuracy, there is no justification for the use of parameters other than $\bar{M}_w$ and Q to characterize the *MWD* of unblended polymers. This also means that any mechanical or rheological property of polydisperse polymers may be described as a function of $\bar{M}_w$ and Q.

For polymer blends, complications in the rheological behaviour must be expected in agreement with the conclusions of Cote and Shida.

None of the commonly used theoretical *MWDs*, such as Schulz–Flory, Lansing–Kraemer, Tung, Poisson, etc., is in agreement with the experimental relationships given in this paper. Clearly, there is a need for a new theoretical approach.

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Table 1 Experimentally determined molecular weight distributions*

Polymer	$\bar{M}_n$ x 10^3	$\bar{M}_w$ x 10^3	$\bar{M}_z$ x 10^3	$\bar{M}_{z+1}$ x 10^3	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$	$\bar{M}_{z+1}/\bar{M}_z$	$\bar{M}_z \cdot \bar{M}_{z+1}/\bar{M}_w^2$
1 Polyisobutylene	171	597	1730	5012	3.5	2.9	2.9	24.3
	565	3382	10930	24372	6.0	3.2	2.2	23.3
2 Polystyrene	74	165	304	479	2.2	1.8	1.58	5.3
3 Poly(vinylidene fluoride)	75	191	409	689	2.6	2.1	1.68	7.7
4 Poly(vinyl alochol)	66	294	941	1846	4.5	3.2	1.96	20.1
5 Poly(vinyl acetate)	217	611	1821	5287	2.8	3.0	2.90	25.8
6 Poly(vinyl pyrrolidon)	10	24	54	100	2.5	2.3	1.85	9.4
7 Poly(methyl methacrylate)	252	481	766	1196	1.9	1.6	1.56	4.0
8 Polyacrylonitrile	38	116	249	405	3.1	2.1	1.63	7.5
9 Polybutadiene	142	443	1076	1745	3.1	2.4	1.6	9.6
10 Poly(2,6-dimethyl-1, 4-phenylene oxide)	26	56	88	117	2.2	1.6	1.33	3.3
11 Poly(2,6-diphenyl-1, 4-phenylene oxide–	297	550	875	1319	1.9	1.6	1.51	3.8
12 Poly(ethylene terephthalate)	27	62	116	198	2.3	1.9	1.71	6.0
13 Poly(6-aminohexanoic acid)	50	118	233	371	2.4	2.0	1.59	6.2

* All molecular weights were obtained from g.p.c. curves

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Book Reviews

Progress in Polymer Science Japan Volume 8

Edited by K. Imahori and T. Higashimura

Wiley, New York, 1975, 244 pp. £14.75

The latest volume of this series continues the established pattern and presents five chapters, devoted to quite different aspects of polymer science, in which the authors mainly review their own contribution (and sometimes that of other Japanese workers) to the subject under discussion.

The first chapter 'Copolymerization of Carbon Dioxide' by S. Inoue is primarily devoted to copolymerizations with ethylene and propylene oxides using diethylzinc based initiators to produce alternating copolymers. The author describes the collates recent kinetic and mechanistic data obtained in Toykyo University and presents arguments used to establish mechanisms of initiation and propagation. Brief descriptions of related zinc chemistry and the properties of the alternating copolymers are given along with mechanisms of copolymerization of carbon dioxide with imines (proposed by other workers) and reports of a condensation polymerization with diamines to form polyureas.

Following reports that so-called uncatalysed polymerizations of methyl methacrylate in the presence of various polymers are influenced by traces of copper, K. Takemoto and Y. Inaki have investigated polymerizations initiated by metal complexes in the presence of carbon tetrachloride. In a long article they describe many cursory kinetic studies of methyl methacrylate and acrylonitrile polymerizations initiated by complexes of Cu^{II} and Fe^{III} with various polymers and model compounds. Spectroscopic data are described and plausible mechanisms are suggested.

'Photo-induced Ionic Polymerizations' by M. Irie and K. Hayashi provides a detailed discussion of the mechanism of photoinitiation of the cationic polymerization of α-methylstyrene in the presence of tetrahydrofuran as electron acceptor and continues with discussions of the basic features of photo-induced cationic polymerizations of α-methylstyrene and cyclohexene oxide in the presence of various electron acceptors and anionic polmerizations of acrylonitrile and nitroethylene in the presence of electron donors. Evidence for simultaneous cationic and anionic polymerizations in cyclohexene oxide–nitroethylene mixtures is given.

As an introduction to 'Structural Studies of Crystalline Polymers', H. Tadokoro briefly considers problems and techniques relevant to the determination of polymer crystal structures. He then considers crystal structures of a number of polymers which have been determined (or to which a significant contribution has been made) in his laboratory, clearly describing the logic used to discriminate between possible structures. He concludes with a discussion of the relative importance of intra- and inter-molecular interactions in determining crystal structures.

Finally, H. Noguchi gives a general discussion of hydration of biopolymers with some concentration on his (and other Japanese workers) contributions to the field. Aspects considered include changes in volume and of velocity of sound accompanying order–disorder transitions in solutions of polypeptides, the hydration of polysaccharides and polyelectolytes.

The original aim of this series was to make available a knowledge of Japanese research since (to quote from the dust-cover) '. . . most is not well-known internationally since the vast proportion of papers are published only in Japanese'. This volume contains very few references to Japanese language publications but still serves a useful purpose by providing an opportunity for authors to present a coherent overview of their recent research which is often fragmented in the literature. Given the present value of Sterling sales must be to libraries only.

G. C. Eastmond

Conference Announcement

Statistical and Dynamic Behaviour of Chain Molecules

St. John's College, Oxford, 20 and 21 September 1977

The Statistical Mechanics and Thermodynamics Group in association with the Macromolecular group of the Chemical Society are organizing the meeting 'Statistical and Dynamic Behaviour of Chain Molecules' to be held at St. John's College, Oxford, 20 and 21 September 1977. It is anticipated that the meeting will cover both theoretical and experimental aspects of the above topic. Further information may be obtained from: Dr. M. Lal, Unilever Research, Port Sunlight, Wirral L62 4XN.

Advances in Polymer Science

Volume 21: Mechanisms of Polyreactions – Polymer Characterization

Springer Verlag, Berlin, 1976, 151 pp. $26.30

Volume 21 of Advances in Polymer Science contains three interesting and timely reviews together with, and unusually for this series, an original account of the preparation and properties of poly (isobutylene-*co*-β-pinene) by Kennedy and Chou.

Semlyen (28 pp. 224 refs) reviews ring-chain equilibria in polymers. Molar cyclization equilibrium constants are presented for a wide variety of systems : usually they are adequately described by the Jacobson – Stockmayer (Gaussian coil) theory. Particular emphasis is placed upon the conformational information provided by experimental and theoretical studies of ring-chain equilibria.

Inoue (27 pp, 67 refs) reviews the assymetric catalytic, formation and chain modification reactions of synthetic polypeptides. The important effect of chain conformation (secondary structure) on all these assymetric reactions is emphasized : and the relevance of these studies to the elucidation of the mode of reaction and the mode of evolution of enzymes is pointed out.

Braun and Guillet (35 pp. 116 refs) review the uses of inverse gas chromatography in polymer science. This technique, involving the molecular probing of a polymeric stationary phase with a volatile solute, has become prominent in the last few years as a source of thermodynamic data for polymer – liquid systems. This work is discussed, together with the wider applications of the technique, e.g. detection of transitions (T_g, T_m), measurement of crystallinity, study of adsorption and diffusion.

C. Booth

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