EXHIBIT V

PART 17

27

THE MARKETING CHALLENGE CREATED BY SINGLE SITE CATALYSTS IN POLYOLEFINS

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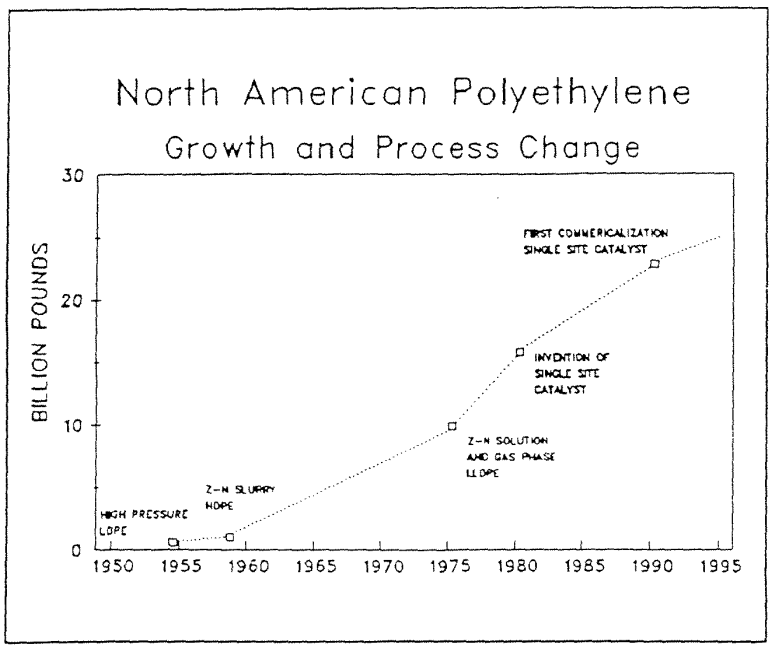
Michael P. Jeffries
EXXPOL Ethylene Polymers Venture Manager

Ladies and gentlemen thank you for attending today. I would like to thank Ron Schotland and Paul Smith for inviting me to speak. I am excited about what is happening in our polyolefins industry today and, as a marketer, see both challenge and opportunity. The material I will share with you today reflects a personal vision. A vision of how single site catalyst technology, Exxon's EXXPOL TECHNOLOGY, will change our industry and how it will challenge the marketing skills of those serving specialty and volume polyolefin markets alike.

Before examining the changes we need a good definition of marketing. Webster's dictionary calls marketing "an aggregate of functions involved in moving goods from producer to consumer".

My personal definition for polyolefins marketing is "the function that places new products into the marketplace, by matching their value to the needs of the customers". This definition of marketing tends to define our role as reactive. Historically I believe that is true. I also believe that this definition is rapidly changing, in part, because of the invention of single site catalysts. Tomorrow's marketing function must be more proactive and provide better quality information. As a way of supporting this argument examine with me the assumptions that support this assertion.

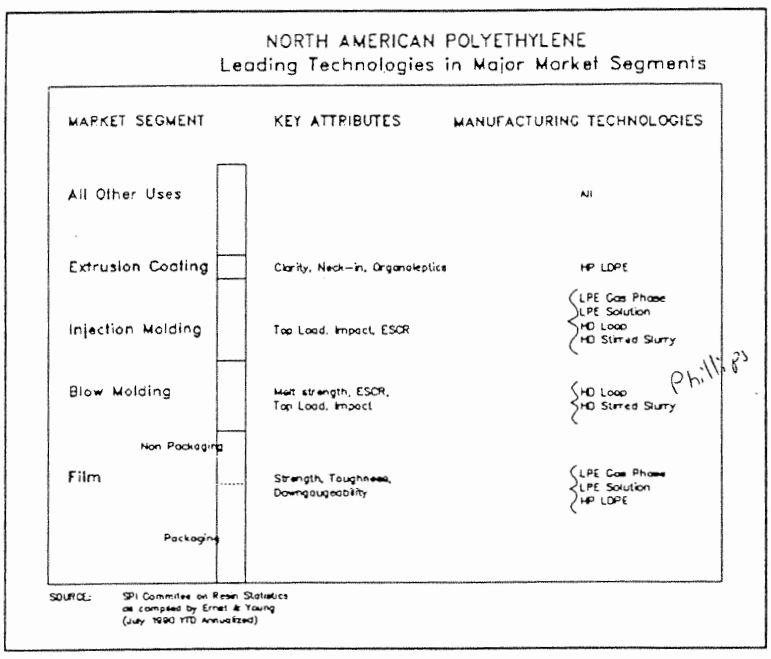
My first assumption is that polyolefins industry change is driven by technological innovation. Historically, change and growth have been driven by creation of new processes or products. Marketing has helped fit those innovations into the market.



The polyethylene business provides a good example. The polyethylene business in the early 1960's was comprised of two basic processes and produced less than a billion pounds. Through the 1960's and early 1970's growth rates were high but the number of processes remained relatively limited and the result was a fairly homogeneous product offering. Despite some early alignment of processes with specific markets, marketing was more "selling" and differentiation between competitive products was difficult. Beginning in the late 1970's as the growth rates of the industry began to slow new processes began to emerge commercially. Markets reacted to each new entry by aligning themselves with these new products through the open market process. LLDPE became a reality in both the solution and gas phase processes and each established a market position. Specialization of LDPE and LDPE copolymers from the high pressure process occurred driven by the price pressure from LLDPE. Even now HMW HDPE is establishing a position in industrial films and blow

molding markets. Clearly our industry's market changes are driven by process and product evolution. Historically marketing followed, and reacted to, technology change.

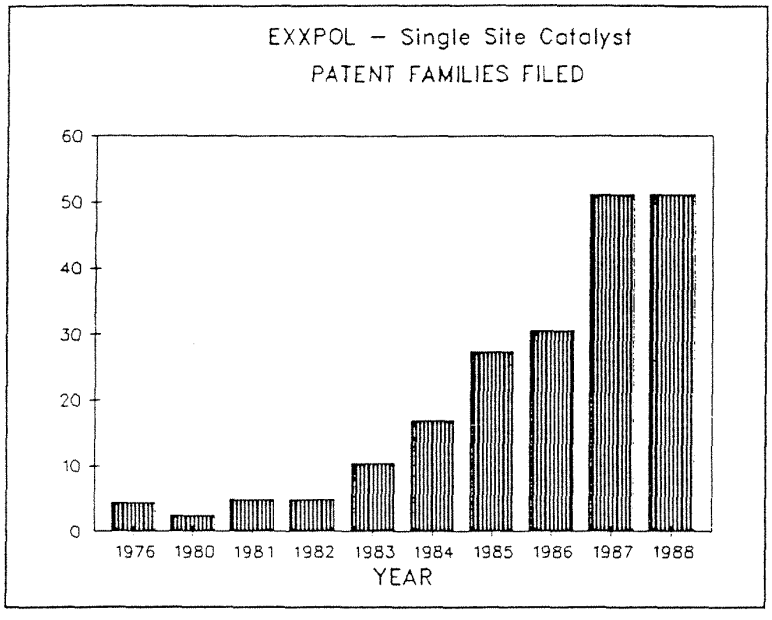
My second assumption is that today's market for polyolefins is maturing and beginning to segment. As a result, leadership will belong to those companies who are able to align their polymerization processes with the needs of the market and deliver added value. The examples just given show some of that trend. As customers downstream requirements become more sophisticated the demands on the polymers we sell change. I will not argue which came first, the market need or the technological innovation. What I will conclude is that growth in our industry is being captured by those who deliver PERFORMANCE improvements to the market.



For example, today's polyethylene market is a mixture of processes with the most successful companies having generated a strong alignment between what their process can produce and the performance needs of the markets. Within each of these large segments are specific examples of high growth penetration where alignment of product and market need create a success story.

With most of our rapid growth behind us, the broad trend driving our industry is what I call SEGMENTATION based on PERFORMANCE. This trend towards segmentation of markets will be accelerated by the invention of single site catalysts and will create THE MARKETING CHALLENGE for the 1990's. Indeed, single site catalysis will give our industry the ability to create polymerization systems to match specific market needs...but we will come to more of that later.

My third assumption is that the pace of change is quickening and technology development is becoming increasingly expensive and risky. Our business will never change as rapidly as some industries, but pace of change is accelerating. I would characterize it as faster than the steel industry but slower than electronics such as computers. To appreciate the pace of change we need only look at the volume of patent literature in the area of single site catalysis.



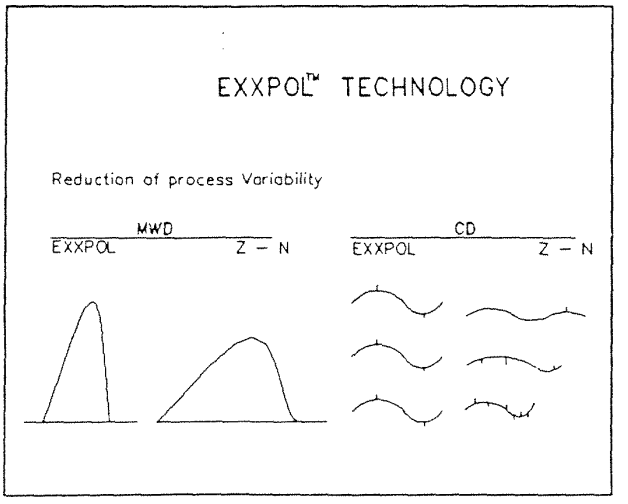
The pace of change is quickening. As an industry we already have a first generation of EXXPOL ethylene polymers in the market and a second generation is in development. The first generation process and catalyst are designed to address specialty markets and the second is targeted at the needs of larger markets such as packaging films.

The cost of research today has been documented in any number of places. In our capital intensive industry growth has historically fueled research and the payout came in the form of increased sales. Even when marketing found that a new technology had less value or was a little slow to develop, the rapid growth of the industry protected us from financial failure. Today the rules are different...we must provide performance and be able to charge the right price for it. In today's environment the cost of new process, product and catalyst development is staggering. Companies must carefully examine the affordability of research and development programs. The cost of failure

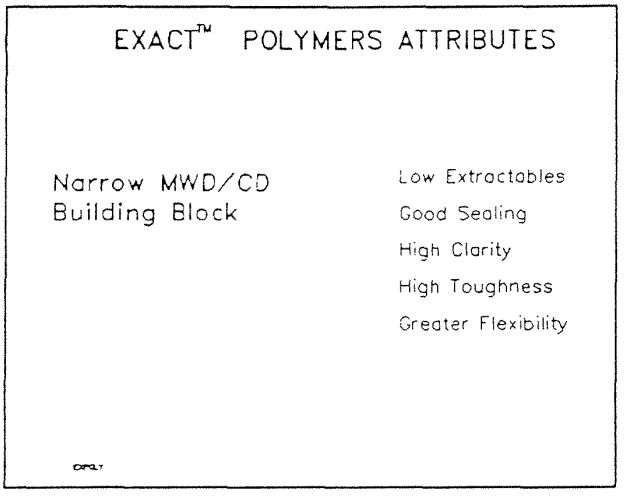
today is very high. Market knowledge can reduce the risks of development. Knowing what will sell, to whom and at what price is more important today. If single site catalysis offers our industry the opportunity to design plants to serve markets, then marketing's role will indeed need to change.

My fourth assumption is that single site catalyst technology is the next major technological change in our industry. The data available comes from Exxon Chemical's own experiences with EXXPOL TECHNOLOGY and EXACT polymers produced at our Baton Rouge Plant. We have concluded that it is a major new tool that will differentiate products, provide improved performance and further segment our markets. It is here, at the market interface that we begin to build an argument for a new marketing role.

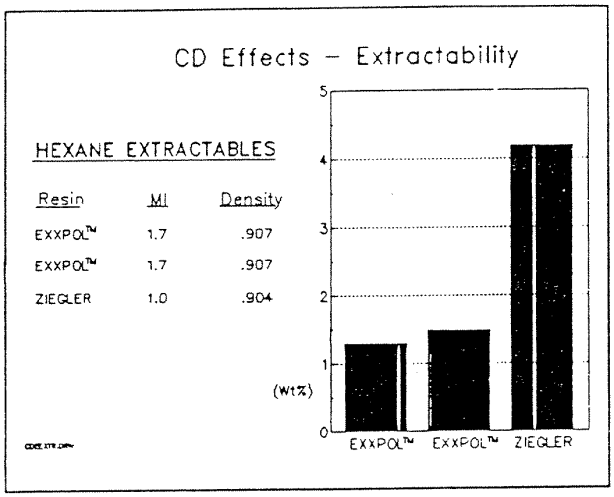
To judge the impact these polymers will have they must be viewed as our customers see them...for their value in use. Exxon Chemical Company has been working with selected customer partners for several years and has cooperatively developed powerful insights into the performance advantages of EXACT POLYMERS, what we call attributes, and the performance needs of markets.



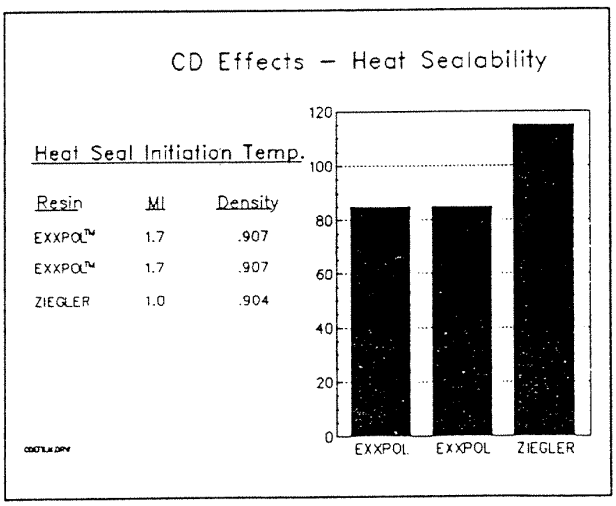
The basic building block of our future industry will be this narrow molecular weight distribution (NMWD), narrow composition distribution (NCD) molecular unit. To a first approximation every molecule in this building block has the same length (molecular weight) and the same comonomer content (composition). This gives rise to properties, or attributes, that we can recognize as having value in our markets. For manufacturing operations these catalyst systems open up more "product geography" and provide more control over the product produced.



As marketers our challenge is to place those attributes in the hands of customers who will pay for them. As marketers, advisors to management on the value of such products, we must accurately reflect the value our companies can expect to get for such innovations. At Exxon Chemical, our methodology has been to thoroughly understand the polymer and the application needs in the real world...the shop floor.



For packaging applications, single site catalysis produces a unique combination of very low extractables, outstanding heat seal and hot tack performance, and superior toughness properties.



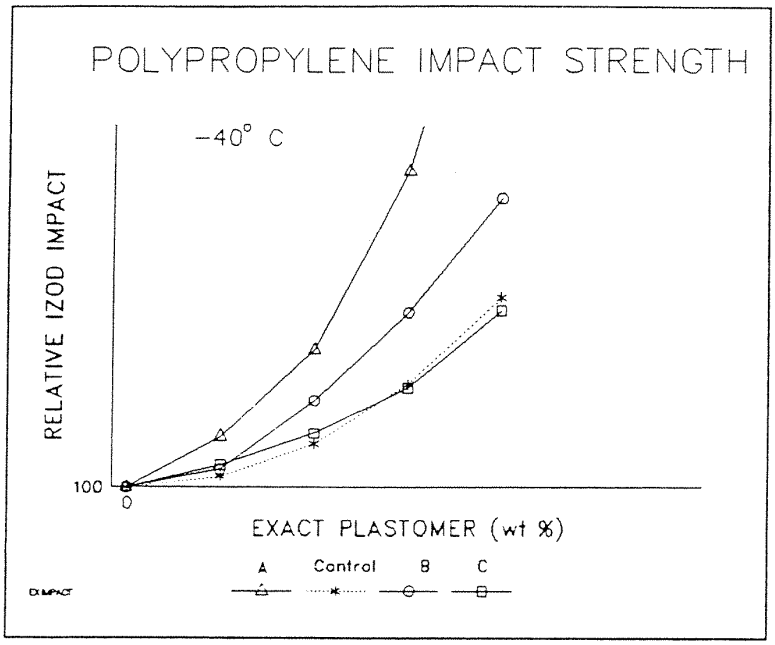
Food approved sealing layers with lower heat seal initiation temperatures will allow faster line speeds in form-fill-seal applications.

PROPERTIES OF MEDIUM VOLTAGE INSULATION COMPOUND*

PROPERTIES	COMPOUND BASED on EPR [25 MOONEY (=11,000 Mw), 67% C	COMPOUND BASED on EXXACT PLASTOMER [3MI (=80,000 Mw), 0.8800 (=75% C)	COMPOUND BASED on COMMERICAL VLDPE [1MI (=100,000Mw),0.9060 (=8. WT% C)
Tensile Strength (PSI)	1300	2100	Compound integrity poor. Today's competitive, commerical polyethylenes (VL,LL) show comparatively poorer filler acceptance, resulting in poor quality, non-optimum end product.
% Tensile Retained	100	100	
Elongation (%)	300	425	
% Elongation Retained	90	95	
Hardness, Shore 'A'	80	90	
Dielectric Constant, Original	2.85	2.75	
Power Factor, Original (%)	0.40	0.23	
Power Factor, 14 Days/90 C Water (%)	0.70	0.50	

For compounders a selection of high comonomer content rubber like materials are created with EXXPOL. Lower density EXACT PLASTOMERS combine rubber properties with a convenient pellet form and excellent filler acceptance. Compounds have shown better physical properties with EXACT POLYMERS compared to current ethylene polymers. In the electrical industry, for instance, polymer uniformity...molecular weight and composition distribution described earlier....translates into some very attractive and patentable performance.

Looking for 5 years with selected customer/partners



For impact modification and blending EXACT polymers are ideal. The pelletized form and the very low densities of EXACT PLASTOMERS offer a new range of convenience and impact performance. For those serving the automotive industry, control over MWD and CD means PLASTOMERS will mix intimately with a wide range of polypropylenes and other olefins. For those packaging film producers who want to differentiate their products the superior toughness, more dependable sealing and low extractables of EXACT offer considerable value.

For those customers interested in the sophisticated functionalization of polymers EXXPOL offers a truly new tool....control over the type and level of unsaturation. With the high level of unsaturation possible with EXXPOL TECHNOLOGY correspondingly high levels of functionalization are possible. We expect new compatabilizers and additives to emerge.

Exxon Chemical believes that first generation EXACT single site catalyzed materials offer a new combination of value and performance and our specialty customer partners agree. Understanding products and their value is at the heart of the changed role for marketing.

Having looked at the assumptions it is time to draw some conclusions. Unlike innovations of the past, today's marketing challenge will not be limited to simply placing new capability into a growing market. It will offer marketing an opportunity to lead change rather than react to change.

Our polyolefins industry has been successful in placing technological innovation in the market over the long term, but our track record in predicting value and market acceptance has not been as good. Innovations such as ionomers were originally targeted at producing clear bottles but found their niche in very different places. In the past our function as marketers was to facilitate the process of fitting a technology or innovation into the market. We needed to know our polymers and our markets, but at best we were advisors as the process of change proceeded. In the worst cases we became followers and bystanders to a technically driven development.

Any company faced with today's cost of development will need a clear understanding of the market values BEFORE beginning a development program. What single site catalysts have created is the opportunity to design plants and produce very specific products. This in turn creates a dramatic need to understand market values as input to the management process. Some of you may comment that what I have described is classical marketing and nothing more. You may argue that our polyolefins industry should have been doing this all along. You would be 100% correct...we should have been doing it but in most cases it has not been necessary and it has not happened.

I argue that in today's competitive markets where speed is important and development costs high we can no longer afford a passive marketing role. Where we have traditionally followed and advised we must now lead by defining market value. The EXXPOL technology can deliver so much from so many different polymerization systems that it is possible to redefine our processes from technology driven to market driven.

As an example, we can look at the capabilities of a second generation of single site catalyzed materials.

MWD/CD MODIFICATION

	EXACT	ZIEGLER
MI	5	5
DENSITY	.913	.918
MD TEAR	65	35
IMPACT	170	40
EXTRACTABLES	2.3	8.1
Processability	Improved Relative to .918 Ziegler	

These products, already in development, will serve the needs of larger more price sensitive markets. This application of EXXPOL TECHNOLOGY will take advantage of the ability to combine and manipulate the basic molecular building block produced with single site catalyst. When combined with the proper process technology, new materials can be created that are tailored to the specific needs of markets. This slide illustrates only one of the ways that MWD and CD can be manipulated to meet customer needs.

Our polyolefins world is changing. Our business is indeed driven by technology change. Our business is maturing and growth rates are slowing. Our markets are segmenting, asking us to provide greater and more specific polymer performance. Change is accelerating and single site catalysis is a real and major development.

In this environment marketing has a renewed role, a leadership role. Market information can make the difference between success and failure in today's more costly environment. We need to understand the technology changes impacting our industry and value them through the eyes of our customers.

Ladies and gentlemen, the companies that will be the most successful in the future will be the ones that take can control and guide technological change. They will design facilities to meet specific market needs. They will have the lowest development costs and the best alignment of manufacturing capability with market needs. This will translate into higher margins as our volume markets are further segmented on the basis of polymer performance.

Thank you for your attention. The future of the polyolefins business will indeed be interesting.

31

Modern Methods of Polymer Characterization

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CHAPTER

3

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MEASUREMENT OF LONG-CHAIN BRANCH FREQUENCY IN SYNTHETIC POLYMERS

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1. **Introduction**
2. **Measurements of Long-Chain Branching**
3. **Conclusions**
   References

1. INTRODUCTION

This chapter summarizes the current state of size exclusion chromatography (SEC) techniques for measuring the variation of long-chain branching with molecular weight in synthetic polymers. The analysis of molecular weight distribution of branched polymers is not treated explicitly, although this information is necessary for the measurement of long-chain branching.

It has been widely recognized that long branching may have profound effects on the properties of polymers in which this feature may occur. Although many attempts have been made to quantify long-branch concentrations, these efforts have been hampered by analytical problems and the estimates that have been reported have perforce rested on unverifiable assumptions of relations between molecular weight and long-branch frequency. The more modern equipment and techniques of recent years have improved the analysis for long-branch concentrations and permitted more objective testing of the assumptions on which such estimates are based. Not surprisingly, SEC plays a central role in such advances.

Full characterization of a polymer that contains long branches requires at least the measurement of the concentration of such branches as a function of

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polymer molecular weight. In a polydisperse material, the more extended molecules are more likely to participate in entanglements than more compact species. Melt elasticity and flow behavior are thought to be influenced particularly by the rheological characteristics of the larger macromolecules in the sample. The low-molecular-weight tail of the molecular weight distribution, however, may have a very significant effect on mechanical properties. In general, a branched molecule will be more compact and less entangled with its neighbors than a linear molecule with the same molecular weight. Therefore, we may expect that the processability of a thermoplastic may be relatively unaffected by long branching in the low-molecular-weight region, while such isomerism in high-molecular-weight polymer molecules may be extremely important in this regard.

Size exclusion chromatography is the only current analytical technique that may provide information on the variation of long branching with molecular weight, without fractionation of the sample. Information about details of branch length and structure are highly desirable, but these parameters are beyond our reach at present, at least for long branches.

2. MEASUREMENT OF LONG-CHAIN BRANCHING

Universal calibration based on hydrodynamic volumes of linear polymers is not valid for isomers with branches that are longer than a certain minimum. This is because such long-branched species are more compact than linear macromolecules with the same molecular weight. More is said later on the minimum branch length for long branching.

At equal SEC elution volume and infinite dilution, the molecular weights of linear and branched species with the same constitution are related by (1–3)

$$[\eta]_b M_b = [\eta]^* M^* \tag{1}$$

where the subscript b and superscript * refer to branched and linear macromolecules, respectively, that have the same SEC retention time. This implies that branched species with molecular weight M_b have the same solvodynamic volume in the SEC solvent as linear polymers with molecular weight M^*.

In general $M_b \geqslant M^*$, with the equality prevailing only for short branches. (The lengths of short and long branches are defined operationally below.) Presumably, also, the inequality would not apply even for short branches if these were very frequent.

Now, consider a branched and a linear polymer, both with the same

molecular weight. In that case the intrinsic viscosity $[\eta]_l$ of the linear species will be greater than that of the branched polymer $[\eta]_b$ in the SEC solvent. The ratio of intrinsic viscosities may be expressed as follows:

$$g' = \frac{[\eta]_b}{[\eta]_l} \tag{2}$$

Note that the corresponding molecular weights considered to this point are related by $M_b = M_l \geqslant M^*$.

For monodisperse versions of the linear polymer in the SEC solvent

$$[\eta] = KM^a \tag{3}$$

where K and a are the Mark–Houwink constants. Then,

$$[\eta]_b = g'[\eta]_l = g'KM_l^a = g'KM_b^a \tag{4}$$

in which $M_b = M_l$ and a is the value from the linear polymer. From Eqs. 1 and 3

$$[\eta]^*M^* = K(M^*)^{a+1}$$

and Eq. (1) is therefore equivalent to

$$g'KM_b^{a+1} = K(M^*)^{a+1} \tag{5}$$

So that

$$g' = \left(\frac{M^*}{M_b}\right)^{a+1} \tag{6}$$

In order to relate g' to actual molecular size it is necessary to consider the ratio g of the mean-square radii of gyration $\langle S^2 \rangle$ of the branched and linear polymers with respective molecular weights equal to $M_l = M_b$. That is

$$g = \frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l} < 1 \tag{7}$$

Various relations have been proposed of the form (4, 5):

$$g' = g^k \tag{8}$$

the value of k will be considered later in this chapter. With Eqs. 6 and 8

$$g' = \left(\frac{M^*}{M_b}\right)^{a+1} = g^k \tag{9}$$

Recall that the exponent a is the Mark–Houwink constant for the linear polymer in the SEC solvent.

Equation 9 can serve as the basis for a technique to measure the relation between long-chain branching and molecular weight using SEC with a detector that measures molecular weight directly. At any given elution volume M_b is measured directly, while M^* is calculated from the universal calibration curve for linear species. At present, there are two commercially available detectors that permit the direct measurement of the molecular weights of eluting polymers. One is the low-angle laser light scattering detector (LALLS), which measures $\bar{M}_w$ of the macromolecules (6) (see Chapter 9).

An alternative detector is an online viscometer that can be used to measure intrinsic viscosities of the polymers in the eluant stream. Several designs have been reported (7, 8), based on monitoring pressure drops across capillaries. Room temperature operation of a continuous viscometer detector is less difficult than high temperature use, where the output may be affected by thermal as well as mechanical and electrical noise. Analysis of the most widely used branched polymer, that is, low-density polyethylene (LDPE), requires experiments at temperatures near 145 °C. A continuous viscometer has been described for operation under these conditions (9, 10) (also see Chapter 7).

The viscometer detector is the more generally appropriate device for studying branched polymers. The LALLS detector gives correct results only if all species viewed by the detector are uniform with respect to long-chain branching. If the polymers in the detector cell consist of species with different extents or types of long branching then M_b in Eq. (1) is actually equal to $\bar{M}_n$ (11). Since the LALLS detector measures $\bar{M}_w$, it is not suitable for measurements of molecular weights or long-chain branch distribution of polymers in which various species may have the same solvodynamic volumes and different molecular weights.

Such a situation will arise when the branched polymers have higher molecular weights than less branched or linear analogs. One expects such a mixture to be produced in the isothermal free-radical polymerization of vinyl monomers, where long branches result from radical chain transfer to dead polymer (12, 13). Larger molecules are more likely targets for such chain transfer and are therefore more likely to contain long branches from purely statistical reasoning.

Poly(vinyl chloride) is possibly a polymer of the type mentioned. Universal

calibration and direct detection of molecular weights by LALLS may be invalid if the sample contains an appreciable concentration of long branches.

The LALLS technique appears to provide correct results, however, for high-pressure LDPE (14). This is because radical chain transfer to polymer, which produces long branches, occurs most frequently at higher temperatures in this nonisothermal polymerization. These are also the conditions that yield lower molecular weight polyethylene (15).

Equation 9 has been used recently to measure long-chain branch frequency in polyethylene (15, 16). At any given elution volume, M_b is measured directly with a LALLS detector, while M^* is calculated from the universal calibration curve for linear polymers. The long-chain branch frequency is expected to be reflected in the value of the parameter g'. Several assumptions must be invoked in order to proceed further and to estimate the actual number of long branches per molecule. In particular, one must assume a branch structure for the branched macromolecules and a value for the exponent k in Eq. 9.

Most such calculations use the Zimm–Stockmayer (17) relation for a randomly branched polymer with trifunctional branch points. This is,

$$g = \frac{6}{n_w}\cdot\frac{1}{2}\left[\frac{2+n_w}{n_w}\right]^{1/2} \ln\left[\frac{(2+n_w)^{1/2}+n_w^{1/2}}{(2+n_w)^{1/2}-n_w^{1/2}}-1\right] \tag{10}$$

where n_w is the number of long branches per weight average molecule.

An alternative Zimm–Stockmayer relation may be used to estimate the number of trifunctional long branches per number average molecule n_n

$$g = \left[\left(1+\frac{n_n}{7}\right)^{1/2}+\frac{4n_n}{9\pi}\right]^{-1/2} \tag{11}$$

If one assumes that the branch points are tetrafunctional then the appropriate equation is:

$$g = \left[\left(1+\frac{n_n}{6}\right)^{1/2}+\frac{4n_n}{3\pi}\right]^{-1/2} \tag{12}$$

Analytical solutions to Eqs. 10–12 are not available. An iterative computer program is used to calculate n_w or n_n at each value of M_b, from Eqs. 9 and 10, 11 or 12, with a given value of k (15).

There are evidently some serious assumptions involved in proceeding from the experimental values of M^*/M_b to the estimated value of n_w. One may question, for example, whether the polyethylenes are randomly branched. Theoretically, short branches in polyethylene made by free radical initiation

are expected to be clustered and to contain quaternary as well as tertiary carbon branch points (12, 18). Evidence on long-branch occurrence is lacking.

Furthermore, the Zimm–Stockmayer model was derived for molecular sizes in theta solvents, whereas the SEC analyses should be made in good solvents. It has been reported, however, that the solvent–temperature system does not affect the measurement of long-chain branches in polyethylene (19, 20).

The absolute value of branch frequency may be uncertain for these reasons, and because the exponent k may have been assumed incorrectly in the calculations. The data should be valid at least in a relative sense, however, if the same value of k in Eq. 9 can be assumed for species of all molecular weights.

Various values of k have been suggested between 0.5 and 1.5 (4, 21, 22). Some experimental information on this point has become available recently. Copolymers of ethylene with 1-olefins were analyzed by SEC and it was shown that k varied from 0.68 to 0.88 as the number of long branches increased from 10/1000 carbon atoms to 49/1000 carbon atoms (22). Clearly, k is not the same for samples with different long-branch concentrations, at least in this concentration range.

Studies with copolymers of 1-olefins and ethylene have shown that the C_6 branches are not registered as long branches in SEC–LALLS analyses, whereas C_{12} branches are measured as long branches. The minimum branch length for "long branching" is therefore between C_6 and C_{12} (15, 23), at least for such copolymers in which the 1-olefin concentration is less than 7 mol%.

Nuclear magnetic resonance (NMR) analyses can be used with SEC characterizations to estimate k for different polymers if k is assumed to be uniform through the molecular weight distribution. Present-day ^{13}C NMR analyses measure polyethylene branches of six carbon atoms or longer. This is approximately the minimum length that is apparently recognized by SEC. NMR results will produce a mean long-chain branch frequency, in terms of branches per 1000 carbon atoms, for the whole polymer sample. The same value can be estimated from SEC. In this case, it is appropriate to use Eq. (11) with Eq. (9) and to take a weighted sum across the molar size distribution. Presumably, then, k can be iterated in Eq. (9) to produce a value of g that yields the same number average of n_n as that determined by ^{13}C NMR. A variation of this approach has been reported by Bugada and Rudin (24). The method suggested here is straightforward in principle. It will, however, be subject to the uncertainty in SEC and ^{13}C NMR measurements, which are not insignificant. Also, while Eq. (11) is correct for comparisons with the results of NMR analyses, this relation has been reported to provide unreasonably high estimates of long-branch frequency as compared to those from application of Eq. (10) (25–27).

Hama et al. (20) characterized low-density polyethylenes fractions and

reported in this case that $g' = g^{1.0 \pm 0.3}$. In studies with ethylene copolymers with 1-olefins k was found to vary with branch frequency and to lie between 0.68 and 0.81 (23). These figures are compatible with those derived by Hert and Strazielle (28) from measurements on polyethylene fractions. Other workers have studied different polymers and reported or assumed different values of k (29–32). It seems likely that this exponent may depend on branch point functionality and branch frequency, at least. Assumption of any particular value is likely to produce estimates of long-branch frequency that are relatively, but not necessarily absolutely accurate.

The present rather cloudy state of the art can probably be summarized best by comparing reports on the long-chain branch character of low-density polyethylene, which is the most widely studied polymer.

Constantin (33) reported a study of long branching in polyethylene, using continuous detection of the intrinsic viscosity of the SEC eluant. In this case g' (Eq. 2) decreased with increasing molecular weight, indicating that long branching increased at higher molecular weights, but the author notes that the absolute values of long-branch frequency estimated at high molecular weights are not credible.

More recently, Hert and Strazielle (28) studied fractions of polyethylene obtained from large scale SEC. These fractions were characterized by light scattering and intrinsic viscosity. It was shown that the parameter k varied with molecular weight and even with the source of the LDPE. This is consistent with later SEC–LALLS conclusions (23). Also, long-branch frequency decreased with increasing molecular weight.

Lecacheux et al. (34) characterized branched polyethylene and ethylene–vinyl acetate copolymers by coupling the SEC apparatus to a high temperature continuous viscometer of their design. Long-chain branching was found not to vary with molecular weight, for the range of samples studied by these workers.

The most recent analyses (15, 27) agree that long-branch frequency decreases with increasing molecular weight in low-density polyethylenes. This is consistent with the results of Hama et al. (20) and also with theoretical considerations of the polymerization process (35).

3. CONCLUSIONS

The conclusions of different laboratories regarding long-branch frequency–molecular weight relations in polyethylene appear to vary widely. One possible explanation is that these discrepancies reflect differences in the polymers studied. It is more likely, however, that there are fundamental differences in analytical techniques or interpretations that have not been

identified. The analysis is hampered at present by uncertainties in the tails of the SEC chromatograms because of differing sensitivities of the concentration and molecular weight detectors (36, 37).

Long branches are usually defined as being approximately as long as the main polymer chain. The branches that are detected as long branches in SEC analyses may be much shorter than this length. The connection has yet to be made between SEC measurement of long-branch concentrations and effects on polymer melt rheology or mechanical properties.

REFERENCES

1. Z. Grubisic, P. Rempp, and H. Benoit, "A Universal Calibration for Gel Permeation Chromatography," *J. Polym. Sci. Part B*, **5**, 753 (1967).
2. A. Rudin and R. A. Wagner, "Solvent and Concentration Dependence of Hydrodynamic Volumes and GPC Elution Volumes," *J. Appl. Polym. Sci.*, **20**, 1483 (1976).
3. H. K. Mahabadi and A. Rudin, "Effect of Solvent on Concentration Dependence of Hydrodynamic Volumes and GPC Elution Volumes," *Polymer J.*, **11**, 123 (1979).
4. B. H Zimm and R. W. Kilb, "Dynamics of Branched Polymer Molecules in Dilute Solution," *J. Polym. Sci.*, **37**, 19 (1959).
5. G. C. Berry, "Thermodynamic and Conformational Properties of Polystyrene. III. Dilute Solution Studies on Branched Polymers," *J. Polym. Sci. Part A2*, **9**, 687 (1971).
6. A. C. Ouano and W. Kaye, "GPC. A Molecular Weight Detection by Low Angle Laser Light Scattering," *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1151 (1974).
7. A. C. Ouano, "Quantitative Data Interpretation Techniques in GPC," *J. Macromol Sci., Rev. Macromol Chem.*, **C9**, 123 (1973).
8. F. B. Malihi, C. Kuo, M. E. Kohler, T. Provder, and A. F. Kah, "Application of an In-line Continuous GPC Viscosity Detector for the Characterization of Molecular Weight and Branching in Polymers," *Org. Coat. Appl. Polym. Sci. Proc.*, **48**, 760 (1983).
9. M. Haney, "The Differential Viscometer. I. A New Approach to the Measurement of Specific Viscosities of Polymer Solutions," *J. Appl. Polym. Sci.*, **30**, 3023 (1985).
10. M. Haney, "The Differential Viscometer. II. On-line Viscosity Detector for SEC," *J. Appl. Polym. Sci.*, **30**, 3037 (1985).
11. A. E. Hamielec and A. C. Ouano, "Generalized Universal Molecular Weight Calibration Parameter in GPC," *J. Liq. Chromatogr.*, **1**, 111 (1978).
12. M. J. Roedel, "The Molecular Structure of Polyethylene. I. Chain Branching in Polyethylene during Polymerization," *J. Am. Chem. Soc.*, 75, 6110 (1953).
13. J. K. Beasley, "The Molecular Structure of Polyethylene. IV. Kinetic Calculations of the Effect of Branching on Molecular Weight Distribution," *J. Am. Chem. Soc.*, **75**, 6123 (1953).

14. V. Grinshpun, A. Rudin, and D. Potter, "Comments on the Measurement of Long-Chain Branching by SEC," *Polym. Bull.*, **13**, 71 (1985).
15. A. Rudin, V. Grinshpun, and K. F. O'Driscoll, "Long-Chain Branching in Polyethylene," *J. Liq. Chromatogr.*, **7**, 1809 (1984).
16. D. E. Axelson and W. C. Knapp, "SEC and Low-Angle Laser Light Scattering," *J. Appl. Polym. Sci.*, **25**, 119 (1980).
17. B. H. Zimm and W. H. Stockmayer, "The Dimensions of Chain Molecules Containing Branches and Rings," *J. Chem. Phys.*, **17**, 1301 (1949).
18. A. H. Willbourn, "Polymethylene and the Structure of Polyethylene: Study of Short-Chain Branching, Its Nature and Effects," *J. Polym. Sci.*, **34**, 569 (1959).
19. G. Williamson and A. Cervenka, "Characterization of Low-Density Polyethylene by GPC. II. The Drott Method Using Fractions," *Eur. Polym. J.*, **10**, 295 (1974).
20. T. Hama, K. Yamaguchi, and T. Suzuki, "Long-Chain Branching and Solution Properties of Low-Density Polyethylene," *Makromol Chem.*, **155**, 283 (1972).
21. G. C. Berry and E. F. Casassa, "Thermodynamic and Hydrodynamic Behavior of Dilute Polymer Solutions," *J. Polym. Sci. D, Macromol. Rev.*, **4**, 1 (1970).
22. M. Kurata, H. Okamoto, M. Iwama, M. Abe, and T. Homma, "Randomly Branched Polymers. II. Computer Analysis of the Gel-Permeation Chromatogram," *Polym. J.*, **3**, 739 (1972).
23. V. Grinshpun, A. Rudin, K. E. Russel, and M. V. Scammell, "Long-Chain Branching Indexes from SEC of Polyethylenes," *J. Polym. Sci., Polym. Lett. Ed.*, **24**, 1171 (1986).
24. D. C. Bugada and A. Rudin, "Sizes of Long Branches in Low-Density Polyethylenes," *J. Appl. Polym. Sci.*, **33**, 87 (1987).
25. E. E. Drott and R. A. Mendelson, "Determination of Polymer Branching with GPC. I. Theory," *J. Polym. Sci. Part A2*, **8**,1361, 1373 (1970).
26. L. Westermann and J. C. Clark, "Low-Density Polyethylene: Variation of Branching Frequency with Molecular Weight and Its Influence on Molecular Weights as Determined by GPC," *J. Polym. Sci., Phys. Ed.*, **11**, 559 (1973).
27. F. H. Mirabella and L. Wild, "Determination of Long-Chain Branching Distributions of Polyethylenes by Combined Viscometry SEC Technique," *Am. Chem. Soc. Polym. Mater. Sci. Eng. Div. Prepr.*, **59**, 7 (1988).
28. M. Hert and C. Strazielle, "Study of the Branching Structure of Low-Density Polyethylene by Viscosity and Light Scattering Measurements on Fractions from GPC," *Makromol. Chem.*, **184**, 135 (1983).
29. R. Dietz and M. A. Francis, "Characterization of Long-Chain Branching in Poly (vinyl acetate): A Comparison of Two Methods," *Polymer*, **20**, 450 (1979).
30. H. Voelker and F. J. Luig, "Long-Chain Branching in Polyethylenes," *Angew. Makromol. Chem.*, **12**, 43 (1970).
31. K. Yamamoto, "An Analytical Method for Long-Chain Branching in Free-Radical Polymerization of Ethylene," *J. Macromol. Sci. Chem.*, **A17**, 415, (1982).
32. S. Shiga, "Modern Characterization of Long-Chain Branching," *Polym. Plast Technol. Eng.*, **28**, 17 (1989).

33. D. Constantin, "Coupling of GPC and Automatic Viscometry. Application to the Study of Long-Chain Branched Polyethylene," *Eur. Polym. J.*, **13**, 907 (1977).

34. D. Lecacheux, J. Lesec, and C. Quivoron, "Characterization of Branched Polyolefins by Coupling High-Speed GPC with a High Temperature Viscometer," *Am. Chem. Soc. Polym. Div. Prepr.*, **23**(2), 126 (1982).

35. A. Rudin, "Molecular Weight Distributions in Free Radical Polymerizations," *Makromol. Chem., Macromol. Symp.*, **10/11**, 273 (1987).

36. V. Grinshpun, K. F. O'Driscoll, and A. Rudin, "On the Accuracy of SEC Analysis of Molecular Weight Distributions of Polyethylene," *J. Appl. Polym. Sci.*, **29**, 1071 (1984).

37. O. Prochazka and P. Kratochvil, "Analysis of the Accuracy of Determination of Molar Mass Distribution by GPC with On-line Light-Scattering Detector," *J. Appl. Polym. Sci.*, **31**, 919 (1986).

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The Dimensions of Chain Molecules Containing Branches and Rings

32

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Formulas for the mean square radii of various branched and ringed polymer molecules are developed under the usual assumptions regarding the statistics of chain configuration. For branched molecules, the mean square radii vary less rapidly with molecular weight than for strictly linear molecules, while for systems containing only rings and unbranched chains the variation is more rapid than for the linear case. These results show that in principle the quantity of branches or of rings can be determined from light-scattering measurements.

I. INTRODUCTION

It is well known that no quantitative methods of determining the presence of branching in a high polymer chain molecule are now in use. Recently, however, it has been shown that the light-scattering phenomenon may be employed to measure the mean square radius of a molecule.[1–3]

The purpose of this paper is to calculate the mean square radii of molecules containing branches and rings in order to develop a method of demonstrating the presence or absence of such structures. It has been known for some time that the mean square of the distance between any two points on a flexible polymer chain is proportional to the number of segments between these points, as long as certain assumptions hold. It will be shown that as long as this proportionality exists, the calculation of the mean square radius of branched molecules is not a difficult matter.

The most significant and questionable assumption involved here is the neglect of what has been called the "volume effect," i.e., the prohibition of configurations of the chain in which two segments occupy the same position.

Fortunately there is at least one way out of the difficulty. Since the bonds in polymer chains are generally rather stiff, a collision of two segments of the same chain is only likely to occur if the loop between the segments is large compared to the segments. Consider now that around one of the segments a sphere is described, whose diameter is several times the diameter of the segment but much less than that of the loop. Unless there are attractive forces between the segments, the second segment will be less likely to lie inside the circumscribed sphere than it would in an equal volume outside, because of the volume excluded in the sphere by the first segment. But if there are attractive forces between the segments, over and above those normally existing between segments and solvent, the probability of the second segment lying in the sphere may be increased again. In fact, the probability may become equal to what it would be in an equal neighboring volume which does not include a segment initially. In this condition, therefore, the volume effect may properly be neglected.

It has also been shown[4] that when the probability of occupancy of a region by a segment is independent of the possible previous presence of another segment in the region, the "second virial coefficient" (A_2 below) in the power series expansion of the osmotic pressure of the solution vanishes. That is, when A_2 in the expression for the osmotic pressure, π, in terms of concentration, c,

$$\pi = A_1c + A_2c^2 + A_3c^3 + \cdots,$$

is zero, the volume effect may be neglected in the calculation of the mean square radius of the molecule.[4a]

Of course, further investigation may show that the volume effect may also be negligible under other circumstances as well. In any case, it will be omitted in the following calculations.

II. PRELIMINARY OPERATIONS

Chain molecules may generally be divided, in a more or less arbitrary way, into small units which by repetition may be considered to generate the chain. Such units will be called *segments*. While most of these segments will be attached to only one or two others, certain ones may be attached to three or more. Such segments will be termed *branch units*. The number of segments attached to a branch unit will be called the *functionality* of the branch unit.

In a chain molecule we may select a certain segment for particular attention, referring to it as the *reference segment*. Let the vector to some other segment, e.g., the i'th segment, from the reference segment be $\mathbf{x}_i$, while the vector from the center of mass of the molecule to

[1] P. Debye, J. Phys. Coll. Chem. 51, 18 (1947).
[2] Doty, Affens, and Zimm, Trans. Faraday Soc. 42B, 66 (1946).
[3] B. H. Zimm, J. Chem. Phys. 16, 1099 (1948).
[4] B. H. Zimm, Polymer Bull. 1, 53 (1945); J. Chem. Phys. 14, 164 (1946).
[4a] Since the above was written, an interesting discussion of the volume effect has been presented by P. J. Flory, J. Chem. Phys. 17, 303 (1949). But the point that the volume effect becomes zero when A_2 is zero does not appear in his discussion, apparently because of the particular statistical method he used.

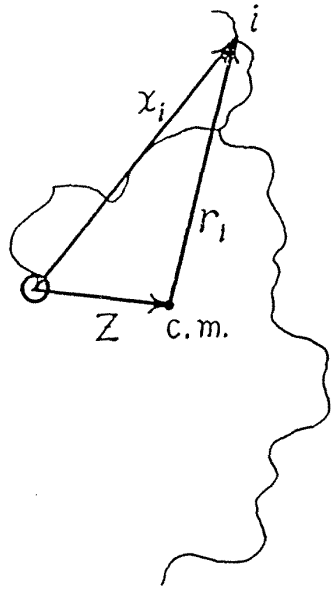


FIG. 1. Relations between the reference segment (circle), the center of mass (c.m.), and an arbitrary segment i of a chain molecule.

the i'th segment is $\mathbf{r}_i$. In particular, let the vector *from* the reference segment *to* the center of mass be $\mathbf{Z}$, so that

$$\mathbf{r}_i=\mathbf{x}_i-\mathbf{Z}. \tag{1}$$

These relations are indicated in Fig. 1.

We may now establish a useful lemma. The definition of the $\mathbf{r}_i$ as vectors to the center of mass requires that their sum be zero:

$$\sum\mathbf{r}_i=0, \tag{2a}$$

or alternatively this may be written,

$$\mathbf{Z}=(1/N)\sum\mathbf{x}_i \tag{2b}$$

$$Z^2=(1/N^2)\sum_i\sum_j\mathbf{x}_i\cdot\mathbf{x}_j, \tag{2c}$$

if N is the total number of segments in the molecule. Now from Eqs. (1) and (2a) the following relations succeed:

$$\begin{aligned}(1/N)\sum r_i^2&=(1/N)\sum(\mathbf{r}_i+\mathbf{Z})\cdot\mathbf{r}_i\\&=(1/N)\sum\mathbf{x}_i\cdot(\mathbf{x}_i-\mathbf{Z}).\end{aligned}$$

Combination with Eqs. (2b) and (2c) produces the desired lemma:

$$(1/N)\sum r_i^2=(1/N)\sum x_i^2-(1/N^2)\sum_i\sum_j\mathbf{x}_i\cdot\mathbf{x}_j. \tag{3a}$$

Again, since $\mathbf{x}_i\cdot\mathbf{x}_j=(x_{ij}^2-x_i^2-x_j^2)/2$, where $\mathbf{x}_{ij}=\mathbf{x}_i-\mathbf{x}_j$, it can be shown that

$$(1/N)\sum r_i^2=(1/2N^2)\sum_i\sum_j x_{ij}^2, \tag{3b}$$

an alternative form of the lemma.

If the chain is flexible, it may assume many configurations. Without considering further, for the moment, the nature of these, we shall assume that it is possible to average functions of the several defined vectors over the configurations, indicating the process by angular brackets with a subscript Av. In particular,

$$\langle\mathbf{A}\cdot\mathbf{x}_i\rangle_{Av}=\langle\mathbf{A}\cdot\mathbf{r}_i\rangle_{Av}=\langle\mathbf{A}\cdot\mathbf{Z}\rangle_{Av}=0,$$

where A is any constant vector (assumption of isotropy). Also we shall assume that the chain is so flexible that the average of the scalar product of two chain vectors which end in the same segment vanishes,

$$\langle(\mathbf{x}_i-\mathbf{x}_j)\cdot(\mathbf{x}_j-\mathbf{x}_k)\rangle_{Av}=0, \tag{4a}$$

provided that j lies on a chain connecting i and k, *and provided that* there are no other chains connecting i and k. As corollaries we obtain:

$$\langle\mathbf{x}_i\cdot(\mathbf{x}_i-\mathbf{x}_j)\rangle_{Av}=0, \tag{4b}$$

$$\langle\mathbf{x}_i\cdot\mathbf{x}_j\rangle_{Av}=\langle x_i^2\rangle_{Av}, \tag{4c}$$

if segment i lies on the chain connecting segment j and the reference segment, and

$$\langle\mathbf{x}_i\cdot\mathbf{x}_j\rangle_{Av}=0, \tag{4d}$$

if the reference segment lies on the chain connecting i and j.

We may now define R^2, the mean square radius of the molecule, as

$$R^2=(1/N)\sum_i\langle r_i^2\rangle_{Av}. \tag{5}$$

Likewise a quantity X^2 may be defined as

$$X^2=(1/N)\sum_i\langle x_i^2\rangle_{Av}. \tag{6}$$

Now returning to Eqs. (3a) and (3b), it is seen their averages may be written in terms of R^2 and X^2:

$$R^2=X^2-\langle Z^2\rangle_{Av} \tag{7a}$$

$$R^2=(1/2N^2)\sum_i\sum_j\langle x_{ij}^2\rangle_{Av}. \tag{7b}$$

In the first equation the mean square radius, R^2, is expressed as the mean square distance, X^2, of the rest of the chain from a reference segment, less the mean square distance, $\langle Z^2\rangle_{Av}$, of that segment from the center of mass. This form is particularly useful for branched molecules, where one of the branch units may be taken as the reference segment.

The latter Eq. (7b) is more useful in treating rings, in which $\langle Z^2\rangle_{Av}$ is not as simply evaluated.

We may further observe that if the reference segment is a branch unit, from which grow several branches of M_ν segments each (where ν is the distinguishing index of the branch), $\langle Z^2\rangle_{Av}$ and X^2 may be given as sums of parts, X_ν^2 and $\langle Z^2\rangle_{Av}$, one from each branch:

$$X^2=(1/N)\sum_\nu M_\nu X_\nu^2, \tag{8a}$$

$$\langle Z^2\rangle_{Av}=(1/N^2)\sum_\nu M_\nu^2\langle Z_\nu^2\rangle_{Av}. \tag{8b}$$

The latter relation follows particularly from Eq. (2c) combined with Eq. (4d).

Finally, if the chains are reasonably flexible, the usual proportionality will hold between $\langle x_i^2\rangle_{Av}$ and n_i, the number of segments between the reference segment and the i'th segment:

$$\langle x_i^2\rangle_{Av}=b^2n_i. \tag{9}$$

The quantity b is determined by the detailed structure of the chain, especially the length and flexibility of its bonds.[5]

III. CALCULATIONS FOR BRANCHED MOLECULES CONTAINING NO RINGS

III.1. Linear Chains

We first consider the[4,6a] case of linear chains, i.e., those with no branch units. This problem has been studied before but it is included here as an introduction to the more complicated cases.

Let the reference segment be one of the end segments of the chain. Using Eqs. (6) and (9), we obtain

$$X^2=(b^2/N)\sum_1^N n_i,$$

where $n_i=i$. Recognizing that

$$\sum_1^N i=N(N+1)/2,$$

the result is

$$X^2=b^2N/2. \tag{10}$$

Terms of order unity have been dropped.

Now using successively Eqs. (2c), (4c), and (9), we obtain

$$\langle Z^2\rangle_{Av}=(2b^2/N^2)\sum_1^N (N-n_i)n_i,$$

where $n_i=i$. Again recognizing that

$$\sum_1^N i^2=N(N+1)(2N+1)/6,$$

and dropping terms of order unity, the result is:

$$\langle Z^2\rangle_{Av}=b^2N/3. \tag{11}$$

Combination of these results according to Eq. (7a) yields R^2;

$$R^2=b^2N/6. \tag{12}$$

It may be noted that R^2 is just one-sixth of the mean square end-to-end length of the chain, b^2N.

[5] See Wm. J. Taylor, J. Chem. Phys. 15, 412 (1947); 16, 257 (1948). References to previous work are given in these papers.

[6] P. Debye, J. Chem. Phys. 14, 636 (1946).

[6a] A closely related study has been made by H. A. Kramers, J. Chem. Phys. 14, 415 (1946).

III.2. Chains of One Branch Unit

We will let the functionality of the branch unit, i.e., the number of branches that grow from it, be f. The number of segments in the ν'th chain growing from it will be N_ν, with ν an index running from one to f, and

$$\sum_1^f N_\nu=N.$$

By Eqs. (10) and (8a), the value of X^2 is

$$X^2=(b^2/2N)\sum_\nu N_\nu^2. \tag{13}$$

Likewise, by Eqs. (11) and (8b), the value of $\langle Z^2\rangle_{Av}$ is

$$\langle Z^2\rangle_{Av}=(b^2/3N^2)\sum_\nu N_\nu^3. \tag{14}$$

Finally by Eq. (7a), R^2 is found:

$$R^2=(b^2/N)\sum_\nu[(N_\nu^2/2)-(N_\nu^3/3N)]. \tag{15}$$

For convenience, we symbolize by g the ratio of R^2 of the branched molecule to that for a linear molecule, $b^2N/6$. Thus:

$$g=\sum_\nu[(3N_\nu^2/N^2)-(2N_\nu^3/N^3)]. \tag{15a}$$

III.3. Chains of Two Branch Units

Before attacking the main problem, it is necessary to find X^2 and Z^2 for a chain of one branch unit, when the unattached terminal segment of one of the chains is chosen as the reference segment.

Let the molecule be described otherwise as above, but with the reference segment at the outer end of chain one, of length N_1; assign the segments of chain one numbers in increasing order from the reference segment toward the branch unit, and assign those of the other chains numbers, i, in order outward from the branch unit. Let M be the total number of segments. Then by Eq. (9),

$$\begin{aligned}\langle x_{i,\nu}^2\rangle_{Av}&=b^2(N_1+i_\nu) \quad (\nu\neq 1)\\ &=b^2i_1 \quad (\nu=1).\end{aligned}$$

$$\begin{aligned}X^2&=\frac{1}{M}\sum_1^f\sum_1^{N_\nu} i_\nu\langle x_{i,\nu}^2\rangle_{Av}\\ &=\frac{b^2}{M}\left[\sum_1^f\frac{N_\nu^2}{2}+N_1\sum_2^f N_\nu\right].\end{aligned} \tag{16}$$

Since R^2 has already been shown to be given by Eq. (15), $\langle Z^2\rangle_{Av}=X^2-R^2$ can be found:

$$\langle Z^2\rangle_{Av}=\frac{b^2}{M}\left[\sum_1^f\frac{N_\nu^3}{3M}+N_1\sum_2^f N_\nu\right]. \tag{17}$$

It is now possible to proceed to the case of two branch units. Here we will designate the two branch units by

a and b, and their functionalities by f_a and f_b. The indices of the linear branches growing from a will be ν_a, and those from b, ν_b; the index of the chain connecting the two units will be ab.

Let us consider branch unit a as the reference segment. There will be f_a-1 linear branches, whose X^2 and $\langle Z^2\rangle_w$ are given by Eqs. (10) and (11), and one ramified branch, which includes unit b, and whose X^2 and $\langle Z^2\rangle_w$ are given by Eqs. (16) and (17). These may all be combined by Eqs. (8a) and (8b), yielding the following:

$$g=\frac{6R^2}{b^2N}=6\Big[\sum_{\text{all chains}}\Big(\frac{N_\nu^2}{2}-\frac{N_\nu^3}{3N}\Big)+6\Big(1-\frac{N_{ab}+\sum_{\nu b}N_{\nu b}}{N}\Big)N_{ab}(\textstyle\sum_{\nu b}N_{\nu b})\Big]$$
$$=6\Big[\sum_{\text{all chains}}\Big(\frac{N_\nu^2}{2}-\frac{N_\nu^3}{3N}\Big)+6\frac{N_{ab}}{N}(\sum_1^{f_a-1}N_{\nu a})(\sum_1^{f_b-1}N_{\nu b})\Big]. \quad (18)$$

III.4. Chains of Three Branch Units

In any molecule of three branch units and containing no rings, one of the three units must be unique in that it is connected to both the other two. We will designate this unit as unit a, the others as b and c. The chains connecting a with b and c will be designated ab and ac; the remaining symbols will be obvious extensions of the preceding ones.

If the reference segment is taken as branch unit a, the present case differs from the preceding one only in that there are two ramified branches and f_a-2 linear branches on the reference segment.

As a result, the ratio, g, is immediately found to be

$$g=\frac{6R^2}{b^2N}=6\Big[\sum_{\text{all chains}}\Big[\Big(\frac{N_\nu^2}{2}\Big)-\Big(\frac{N_\nu^3}{3N}\Big)\Big]+N_{ab}\Big(1-\frac{N_{ab}+\sum_{\nu b}N_{\nu b}}{N}\Big)(\textstyle\sum_{\nu b}N_{\nu b})+N_{ac}\Big(1-\frac{N_{ac}+\sum_{\nu c}N_{\nu c}}{N}\Big)(\textstyle\sum_{\nu c}N_{\nu c})\Big],$$
$$=6\Big[\sum_{\text{all chains}}\Big[\Big(\frac{N_\nu^2}{2}\Big)-\Big(\frac{N_\nu^3}{3N}\Big)\Big]+\frac{N_{ab}}{N}(\sum_1^{f_a-2}N_{\nu a}+\sum_1^{f_c-1}N_{\nu c}+N_{ac})(\sum_1^{f_b-1}N_{\nu b})+\frac{N_{ac}}{N}(\sum_1^{f_a-2}N_{\nu a}+\sum_1^{f_b-1}N_{\nu b}+N_{ab})(\sum_1^{f_c-1}N_{\nu c})\Big]. \quad (19)$$

This kind of process could be extended stepwise to more and more complicated molecules. It does not seem desirable to carry it further here, since the general formulas become excessively unwieldy. Specific cases of four and five branch units will be treated below.

However, before proceeding we should recognize that pure samples of molecules all with the same definite chain lengths seldom occur in practice. To apply these formulas to actual materials, therefore, it is required that averages be made over the varying chain lengths. We are thus led to consider the following topic.

III.5. Materials With Branch Units Distributed at Random

Any real polymeric material will have a characteristic distribution of chain lengths, number of branch units per molecule, distribution of branch units in the molecule, and so on, which will usually depend on the chemical process that creates the material. For many materials these distributions are still a matter of surmise, although in some special cases they have been studied.[7,8] It would be premature in any case to calculate the average R^2 of materials of all the possibly important distributions. Therefore we study only an idealized example, which may, however, not be so different from actuality as to be useless.

For the beginning it will be assumed that the material is of uniform molecular weight, with a given number, p, of branch units per molecule, but that all possible arrangements of chains of varying lengths occur with equal frequency. More specifically, if it is assumed that each chain of the molecule is labeled, and the "arrangement" of the molecule is defined by the number of segments in each chain, all arrangements with the correct total number of segments are considered to be equally probable.

The process of averaging the expressions for R^2 over the different arrangements then consists of summing the values of R^2 of all the possible arrangements and dividing by the total number of arrangements. When integration is substituted for summation, the general formula for the average of R^2 becomes:

$$\langle R^2\rangle_w=\frac{\int_0^N dn_{\Omega-1}\int_0^{N-n_{\Omega-1}}dn_{\Omega-2}\cdots\int_0^{N-\Sigma_2^{\Omega-1}n_\nu}R^2dn_1}{\int_0^N dn_{\Omega-1}\cdots\int_0^{N-\Sigma_2^{\Omega-1}n_\nu}dn_1} \quad (20)$$

Ω is the total number of chains in the molecule.

[7] P. J. Flory, Chem. Rev. 39, 137 (1946); for experiments relating to the problem of this paper, see J. R. Schaefgen and P. J. Flory, J. Am. Chem. Soc. 70, 2709 (1948).

[8] W. H. Stockmayer, J. Chem. Phys. 11, 45 (1943).

By elementary integrations it is found that for molecules of N segments in Ω chains,

$$\langle N_\nu^x\rangle_w = \frac{x!(\Omega-1)!}{(\Omega+x-1)!}N^x \tag{21a}$$

$$\langle N_\mu^x N_\nu^y\rangle_w = \frac{x!y!(\Omega-1)!}{(\Omega+x+y-1)!}N^{x+y} \tag{21b}$$

$$\langle N_\lambda^x N_\mu^y N_\nu^z\rangle_w = \frac{x!y!z!(\Omega-1)!}{(\Omega+x+y+z-1)!}N^{x+y+z}. \tag{21c}$$

For molecules of one branch unit of functionality f, use of these equations on the previous result, Eq. (15), gives:

$$g = \frac{6\langle R^2\rangle_w}{b^2N} = \frac{6f}{(f+1)(f+2)}. \tag{22}$$

Likewise, if we consider molecules containing two branch units, each of functionality f, the result from Eq. (18) is

$$g = \frac{6\langle R^2\rangle_w}{b^2N} = \frac{3(5f^2-6f+2)}{f(4f^2-1)}. \tag{23}$$

If there are three branch units the result from Eq. (19) is

$$g = \frac{6\langle R^2\rangle_w}{b^2N} = \frac{2(13f^2-20f+8)}{f(9f^2-9f+2)}. \tag{24}$$

As a partial check on the work, we observe that all three formulas reduce to the value unity for the linear molecule when $f=1$ or 2.

III.6. Molecules with Four and Five Tri-Functional Branch Units

The preceding may be extended without much trouble to molecules containing four or five branch units. Considering that the results will be of interest principally when the units are tri-functional, the discussion will be restricted to these with some gain in simplicity.

It is first necessary to find X^2 and $\langle Z^2\rangle_w$ for a form with two branch units, when one terminal segment is considered as the reference segment. Let the form be represented as in Fig. 2*a*, with the individual chains indexed as shown. Then the individual $\langle x_{i\nu}^2\rangle_w$, where i is the index of a segment and ν is the index of the chain, will be given by the following:

$$\begin{aligned}\langle x_{i\nu}^2\rangle_w &= b^2(N_1+N_3+i_\nu); && \nu=4,5,\\ &= b^2(N_1+i_\nu); && \nu=2,3,\\ &= b^2 i_1; && \nu=1.\end{aligned} \tag{25}$$

Then X^2, which is equal to $\sum_\nu^5 \sum_{i_\nu}^{N_\nu} \langle x_{i\nu}^2\rangle_w / M$ where M is the total number of segments, will be given by the expression:

$$\langle X^2\rangle_w = \frac{b^2}{M}\left[\sum_{\text{all chains}}\frac{N_\nu^2}{2} + N_1(N_2+N_3) + (N_1+N_3)(N_4+N_5)\right]. \tag{26}$$

Since R^2 is already known, Eq. (18), $\langle Z^2\rangle_w$ is soon found from $\langle Z^2\rangle_w = X^2 - R^2$;

$$\langle Z^2\rangle_w = \frac{b^2}{M^2}\left[\sum_{\text{all chains}}\frac{N_\nu^3}{3} + MN_1(M-N_1) + MN_3(N_4+N_5) - N_3(N_1+N_2)(N_4+N_5)\right]. \tag{27}$$

From consideration of the averages given by Eqs. (21a, 21b, 21c), and by means of Eqs. (7a), (26), and (27), it may be seen that in any molecule of Ω chains each doubly ramified (d.r.) branch will contribute

$$b^2N\left[\frac{6\Omega-26-(\Omega-5/\Omega-3)}{\Omega(\Omega+1)(\Omega+2)}\right] \tag{28}$$

to $\langle R^2\rangle_w$, over and above what its five chains contribute individually, Eq. (30).

Likewise, each singly ramified (s.r.) branch will contribute

$$b^2N\left[\frac{2\Omega-6}{\Omega(\Omega+1)(\Omega+3)}\right], \tag{29}$$

by virtue of Eqs. (21) applied to Eqs. (16) and (17).

In addition every chain wherever located in the molecule contributes the quantity:

$$b^2N/(\Omega+1)(\Omega+2). \tag{30}$$

Linear branches contribute nothing further.

It now follows that $\langle R^2\rangle_w$ can be found by adding the above contributions for any molecule that can be analyzed into one branch unit bearing linear, singly ramified, or doubly ramified branches, if all the branch units are trifunctional. All molecules of four and five trifunctional branch units may be analyzed in this way.

Two types of molecules containing four branch units exist, a "normal" form and an "iso" form, as illustrated in Figs. 2*b* and 2*c*. The "normal" form may be thought of as a branch unit bearing one d.r., one s.r., and one linear branch. There are nine chains ($\Omega=9$). Adding Eqs. (28), (29), and nine times Eq. (30) yields $\langle g\rangle_w$:

$$g = \frac{6\langle R^2\rangle_w}{b^2N} = \frac{361}{495}. \tag{31}$$

The second kind of molecule of four branch units, the "iso"-form, consists of a branch unit bearing three s.r. branches. Again Ω is nine. Adding three times Eq.

(29) and nine times Eq. (30), we find,

$$g=\frac{6\langle R^2\rangle_w}{b^2N}=\frac{117}{165}, \tag{32}$$

somewhat smaller than for the "normal" form.

The ratio of abundance of the normal- and iso-forms of the molecule of four branch units in any material will depend on the nature of the polymerization reactions. If all molecules of four branch units are formed by the irreversible addition of single branch units to chain-ends of molecules of three units, the normal form should be just four times as abundant as the iso-form. If the reaction is reversible, or if molecules of four branch units can also form by combination of two molecules of two units each, a somewhat different ratio of isomers[7,8] obtains. This latter case is discussed fully in the next section. A chain transfer reaction acting on the middle of the chains of a previously formed three-unit molecule would also favor the normal form, though by a still different ratio.

In molecules with five trifunctional branch units, there also exist two structural isomers, as illustrated in Figs. 2d and 2e. Again, the proportions of these isomers will depend on the polymerization mechanism. The "normal" form of the five-unit molecule may be analyzed as a branch unit bearing two d.r. branches and a linear branch. The number of chains, Ω, is 11; g may be found as described above.

$$g=399/572. \tag{33}$$

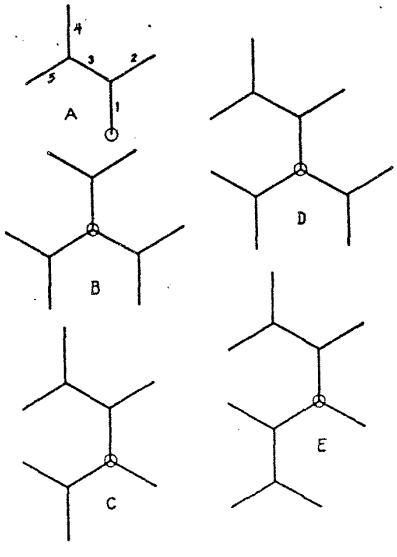


FIG. 2. Types of branched molecules: *A*, doubly ramified (d.r.) branch; *B*, "iso"-form and *C*, "normal" form of molecule of four branch units; *D*, "iso"-form and *E*, "normal" form of molecule of five branch units. Reference segment circled in each case.

The "iso"-form of the five-unit molecule contains two s.r. branches and a d.r. branch, with $\Omega=11$:

$$g=766/1144. \tag{34}$$

III.7. Highly Branched Molecules: Heterogeneous Systems

For treating still more highly branched molecules and heterogeneous polymeric mixtures, the method of the preceding sections becomes unwieldy. An alternative approach, based on a theorem of Kramers,[6a] is more powerful in dealing with such cases, some of which are considered below.

The Kramers theorem may be stated as follows: Consider a polymeric molecule containing any number of branches but no rings, and consisting in all of N segments. Imagine cutting the molecule at one segment into two fragments of N_1 and $N_2(=N-N_1)$ segments respectively. Then the mean square radius of the molecule is given by

$$R^2/b^2=\langle N_1N_2\rangle_w/N \tag{35}$$

where the average in the second member is taken over all possibilities of cutting.* In other words, the contribution of any segment to $\sum\langle r_i^2\rangle_w$ is given by the quantity $b^2N_1N_2/(N_1+N_2)$ for that segment. For heterogeneous systems, the average is taken over all segments, yielding *weight-* or *z-average* values of R^2.[8a] In general, we have

$$\langle g\rangle_w=\langle R^2\rangle_w/\langle R^2\rangle_w^0=6\langle N_1N_2/N\rangle_w/\langle N\rangle_w \tag{36a}$$

and

$$\langle g\rangle_z=\langle R^2\rangle_z/\langle R^2\rangle_z^0=6\langle N_1N_2\rangle_w/\langle N^2\rangle_w. \tag{36b}$$

* The derivation of this theorem is briefly as follows: For any molecule, Σr_i^2 may be expressed as a quadratic form $b^2\sum_j\sum_k\lambda_{jk}(\sigma_j\cdot\sigma_k)$, where σ_j is a unit vector along the jth bond and the λ_{jk} are numerical coefficients. Closely related is the relative kinetic energy with respect to the center of mass, given by $m\sum\dot r_i^2/2=mb^2\sum_j\sum_k\lambda_{jk}(\dot\sigma_j\cdot\dot\sigma_k)/2$ where m is the mass per chain atom. Consider now a special instantaneous phase of the molecular motion such that the relative kinetic energy happens to be simply $(mb^2/2)\lambda_{jj}(\dot\sigma_j)^2$: this would be the case if only the jth link were rotating, all others performing translations only. But then the relative kinetic energy is equal to that of a rotating diatomic molecule with masses mN_1 and mN_2 connected by a rod of fixed length b, and this equality gives $\lambda_{jj}=N_1N_2/N$. Now if the molecule contains no rings, $\langle\sigma_j\cdot\sigma_k\rangle_w=\delta_{jk}$ for flexible chains, and hence $R^2/b^2=\sum_j\lambda_{jj}/N=\langle N_1N_2\rangle_w/N$. Kramers used similar arguments to determine λ_{jk} which is needed for the treatment of rings (see Section V) by this method.

[8a] This usage implies an extension of the common definition of weight average. If ν_N is the number of molecules of N segments in the system, and y is a quantity whose average is to be taken, then the weight average of y is defined as

$$\langle y\rangle_w=\Sigma\nu_NNy/\Sigma\nu_NN.$$

However, since $\Sigma\nu_NN$ is the total number of segments in the system, $\langle y\rangle_w$ may also be written

$$\langle y\rangle_w=\Sigma_{\text{all segments}}\,y/\Sigma\nu_NN,$$

provided that y may be considered as a property of the individual segments. Likewise, the "z-average," $\langle y\rangle_z$, may be written

$$\langle y\rangle_z=\Sigma\nu_NN^2y/\Sigma\nu_NN^2,$$

or alternatively

$$\langle y\rangle_z=\Sigma_{\text{all segments}}\,Ny/\Sigma\nu_NN^2.$$

Where the subscripts w denote weight averages (i.e., over all segments), and the subscripts z denote z-averages. The second of these quantities is pertinent for values of $\langle R^2\rangle_w$ derived from measurements of light scattering. However, this implies that the z-average molecular weight of the sample is known independently, and such is rarely the case. Probably a more common situation would restrict the measurements to $\langle R^2\rangle_z$ and $\langle N\rangle_w$ for a given polymer sample. In this case, the quantity obtainable from the experiments would be

$$6\langle R^2\rangle_z/b^2\langle N\rangle_w=\langle g\rangle_z\langle N^2\rangle_w/\langle N\rangle_w^2=\langle g\rangle_z\langle N\rangle_z/\langle N\rangle_w. \quad (36c)$$

Of course, if fractions of a single molecular weight are involved, the distinction between these various g's becomes unimportant.

In this section, Eqs. (36) will be applied to randomly branched polymers containing branch units of any single functionality f, with the aid of distribution theory previously given.[7,8] By specializing to the case of uniform molecular weight and a uniform number of branches per molecule, we obtain an expression reducing to Eqs. (22)–(24) for molecules of one, two, and three branch units, and corresponding to special proportions of the structural isomers for more highly branched species.

To calculate $\langle N_1N_2/N\rangle_w$, we require the probability that a randomly chosen segment is connected to N_1 segments at one end and to N_2 at the other. But since this probability depends on the frequency of branching, we must first find the chance P_i that one end of the segment is connected to a network of i branch units. For random distribution of branches and chain lengths, it is found in Appendix B that

$$P_i=(1-\alpha)\beta^i\frac{(fi-i)!}{i!(fi-2i+1)!}, \quad (37)$$

where α is Flory's branching probability[7] and $\beta=\alpha(1-\alpha)^{f-2}$.

Now this network of i branch units consists of $\Omega=fi-i+1$ chains. If it contains N_1 segments, these can be distributed among the chains in $\binom{N_1-1}{\Omega-1}$ ways. For long chains, $\Omega\ll N_1$ and approximately $\binom{N_1-1}{\Omega-1}\cong N_1^{fi-i}/(fi-i)!$. Also, for chains randomly distributed in length, the chance that the νth chain has x_ν segments is $(1-q)q^{x_\nu-1}$, where q is the probability of continuation of the chain. Hence, the chance that one end of a chosen segment is connected to a network of $N_1(=\sum x_\nu)$ segments carrying i branch units is

$$P_i\frac{N_1^{fi-i}}{(fi-i)!}q^{N_1}[(1-q)/q]^{fi-i+1}.$$

Then the chance that simultaneously the other end of the chosen segment is connected to a network of N_2 segments and j branch units is

$$Q(N_1,N_2,i,j)=P_iP_j\frac{N_1^{fi-i}N_2^{fj-j}q^{N_1+N_2}[(1-q)/q]^{fi+fj-i-j+2}}{(fi-i)!(fj-j)!}. \quad (38)$$

On substituting for P_i and P_j from Eq. (37), this becomes

$$Q(N_1,N_2,i,j)=(1-\alpha)^2\times\frac{\beta^{i+j}N_1^{fi-i}N_2^{fj-j}q^{N_1+N_2}[(1-q)/q]^{fi+fj-i-j+2}}{i!j!(fi-2i+1)!(fj-2j+1)!}. \quad (39)$$

This equation gives the required distribution over which the quantities $N_1N_2/(N_1+N_2)$ and $N=N_1+N_2$ must be averaged. For unfractionated systems, the sums run over all positive values of i, j, N_1 and N_2. For fractions of a given molecular weight N and a given number of branches n, the sums must be restricted to such values that $i+j=n$ and $N_1+N_2=N$. This latter case is considered first, in order to compare with the earlier results. For such fractions,

$$g_f(n)=\frac{6}{N}\frac{\sum_{i=0}^{n}\sum_{N_1=0}^{N}\left[\frac{N_1(N-N_1)}{N}\right]Q(N_1,N-N_1,i,n-i)}{\sum_{i=0}^{n}\sum_{N_1=0}^{N}Q(N_1,N-N_1,i,n-i)}$$

$$=\frac{3}{(f-1)n+3}\left[1+\sum_{i=1}^{n}(f-1)^i\prod_{i=0}^{j}\frac{n-i}{(f-1)n+2-i}\right], \quad (40)$$

details of summation being given in Appendix B. The sum in the last member appears irreducible. Specialization to $n=1$, 2, and 3 yields Eqs. (22)–(24). For higher values of n, as earlier stated, g_f corresponds to the special proportions of structural isomers subsisting in random polymers.

In Appendix B it is shown that at large values of n an asymptotic relation may be found for $g_f(n)$, of the form:

$$g_f(n)\doteq 3\left(\frac{\pi}{2(f-1)(f-2)n}\right)^{\frac{1}{2}}-\frac{2(6-f)}{(f-1)(f-2)n}. \quad (40a)$$

For f equal to three and four the following modifications represent $g_f(n)$ within the stated limits for n greater than five:

$$g_3(n)\doteq\tfrac{3}{2}(\pi/n)^{\frac{1}{2}}-5/2n \quad \text{(error}<3\text{ percent)} \quad (40b)$$

$$g_4(n)\doteq\tfrac{1}{2}(3\pi/n)^{\frac{1}{2}}-2/3n \quad \text{(error}<5\text{ percent)} \quad (40c)$$

We may note that, at large values of n, $g_f(n)$ tends to decrease as the reciprocal of the square root of n.

TABLE I. Mean square radii of branched molecules.

Number of branch units	Functionality of branch units	$g=6\langle R^2\rangle_w/b^2N$ Fixed equal chain lengths	Random distribution of chain lengths
0	(1 or 2)	1	1
1	3	0.778	0.900
	4	0.625	0.800
	8	0.344	0.533
2	3	0.712	0.829
	4	0.525	0.690
3	3	0.668	0.774
	4	0.496	0.618
4	3n*		0.729
	3i		0.709
	3e		0.728
	4e		0.567
5	3n		0.698
	3i		0.672
	3e		0.693
	4e		0.525
6	3e		0.663
	4e		0.493
7	3e		0.637
15	3e		0.504
	4e		0.345
50	3e		0.318

* n = "normal" form
i = "iso"-form
e = equilibrium mixture, Eq. (40).

For unfractionated polymers, we obtain, by similar methods

$$\langle g_f\rangle_w=\frac{6\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}\frac{N_1N_2}{N_1+N_2}Q(N_1,N_2,i,j)}{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}(N_1+N_2)Q(N_1,N_2,i,j)}=\frac{3(1-\alpha)^2[1-(f-1)\alpha]G_f(\alpha)}{(f-1)\beta^{3/(f-1)}},\tag{41}$$

where

$$G_f(\alpha)=\int_0^{\alpha}\frac{z^{(4-f)/(f-1)}dz}{[1-(f-1)z][1-z]^{3/(f-1)}}.$$

For arbitrary functionality, this result is intractable, but for the cases of major interest ($f=3$ or 4) the integrations are elementary. For these cases, Eq. (41) becomes

$$\langle g_3\rangle_w=\frac{3(1-2\alpha)}{\alpha}\left[\frac{1}{2}\left(\frac{1-\alpha}{\alpha}\right)^{\frac{1}{2}}\times\ln\left(\frac{(1-\alpha)^{\frac{1}{2}}+(\alpha)^{\frac{1}{2}}}{(1-\alpha)^{\frac{1}{2}}-(\alpha)^{\frac{1}{2}}}\right)-1\right],\tag{42}$$

and

$$\langle g_4\rangle_w=[(1-3\alpha)/2\alpha]\ln(1-\alpha/1-3\alpha),\tag{43}$$

These results are more conveniently expressed in terms of n_w, the weight-average number of branch units per molecule. With the relation[3] $\alpha=n_w/[2+(f-1)n_w]$, they become

$$\langle g_3\rangle_w=\frac{6}{n_w}\left[\frac{1}{2}\left(\frac{2+n_w}{n_w}\right)^{\frac{1}{2}}\ln\left(\frac{(2+n_w)^{\frac{1}{2}}+(n_w)^{\frac{1}{2}}}{(2+n_w)^{\frac{1}{2}}-(n_w)^{\frac{1}{2}}}\right)-1\right],\tag{44}$$

and

$$\langle g_4\rangle_w=(1/n_w)\ln(1+n_w),\tag{45}$$

the last equation being particularly simple in form.

These formulas are restricted in application to properties which depend directly on $\langle R^2\rangle_w$, such as intrinsic viscosity in the absence of the shielding effect (see Sect. IV.3.).

In other cases we may be interested in $\langle g_f\rangle_z$, the z-average value of g. Here we find

$$\langle g_f\rangle_z=\frac{6\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}N_1N_2Q(i,j,N_1,N_2)}{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}(N_1+N_2)^2Q(i,j,N_1,N_2)}=\frac{1-(f-1)\alpha}{1+[(f-1)(f-5)/3]\alpha}.\tag{41a}$$

In terms of n_w, this gives

$$\langle g_f\rangle_z=\frac{1}{1+(f-1)(f-2)n_w/6}$$

$$\langle g_3\rangle_z=1/(1+n_w/3)\tag{44a}$$

$$\langle g_4\rangle_z=1/(1+n_w).\tag{45a}$$

Also, we may note the equation,

$$\langle g_f\rangle_z\langle N\rangle_z/\langle N\rangle_w=\tfrac{3}{2}(1-\alpha)^2.\tag{41b}$$

IV. FINAL RESULTS FOR BRANCHED MOLECULES

In Table I are collected numerical results for several types of molecules, expressed in terms of the ratio $g=\langle R^2\rangle_M/\langle R^2\rangle_M^0$. As would be expected, the value of g decreases regularly as the number of branch units increases. Fortunately, the various structural isomers (for molecules with four or more branch units) have almost the same radii, so that even extreme assumptions concerning the proportions of these isomers would scarcely affect the results.

It is noteworthy that as many as five branch units introduced at random decrease $\langle R^2\rangle_M$ by only thirty percent, an effect which would also be achieved by reducing the weight of a linear molecule by the same

amount. One might infer that branching would have to be very extensive before such properties of the material as tensile strength would be significantly affected.

IV.1. Variation of R^2 in a Series of Homologous Fractions

A situation of interest arises when a material of heterogeneous molecular weight containing a proportion of randomly distributed branch units is fractionated. Let us suppose that the fractionation divides the material into a series of samples, each of a different but homogeneous molecular weight, but that the branch units are still randomly distributed.

The distribution of trifunctional branch units is known for fractions derived from polymers of the type considered in Section III.7. If the chains are long, the fraction w_n of molecules in the sample carrying n trifunctional branch units is given by

$$w_n=\frac{1}{I_2(y)}\frac{(y/2)^{2n+2}}{n!(n+2)!}, \tag{46}$$

with

$$y=2N\beta^3/(1-q).$$

In this equation, the symbols N, β, and q are those employed previously, and $I_k(y)=i^kJ_k(iy)$, a familiar type of Bessel function. The average number, m, of branch units per molecule is found to be

$$m=\sum nw_n=yI_3(y)/2I_2(y). \tag{47}$$

In the range of interest ($m<5$), m varies more rapidly than N, but less rapidly than N^2. To find $\langle g_3\rangle_w$ for fractions obeying Eq. (46), the sum $\sum g_3(n)w_n$ is required, where $g_3(n)$ is given by Eq. (40). Finding no closed sum formula, we have made numerical calculations in the range of interest. The results, among others, are included in Table II.

For highly branched samples (y and m large), m becomes asymptotically proportional to N, and the distribution function w_n resembles the simple Poisson formula $m^ne^{-m}/n!$ In order to investigate the dependence of $\langle g_3\rangle_w$ on the detailed form of w_n, calculations were also made on the assumption that the Poisson distribution obtains for *all* values of m. It is gratifying that at $m=1$ the Poisson distribution yields a value of $\langle g_3\rangle_w$ only 0.001 higher than that based on Eq. (46); and for $m\geq 2$ the agreement is exact in the third place. Thus, the values of $\langle g_3\rangle_w$ for fractions are not highly sensitive to the form of the distribution of branch units. Moreover, these values are only slightly different from those of $g_3(n)$ calculated from Eq. (40) with $n=m$, as is seen by comparison of Tables I and II. The latter circumstance is of course due to the approximate symmetry of w_n about its maximum. Similar results are found for the case of tetrafunctional branch units, with the use of the Poisson distribution.

In Table II, the calculations for fractions are summarized, values of $\langle g_3\rangle_w$ and $\langle g_4\rangle_w$ being shown in the third column. For convenience in plotting, the degree of polymerization is expressed in units of $N'=N/m$, the average number of segments in a sample whose molecules contain just one branch unit on the average. Thus, the fourth column gives $m\langle g\rangle_w=6\langle R^2\rangle_w/b^2N'$, a convenient magnitude proportional to $\langle R^2\rangle_w$. Log-log and semi-log plots of the resulting curves are shown in Figs. 3 and 4. In the former, the straight line of unit slope, to which all curves approach as m becomes small, is the plot for strictly linear molecules.

TABLE II. Mean square radius as function of average frequency of branch units with random branching.

Average number, m, of branch units per molecule	$\log_{10}m$	$\langle g\rangle_w$	$m\langle g\rangle_w$	$\log_{10}m\langle g\rangle_w$ $=\log\langle R^2\rangle_w+$const.
	A. Trifunctional branch units			
0.250	−0.602	0.976	0.244	−0.612
0.500	−0.301	0.953	0.477	−0.322
1.000	0.000	0.912	0.912	−0.040
2.000	0.301	0.840	1.680	+0.225
3.000	0.477	0.784	2.352	0.371
4.00	0.602	0.73	2.92	0.465
5.00	0.699	0.69	3.45	0.538
10.00	1.000	0.58	5.8	0.764
15.00	1.176	0.50	7.5	0.875
50.00	1.699	0.32	16.0	1.204
	B. Tetrafunctional branch units			
0.125	−0.903	0.976	0.122	−0.913
0.250	−0.602	0.953	0.238	−0.623
0.500	−0.301	0.910	0.455	−0.342
1.000	0.000	0.835	0.835	−0.078
2.00	0.301	0.70	1.40	+0.146
3.00	0.477	0.62	1.86	0.270
6.00	0 778	0.49	2.94	0.468
15.00	1.176	0.35	5.25	0.720

It has also been found that these results may be represented, with a maximum error of less than two percent, by the relations

$$\langle g_3(m)\rangle_w=[(1+m/7)^{\frac{1}{2}}+4m/9\pi]^{-1} \tag{47a}$$

$$\langle g_4(m)\rangle_w=[(1+m/6)^{\frac{1}{2}}+4m/3\pi]^{-1}. \tag{47b}$$

These formulas have the correct asymptotic behavior at large m, in accordance with Eqs. (40b) and (40c).

IV.2. A Method of Detecting Branching

The curves of Figs. 3 and 4 suggest an experimental method of detecting the presence of branching in a material. The material could be fractionated, on the basis of molecular weight, into a series of samples, and the relative degree of polymerization and mean square radius, $\langle R^2\rangle_w$, of each fraction measured by light scattering. Fitting of the logarithms of these numbers to the curves of Figs. 3 and 4 would reveal the presence or absence of branching and allow an estimate of its frequency.

It is interesting to note that, when branching occurs, $\langle R^2\rangle_w$ increases linearly with N at small values of N but only as $N^{\frac{1}{2}}$ at large values.

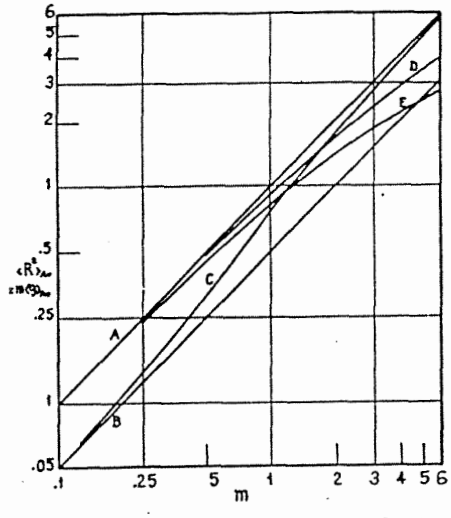


FIG. 3. Mean square radius as function of relative degree of polymerization: *A*, linear chains; *B*, rings; *C*, ring closure incomplete; *D*, trifunctional branch units distributed at random; *E*, tetrafunctional branch units distributed at random.

Since it has been observed[9] that branching alters the solubility of polymers, it is unlikely that an experimental fractionation will be governed only by molecular weight. Nevertheless, it has been seen that the calculated values of $\langle R^2\rangle_w$ given in Table II are quite insensitive to the fine details of the distribution of branch units. Consequently, the proposed method may be considered at least semi-quantitatively useful. The most serious difficulty is due to the "volume effect" discussed in the introduction. It should also be remarked that measurements of high precision are required.

IV.3. Applications to Intrinsic Viscosity

The intrinsic viscosity, $[\eta]$, unlike angular dissymmetry of light-scattering, in general does not permit the direct evaluation of $\langle R^2\rangle_w$, because of the "shielding" effect.[10,11] Thus, although $[\eta]$ is proportional to $\langle R^2\rangle_w$ for the extreme case of no shielding,[6,6a] corresponding to low molecular weights and to Standinger's rule, it becomes proportional to $\langle R^3\rangle_w$ for complete shielding at very high molecular weights. However, it is a simple matter to compare a branched polymer fraction with a chemically similar unbranched fraction of the same molecular weight, using the Debye-Bueche formulas. Denoting the unbranched sample by a subscript zero, we find

$$[\eta]/[\eta]_0 = g^1\phi(\sigma)/\phi(\sigma_0) = g^{2-\epsilon_0}, \qquad (48)$$

where $\phi(\sigma)$ is the shielding function and ϵ_0 is the exponent in the semi-empirical law $[\eta]=KN^{\epsilon_0}$ for the *linear* polymers. For a series of the *branched* polymer fractions, the viscosity exponent is predicted to be

$$\epsilon = \epsilon_0 + (2-\epsilon_0)\, d\ \mathrm{lng}/d\ \mathrm{ln}N. \qquad (49)$$

Since $d\ \mathrm{lng}/d\ \mathrm{ln}N$ is always negative, according to Table II and Fig. 4, branching is seen to lower the value of the exponent.

Returning to Eq. (48), we note that branching is predicted to decrease the intrinsic viscosity according to the factor $g^{3-\epsilon_0}$; that is, shielding amplifies the effect of branching. However, the experiments of Schaefgen and Flory[7] and of Weil[12] show considerably smaller decreases (roughly by half) than those calculated from Eq. (48), even if ϵ_0 is taken as unity. The indication is therefore strong that the "volume effect" restricts g to larger values than those calculated herein, in the systems thus far studied. Clearly it is still hazardous to draw inferences about branching from empirical viscosity-molecular weight relationships, and the method of Section IV.2, based on evaluations of $\langle R^2\rangle_w$ from light scattering, is much to be preferred.

V. MOLECULES CONTAINING RINGS

The average radius of chain molecules in which the chain closes on itself to form a continuous ring may also be treated by similar methods. Their consideration has been deferred to the last because such molecules are less familiar than those containing branch units. Presumably they are of rarer occurrence.

V.1. $\langle R^2\rangle_w$ of Ring Molecules

A molecule consisting of N segments in a simple ring, with no branches, will now be studied. For such a molecule it is necessary to find a new expression for $\langle x_{ij}^2\rangle_w$.

Let $W_r(x_{ij})$ be the function that gives the probability density of x_{ij} for a ring molecule. Two chains emanate in opposite directions from any segment, i. These two chains will be designated a and b. The density of probability that chain a will arrive at x_{ij} after n_a segments will be $W_a(x_{ij})$; likewise there will be a function $W_b(x_{ij})$ for chain b. The density of the probability that both will arrive at x_{ij} is the product of these two functions, but this is also $W_r(x_{ij})$, since when both a and b arrive at x_{ij} a ring is formed.

It is well known[13] that

$$W_a(x_{ij}) = C\exp\left(-\frac{3x_{ij}^2}{2b^2n_a}\right),$$

$$W_b(x_{ij}) = C\exp\left(-\frac{3x_{ij}^2}{2b^2n_b}\right),$$

[9] W. O. Baker, J. Am. Chem. Soc. 69, 1125 (1947).
[10] P. Debye and A. M. Bueche, J. Chem. Phys. 16, 573 (1948).
[11] J. G. Kirkwood and J. Riseman, J. Chem. Phys. 16, 565 (1948).
[12] L. L. Weil, Doctoral Dissertation (Columbia University, 1945).
[13] W. Kuhn, Kolloid Zeits. 68, 2 (1934). E. Guth and H. Mark, Monatsh. 65, 63 (1934).

where C is a constant, so that

$$W_r(x_{ij}) = C' \exp\left(-\frac{3Nx_{ij}^2}{2b^2 n_a n_b}\right), \tag{50}$$

since $n_a + n_b = N$. Given the density function, $\langle x_{ij}^2 \rangle_{Av}$ is found by elementary operations:

$$\langle x_{ij}^2 \rangle_{Av} = b^2(|j-i|)(N-|j-i|)/N. \tag{51}$$

Here $|j-i|$ and $N-|j-i|$ have been substituted for n_a and n_b, respectively.

From Eqs. (7b), (6), and (7a) R^2, X^2, and $\langle Z^2 \rangle_{Av}$ may be found in order.

$$R^2 = \frac{\sum_i \sum_j \langle x_{ij}^2 \rangle_{Av}}{2N^2} = \frac{b^2 N}{12}, \tag{52a}$$

$$X^2 = \frac{\sum_j \langle x_{ij}^2 \rangle_{Av}}{N} = \frac{b^2 N}{6}, \tag{52b}$$

$$\langle Z^2 \rangle_{Av} = X^2 - R^2 = \frac{b^2 N}{12}. \tag{52c}$$

The reference segment in Eqs. (52b) and (52c) may, of course, be any of the segments of the ring, since all are equivalent.

The difference between the mean square radius of a ring and of a linear chain is striking; the former is just half the latter.** The mean square radius of a ring is almost as small as the average for molecules of the same weight containing ninefold branch units, Eq. (22).

The small values of X^2 and $\langle Z^2 \rangle_{Av}$, compared to those of the linear chain, Eqs. (10) and (11), show that rings also would contribute relatively little to the mean square radius of a branched molecule containing rings as well as linear chains.

V.2. The Dependence of $\langle R^2 \rangle_{Av}$ of Samples Containing Ring Molecules on the Degree of Polymerization

If the heterogeneous mixture of chain molecules produced by a polymerization reaction be divided into fractions on the basis of the molecular weight, it would be expected that most of the ring molecules, if any are present, would occur in the fractions of smaller N. This statement is based on the premise that a short chain is more likely to close to a ring than a long one.

In addition polymers, rings may be formed if both ends of a growing chain molecule can react with each other, e.g., if both are free radicals resulting simultaneously from a diradical initiator. In condensation polymers, rings are readily formed by intra-molecular esterification, ester interchange, and similar reactions.[14]

** This result was obtained by Kramers (reference 6a).

[14] A complete treatment of ring formation in condensation polymers, based on the same physical ideas discussed here, has been given by H. Jacobson, Doctoral Dissertation, Columbia University (1948).

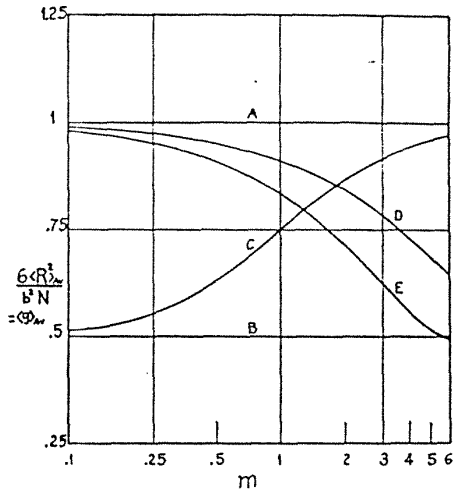


FIG. 4. Ratio of mean square radius to mean square radius of linear molecule of same weight as function of relative degree of polymerization. For curve labels, see Fig. 3.

As a plausible, though perhaps over-simple, assumption it might be postulated that the *a priori* probability of ring closure would be proportional to the probability of the two chain ends lying close to each other. This probability is proportional to L^{-3}, where L^2 is the mean square end-to-end distance of the chain. If, as in polyesters, rings and chains are in chemical equilibrium, the probability of ring closure is further reduced by a factor proportional to N^{-1}, since the ring may be reopened at any one of the inter-monomer linkages.[14] If the reaction is unidirectional, as would probably be the case for combining diradical chains under ordinary polymerization conditions, this factor is omitted. On the other hand, the probabilities of chain growth and of intermolecular termination would be constant, independent of L. Also, we recall that $L^2 = b^2 N$.

From these considerations, it follows for the case of irreversible ring formation that the fraction, $\rho(N)$, of molecules of N units in ring form, and the corresponding fraction, $\lambda(N)$, of N-unit molecules in linear form, are related thus:

$$\rho(N) = \frac{A/b^3 N^{\frac{3}{2}}}{1 + A/b^3 N^{\frac{3}{2}}}; \tag{53a}$$

$$\lambda(N) = \frac{1}{1 + A/b^3 N^{\frac{3}{2}}}; \tag{53b}$$

with A a constant. The fraction of rings, $\rho(N)$, decreases from nearly unity to nearly zero as N increases. For ring-chain equilibrium, the exponent of N in Eqs. (38) becomes 5/2, but the relations are otherwise unaffected. It might be added that in this case the constant A is inversely proportional to the concentration, and can be explicitly formulated.[14]

TABLE III. Variation of $6\langle R^2\rangle_w/b^2N$ with degree of polymerization in samples in which ring closure may occur.

Relative degree of polymerization, m	Fraction of rings, $\rho(m)$	$\frac{1+2m^1}{2+2m^1}=\frac{6\langle R^2\rangle_w}{b^2N}$	$\log\frac{m}{2}\left(\frac{1+2m^1}{1+m^1}\right)$ $=\log\langle R^2\rangle_w+\text{const.}$
0.00	1.000	0.500	—
0.10	0.969	0.515	−1.288
0.25	0.888	0.555	−0.857
0.50	0.739	0.631	−0.501
1.00	0.500	0.750	−0.125
2.00	0.261	0.869	+0.240
4.00	0.111	0.944	0.577
10.00	0.031	0.985	0.994
∞	0.000	1.000	—

The average of R^2 for the mixture of rings and chains can now be found by adding the properly weighted values of R^2 for each type of molecule:

$$\langle R^2\rangle_w=\rho(N)(b^2N/12)+\lambda(N)(b^2N/6),$$
$$=\frac{b^2N}{12}\left(\frac{A+2b^3N^1}{A+b^3N^1}\right),$$
$$=\frac{b^2N}{12}\left(\frac{1+2m^1}{1+m^1}\right). \tag{54}$$

In the last equation a convenient new variable, m, has been introduced as a measure of molecular weight; it is the ratio of N to the number of segments per molecule in the sample of half rings and half chains.

Calculations of $\langle R^2\rangle_w$ from Eq. (54) are given in Table III. When this formula is valid, the samples change from nearly pure rings to nearly pure chains in two decades of N, and altering the exponent of m from 3/2 to 5/2 in Eq. (54) would make the change even sharper.

Eq. (54) is plotted, on a semi-logarithmic scale, in Fig. 3 and on a double logarithmic scale in Fig. 4. Its rising sigmoid curve contrasts with the gentle downward curvature characteristic of branched molecules and the unit slope of the line for linear chains. Thus, while Eq. (54) may not be exactly correct, it is manifest that effects of rings and branches are quite different. Obviously, these curves offer in principle a means of detecting rings, as well as branches, from observable quantities. Estimates of the constant A in Eq. (53) indicate that the crucial range of molecular weights lies far below that required to give angular dissymmetry of light scattering, but intrinsic viscosities have been used to study ring-chain equilibria.[14]

APPENDIX A

The Relation of the Mean Square Radius, R^2, to Light Scattering

A short derivation of the relation between R^2 and light scattering, which offers the principal means of measurement of R^2, may not be out of place.

The intensity of light, $I(s)$, scattered by an isolated polymer molecule may be calculated as a function of angle of scattering by the following well-known formula:

$$I(s)=F\sum_1^N\sum_1^N\int_0^\infty\frac{\sin ksx_{ij}}{ksx_{ij}}W(x_{ij})\,x_{ij}^2dx_{ij} \tag{A1}$$

F is a simple function of the polarization of the incident light, $k=2\pi/\lambda$, where λ is the wave-length, $s=2\sin(\vartheta/2)$, where ϑ is the angle of scattering, and the other symbols are those used previously in this paper.

If $\sin ksx_{ij}$ is expanded in power series, and use is made of the normalization of $W(x_{ij})$, and of the formula defining $\langle x_{ij}^2\rangle_w$, i.e.,

$$\int_0^\infty W(x_{ij})x_{ij}^2dx_{ij}=1,$$
$$\int_0^\infty x_{ij}^2W(x_{ij})x_{ij}^2dx_{ij}=\langle x_{ij}^2\rangle_w,$$

Eq. (A1) becomes:

$$I(s)=F\Sigma_i\Sigma_j\left[1-\frac{\langle x_{ij}^2\rangle_wk^2s^2}{6}+\cdots\right]. \tag{A2}$$

However, Eq. (7b) may now be used and the summation over the unity be performed:

$$I(s)=N^2F[1-(R^2k^2s^2/3)+0(k^4s^4)] \tag{A3}$$

where $0(k^4s^4)$ represents terms of order four and higher in ks.

R^2 may thus be found by obtaining the initial slope of $I(s)$ against s^2 with light of known wave-length. If many molecules of the same number of segments, N, are present at once, $\langle R^2\rangle_w$ will be the quantity measured. However, if molecules of different size are present, the average of R^2 measured will be a "z-average," not a weight average (see reference 3).

APPENDIX B

We first deduce Eq. (37), giving the probability, P_i, that one end of a chain is connected to a network of i branch units of functionality f. For brevity, it is convenient to start from the probability, W_n, that a chain is part of a molecule bearing n branch units. If the chains are long, W_n is given (reference 8, Eq. (41)) by

$$W_n=2(1-\alpha)^2\frac{(fn-n+1)!\beta^n}{n!(fn-2n+2)!} \tag{B1}$$

with $\beta=\alpha(1-\alpha)^{f-2}$, where α is the probability that one end of a chosen chain ends in a branch unit. From the definitions of P_i and W_n, it is clear that

$$W_n=\sum_{i=0}^{n}P_iP_{n-i} \tag{B2}$$

Now, we define a function

$$\phi(\xi)=\sum_{i=0}^{\infty}P_i\xi^i, \tag{B3}$$

and recognize that

$$[\phi(\xi)]^2=\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}P_iP_j\xi^{i+j}=\sum_{n=0}^{\infty}\xi^n\sum_{i=0}^{n}P_iP_{n-i}=\sum_{n=0}^{\infty}W_n\xi^n. \tag{B4}$$

The last member of Eq. (B4) presents a sum that can be evaluated from formulas previously given:[8]

$$\sum_{n=0}^{\infty}(\beta\xi)^n\frac{(fn-n+1)!}{n!(fn-2n+2)!}=\frac{1}{2(1-z)^2}, \tag{B5}$$

with

$$\beta\xi=z(1-z)^{f-2}.$$

Use of this result gives

$$\phi(\xi)=(1-\alpha)/(1-z). \tag{B6}$$

Now, Eq. (B3) shows that P_i is the coefficient of ξ^i in the series defining $\phi(\xi)$. Hence, by Cauchy s theorem,

$$2\pi(-1)^{\frac{1}{2}}P_i=\oint\frac{\phi(\xi)d\xi}{\xi^{i+1}}. \tag{B7}$$

Expressing $\phi(\xi)$ and $d\xi$ by Eqs. (B5) and (B6), we have

$$2\pi(-1)^{\frac{1}{2}}P_i=(1-\alpha)\beta^i\oint\frac{[1-(f-1)z]dz}{z^{i+1}(1-z)^{fi-2i+2}}. \tag{B8}$$

On binomial expansion of the power of $(1-z)$, this becomes

$$2\pi(-1)^{\frac{1}{2}}P_i=(1-\alpha)\beta^i\sum_{\nu=0}^{\infty}\binom{fi-2i+1+\nu}{\nu}\oint z^{\nu-i-1}[1-(f-1)z]dz. \tag{B9}$$

The only terms contributing to the sum are those for which $\nu=i$ and $\nu=-i-1$. Evaluating these, we obtain the expression for P_i stated as Eq. (37) of the text.

We must now perform the summations indicated in Eqs. (40) and (41), leading to the expressions there given for $g_f(n)$ and $\langle g_f\rangle_{Av}$. In each case, the procedure is to replace the summations over N_1 and N_2 by integrations, consistent with the assumption of long chains, and then to evaluate the sums over i and j by making use of Eq. (B5) and other sums already given.[8]

Writing $N_1=Nu$, and using Eq. (39) for Q in Eq. (40), we obtain

$$g_f(n)=\frac{6\sum_{i+j=n}\frac{P_iP_j}{(fi-i)!(fj-j)!}\int_0^1 u^{fi-i+1}(1-u)^{fj-j+1}du}{\sum_{i+j=n}\frac{P_iP_j}{(fi-i)!(fj-j)!}\int_0^1 u^{fi-i}(1-u)^{fj-j}du}$$
$$=\frac{6\sum_{i+j=n}P_iP_j(fi-i+1)(fj-j+1)/(fn-n+3)!}{\sum_{i+j=n}P_iP_j/(fn-n+1)!} \tag{B10}$$

The sum in the denominator is seen to be that for W_n in Eq. (B2). Thus, with the aid of Eqs. (B1) and (37), the equation becomes

$$g_f(n)=\frac{3(n!)(fn-2n+2)!}{(fn-n+3)!}\sum_{i+j=n}\frac{(fi-i+1)!(fj-j+1)!}{i!j!(fi-2i+1)!(fj-2j+1)!}. \tag{B11}$$

The remaining sum is transformed to its more convenient final form as follows. In Eq. (B5), define a new variable y by the relation $\beta\xi=y^{f-2}$, and differentiate Eq. (B5) with respect to y. Expressing the result in terms of z, one finds

$$\sum_{n=0}^{\infty}\frac{(fn-n+1)!(\beta\xi)^n}{n!(fn-2n+1)!}=\frac{1}{(1-z)[1-(f-1)z]}, \tag{B12}$$

a result also useful later. Taking the square of this expression, we have

$$\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\frac{(fi-i+1)!(fj-j+1)!(\beta\xi)^{i+j}}{i!j!(fi-2i+1)!(fj-2j+1)!}=\frac{1}{(1-z)^2[1-(f-1)z]^2}, \tag{B13}$$

and it is clear that the sum of Eq. (B11) is just the coefficient, C, of $(\beta\xi)^n$ in this double sum. Hence, by Cauchy's theorem,

$$2\pi(-1)^{\frac{1}{2}}C=\oint\frac{d(\beta\xi)}{(1-z)^2[1-(f-1)z]^2(\beta\xi)^{n+1}}=\oint\frac{dz}{[1-(f-1)z]z^{n+1}(1-z)^{fn-2n+3}}$$
$$=\sum_{\nu=0}^{\infty}\sum_{\mu=0}^{\infty}\binom{fn-2n+2+\nu}{\nu}(f-1)^{\mu}\oint z^{\nu+\mu-n-1}dz \tag{B14}$$

Only terms with $\mu=n-\nu$ contribute, and thus, on returning to Eq. (B11), the result is obtained:

$$g_f(n)=\frac{3(n!)(fn-2n+2)!}{(fn-n+3)!}\sum_{\nu=0}^{n}\binom{fn-2n+2+\nu}{\nu}(f-1)^{n-\nu}. \tag{B15}$$

This may be rearranged into Eq. (40), in which the magnitudes of the terms of the sum decrease in order.

An asymptotic form, Eq. (40a), may be found for $g_f(n)$ at large n as follows. Eq. (40) may be written:

$$g_f(n)=\frac{3}{(f-1)n+3}\sum_{j=0}^{n}T_j,$$
$$T^0=1$$
$$T_j=\left(1+\frac{2}{(f-1)n}\right)^{-j}\prod_{i=0}^{j-1}\left(1-\frac{i}{n}\right)\left(1-\frac{i}{(f-1)n+2}\right)^{-1},\quad j\neq 0. \tag{B16}$$

However, if x_i are a set of numbers less than unity, the following relation is approximately true:

$$\Pi(1-x_i)=\Pi e^{-x_i}\Pi(1-x_i)e^{x_i}$$
$$\doteq e^{-\Sigma x_i}[1-\Sigma(x_i^2/2)]. \tag{B17}$$

Expression of T_j in this manner, with the neglect of some minor terms, leads to the form:

$$T_j \doteq 1-\frac{f(f-2)j^2}{6(f-1)^2n^2}\exp\left[-\frac{(f-2)j^2-(f-6)j}{2(f-1)n}\right]. \tag{B18}$$

But by the Euler-MacLaurin summation formula $g_f(n)$ may be represented,

$$g_f(n) \doteq \frac{3}{(f-1)n+3}\left(\int_0^n T_j dj+\tfrac{1}{2}T_0\right). \tag{B19}$$

Substitution of (B18) into (B19) and the resolute suppression of all terms of order n^{-1} or less leads to Eq. (40a).

For the unfractionated systems, Eq. (41) can be written

$$\langle g_f\rangle_w = \frac{6\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}[P_iP_j/(fi-i)!(fj-j)!](1-q/q)^{(f-1)(i+j)+2}\int_0^\infty N^{(f-1)(i+j)+2}q^N dN\int_0^1 u^{fi-i+1}(1-u)^{fj-j+1}du}{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}[P_iP_j/(fi-i)!(fj-j)!](1-q/q)^{(f-1)(i+j)+2}\int_0^\infty N^{(f-1)(i+j)+2}q^N dN\int_0^1 u^{fi-i}(1-u)^{fj-j}du}, \tag{B20}$$

by the same procedure used for Eq. (B10). Since long chains are assumed, $(1-q)\ll 1$, and $\ln q \cong (q-1)$. To this approximation, the parameter q cancels and Eq. (B20) simplifies to

$$\langle g_f\rangle_w = \frac{6\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}P_iP_j[(fi-i+1)(fj-j+1)/(fi+fj-i-j+3)]}{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}P_iP_j(fi+fj-i-j+2)}. \tag{B21}$$

On substituting for P_iP_j, the double sum in the numerator becomes

$$\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\binom{fi-i+1}{i}\binom{fj-j+1}{j}\frac{\beta^{i+j}}{(fi+fj-i-j+3)},$$

which is closely related to that of Eq. (B13). With a change of variable, $\beta\xi = v^{f-1}$, and after multiplication by v^2, Eq. (B13) gives

$$\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\binom{fi-i+1}{i}\binom{fj-j+1}{j}v^{fi+fj-i-j+2} = \frac{(\beta\xi)^{2/(f-1)}}{(1-z)^2[1-(f-1)z]^2}. \tag{B22}$$

This equation is now multiplied by dv and integrated, $\beta\xi$ and dv being expressed in terms of z in the second member. Choosing the lower limit at $v=0$ and the upper limit at $v=\beta^{1/(f-1)}$, corresponding to $\xi=1$ or $z=\alpha$, we obtain

$$\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\binom{fi-i+1}{i}\binom{fj-j+1}{j}\frac{\beta^{i+j}}{(fi+fj-i-j+3)} = \frac{1}{(f-1)\beta^{2/(f-1)}}\int_0^\alpha \frac{z^{(4-f)/(f-1)}dz}{[1-(f-1)z][1-z]^{2/(f-1)}}. \tag{B23}$$

A similar procedure serves to evaluate the sum in the denominator of Eq. (B21). From Eqs. (B4) and (B6), after substituting for P_i, we may write

$$\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\frac{(fi-i)!(fj-j)!(\beta\xi)^{i+j}}{i!j!(fi-2i+1)!(fj-2j+1)!} = \frac{1}{(1-z)^2}. \tag{B24}$$

With the auxiliary variable v, this relation can be put in the form

$$\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\frac{(fi-i)!(fj-j)!v^{fi+fj-i-j+2}}{i!j!(fi-2i+1)!(fj-2j+1)!} = \frac{v^2}{(1-z)^2}. \tag{B25}$$

Differentiating with respect to v, dividing by v, and then setting $v=\beta^{1/(f-1)}$, $\xi=1$, and $z=\alpha$ as before, we get

$$\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\frac{(fi-i)!(fj-j)!(fi+fj-i-j+2)\beta^{i+j}}{i!j!(fi-2i+1)!(fj-2j+1)!} = \frac{2}{(1-\alpha)^2[1-(f-1)\alpha]}, \tag{B26}$$

which is the desired sum. On substituting this result and that of Eq. (B23) into Eq. (B21), the final expression for $\langle g_f\rangle_w$, as given by Eq. (41), is obtained.

For $\langle g_f\rangle_n$, the equations required run parallel to Eqs. (B20–B23). Thus,

$$\langle g_f\rangle_n = \frac{6\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}[P_iP_j/(fi-i)!(fj-j)!](1-q/q)^{(f-1)(i+j)+2}\int_0^\infty N^{(f-1)(i+j)+3}q^N dN\int_0^1 a^{fi-i+1}(1-a)^{fj-j+1}da}{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}[P_iP_j/(fi-i)!(fj-j)!](1-q/q)^{(f-1)(i+j)+2}\int N^{(f-1)(i+j)+3}q^N dN\int a^{fi-i}(1-a)^{fj-j}da} \tag{B27}$$

$$= \frac{6\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}P_iP_j(fi-i+1)(fj-j+1)}{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}P_iP_j(fi+fj-i-j+3)(fi+fj-i-j+2)}. \tag{B28}$$

The sum in the numerator has already been given, Eq. (B13), and that of the denominator is easy. Instead of (B25), we need only write

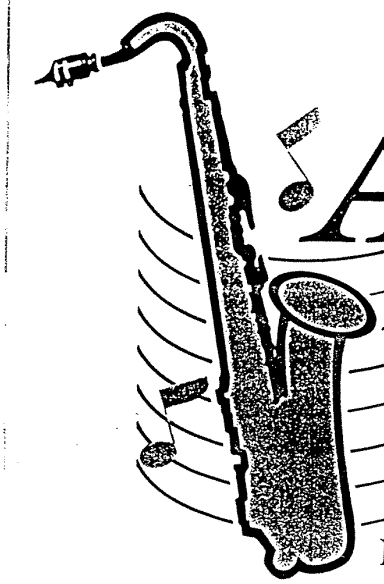
$$\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\frac{(fi-i)!(fj-j)!v^{fi+fj-i-j+1}}{i!j!(fi-2i+1)!(fj-2j+1)!} = \frac{v^2}{(1-z)^2} \tag{B29}$$

and differentiate *twice* with respect to v. The sum (for arbitrary ξ and z) becomes:

$$\frac{6+2(f-1)(f-5)z}{(1-z)^3[1-(f-1)z]^3}. \tag{B30}$$

When this is used with Eq. (B13), putting $z=\alpha$, the stated result, Eq. (41a), appears.

33



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DOW CONSTRAINED GEOMETRY CATALYST TECHNOLOGY (CGCT): NEW RULES FOR ETHYLENE a-OLEFINS INTERPOLYMERS–CONTROLLED RHEOLOGY POLYOLEFINS

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I. INTRODUCTION

The metallocene catalyst or "homogeneous catalyst" technology has been regarded as the future trend in polyolefins technology as shown in recent publications [2-3]. Polyolefin materials made from such technology generally exhibit controlled molecular structure of very narrow short chain branching distribution (SCBD) and narrow molecular weight distribution (Mw/Mn ~ 2) and have many desirable product attributes, such as: low melting temperature, better strength, better optics, low extractables, etc. when compared with polyolefins made from standard Ziegler catalyst technology. However, it has also long been noticed that a narrow molecular weight distribution polyolefin is less shear sensitive, which results in more time and energy consumption during processing or fabricating the resin. Broadening the molecular weight distribution can improve processibility, but will inevitably affect the physical properties[4-5]. Recently, a new series of polyolefins made from Constrained Geometry Catalyst Technology (CGCT) was introduced by The Dow Chemical Company[1]. The shear sensitivity of the CGCT resins can be controlled to the desirable level while maintaining excellent physical properties, narrow SCBD, and narrow MWD[1,6]. In this work we will focus on reporting the unique rheological properties of CGCT polymers. The origin of these unique properties will also be discussed.

II. CGCT POLYMER CHARACTERIZATION

A series of ethylene copolymers and homopolymers polymerized using Constrained Geometry Catalyst Technology (CGCT) is used in this study. The density of these polyolefins ranged from 0.854 to 0.954 gram/cc. For comparison purposes some commercially available homogeneous catalyzed ethylene copolymers were used in this study.

Rheological characterizations were performed using a Melt Indexer, a Melt Tension Tester, and a Rheometrics Mechanical Spectrometer (RMS-800). The molecular weight (MW) and molecular weight distribution (MWD) of the polymers were determined using a Waters 150 GPC at 140 °C, and a differential refractometer detector. RMS-800 experiments were performed in the rate sweep mode at 190 °C, and shear rates were between 0.1 and 100 rad. per second.

III. RHEOLOGICAL PROPERTIES OF CGCT POLYMERS

Figure 1 is a plot of the dynamic complex viscosity (η^*) and elastic moduli (G') vs. shear rate for the a CGCT polymer and a standard Ziegler catalyzed LLDPE at the same melt index and density (1.0 MI and 0.920 g/cc). The data in Figure 1 show that the CGCT polymer has a higher zero shear viscosity, higher melt elasticity and higher shear sensitivity than the standard Ziegler catalyzed polymer. CGCT is capable of producing resins with the same MI and density but different in shear sensitivity or I_{10}/I_2 values. The I_{10}/I_2 values of CGCT polymers correlate very well with higher melt tension, as shown in Figure 2. Note that the standard Ziegler catalyzed LLDPE with broader MWD shows substantially lower melt tension than that of CGCT polymers at the same MI and density level. In an earlier report[6], we postulated a "long chain branching (LCB)" effect to account for these rheological phenomena. We have also theorized that the unique structures with LCB are formed in the CGCT polymerization process due to the "vinyl re-insertion" mechanism (Appendix Figures A-1 and A-2). The postulation is supported by the C^{13} NMR data from a CGCT homopolymerization study[6]. The number of *long chain branches per chain in the homopolymers increases as the* I_{10}/I_2 increases[6] (Appendix Figure A-3). This is further evidenced by the observation that the weight average molecular weight of the same melt index and density CGCT polymers decreases as the shear sensitivity of the melt increases as shown in Table I.

Table I. Correlation between I10/I2 and Mw at constant MI for CGCT Polymers

Polymer #	MI	I10/I2	Mw
1	1.0	7.39	101,300
2	1.0	8.81	90,700
3	1.0	10.5	83,700
4	1.0	12.11	77,600

The melt tension comparison between CGCT polymers and a commercially available homogeneous polyolefin resin is given in Figure 3. Interestingly, the melt tension of CGCT polymers depends not only on MI but also on its density. The melt tension of CGCT polymers is substantially higher than that of the homogeneous polyolefin resin at the similar MI and density. It is an important feature of the CGCT resins that the I_{10}/I_2 ratio and MWD of CGCT polymers can be controlled separately, i.e., I_{10}/I_2 is independent of Mw/Mn as shown in Figure 4. It is important to note that the I_{10}/I_2 ratios of the CGCT polymers can be controlled to the desired value while maintaining a narrow MWD. On the other hand, Figure 4 shows that the I_{10}/I_2 ratio of standard Ziegler catalyzed polyolefins depends strongly on its MWD. For comparison purposes, the shear sensitivity of a typical commercially available homogeneous polyolefin copolymer is rather low (typically less than 6) due to narrow MWD and no LCB. Figure 4 truly exhibits the unique controlled rheological characteristics of CGCT polymers.

The effect of short chain branching on melt rheology of ehtylene α-olefin copolymers has been the subject of scientific as well as technological interest. A study has been made comparing CGCT polymers with LLDPE and commercially available homogeneous copolymers. The zero shear viscosity (η_0) vs. weight average molecular weight (Mw) plot for a highly branched (SCB, but no LCB) elastomeric polyolefins (.880-.885 density) vs. conventional LLDPE is shown in Figure 5. Note that the entire curve for the homogeneous polymers shifts to the right, suggesting that the number of entanglements for the highly

short chain branched polymers is lower than that of linear polymers at the same molecular size. A similar phenomenon has also been reported for narrow MWD comb-shaped polymers[7]. For CGCT elastomeric material, the relationship is complicated by the presence of both LCB and a high level of SCB (Figure 5). Because of this complication, the CGCT polymers at a given zero shear viscosity (η_0), or melt index, no longer correlates with a single molecular weight value (Figure 6). The controlled rheology CGCT polymers are polymerized in such a way that both LCB and SCB are independently controlled. The detailed discussion of the effects of both LCB and SCBs on melt rheology will be reported separately.

In summary, the generally accepted structure/property relationship for conventional Ziegler catalyzed polymers (medium to broad MWD) and homogeneous catalyzed polymers (narrow MWD) are no longer applicable for CGCT polymers. Dow Constrained Geometry Catalyst Technology polymers truly offer advantages through its controlled rheological properties.

IV. CONCLUSION

Substantially linear ethylene copolymers and homopolymers polymerized using Constrained Geometry Catalyst Technology (CGCT) have been successfully developed by The Dow Chemical Company. Unlike other homogeneous catalyzed polyolefins or conventional polyolefins, the rheological properties such as zero shear viscosity (η_0), melt elasticity, and shear sensitivity (I_{10}/I_2), etc. of CGCT polyolefins show unique and different correlations with its structural parameters such as MW and MWD. A unique molecular structure with long chain branching (LCB) has been postulated to account for these rheological effects. Furthermore, a "vinyl re-insertion" mechanism has also been theorized to explain the formation of LCB during the polymerization process. In addition, experimental data show that the presence of a high amount of comonomers or short chain branching (SCB) in an elastomeric material would also affect the resin rheology. The unique rheological properties of these materials can be achieved by independently controlling the length and concentrations of the LCB and SCB during polymerization. The CGCT polymers with controlled rheology characteristics demonstrate a unique structure-processing-property relationship of the next generation polyolefins.

Reference

1. K.W. Swogger, "The Material Properties of Polymers made From Constrained Geometry Catalysts", Schotland Specialty Polyolefins Business Forum, Preprints, pp. 155-165, September 22-24, 1992.
2. D.M. Selman, "Future Trends in Polyolefins Technology", Schotland Specialty Polyolefins Business Forum, Preprints, pp. 11-16, September 22-24, 1992.
3. C.S. Speed, B.C. Trudell, A.K. Mehta, F.C. Stehling, "StructureProperty Relationships in EXXPOL™ Polymers", SPE RETEC, VII Polyolefins International Conference, pp. 45-66, February 24-27 1991.
4. T. Ogawa, "Effects of Molecular Weight on Mechanical Properties of Polypropylene", J. Appl. Polymer Science, Vol. 44, 1869-1871 (1992).
5. I.M. Ward, "Mechanical Properties of Solid Polymers", 2nd edition, John Wiley & Sons (1979)
6. G.W. Knight and S. Lai, "Dow Constrained Geometry Catalyst Technology: New Rules for Ethylene-α Olefins Interpolymers -- Unique Structure and Property Relationships", VIII International Polyolefins Conference SPE RETEC, February 21-24 , 1993.
7. G.V. Vinogradov, A. Ya. Malkin, "Rheology of Polymers", Springer-Verlag, New York (1980).

Figure 1. Dynamic Complex Viscosity
CGCT vs. STD Ziegler Polymers
RMS-800 @ 190 C

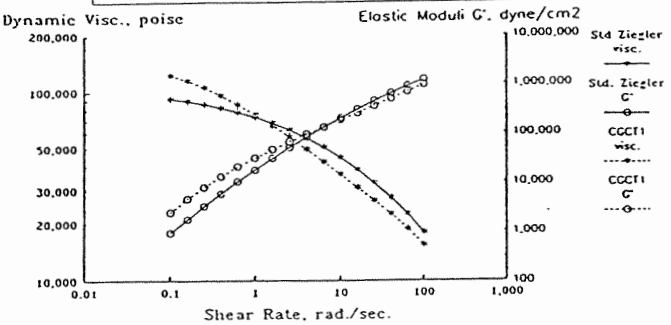


Figure 2. Melt Tension vs. I10/I2
1 MI, .920 density CGCT Polymers
vs. Std. Ziegler Polymer

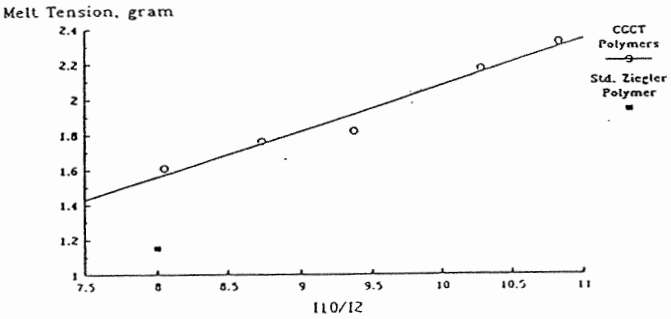


Figure 3. Melt Tension of
CGCT Polymers vs. Homogeneous Polymer

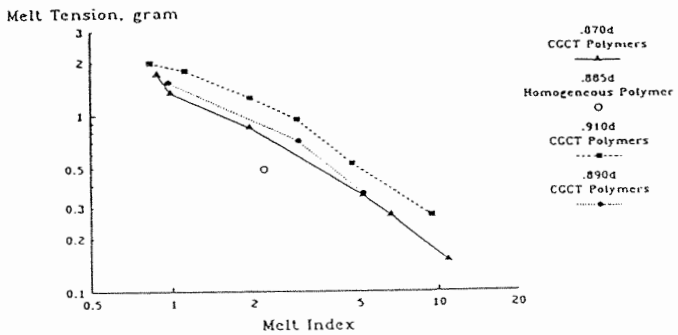


Figure 4. MWD vs. I10/I2 Plot
CGCT Polymers vs. STD Ziegler & Homogeneous Polymers

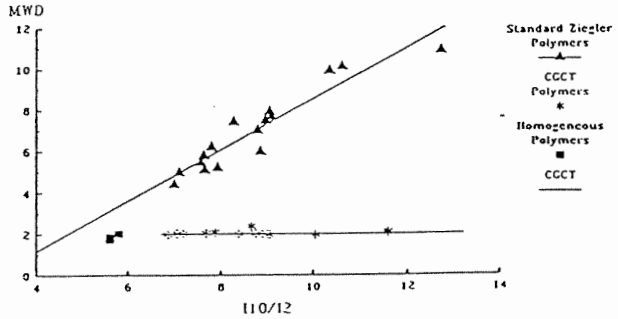


Figure 5. Zero Shear Viscosity vs. Mw
Effects of SCB and LCB

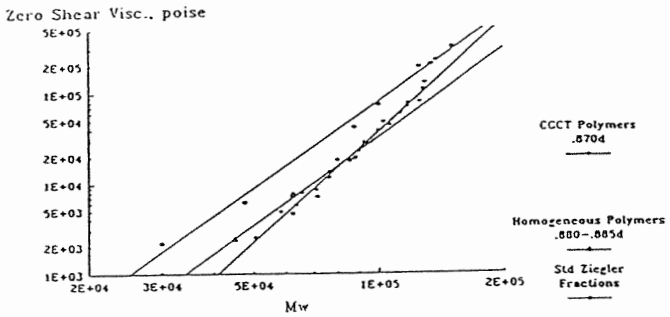
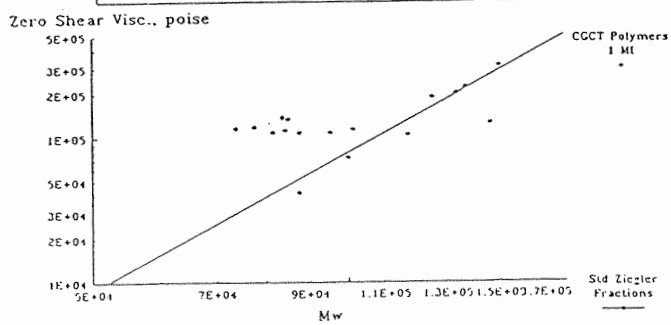


Figure 6. Zero Shear Viscosity vs. Mw
CGCT Polymer @ Constant MI



Appendix

Figure A-1

SOURCES OF UNSATURATION

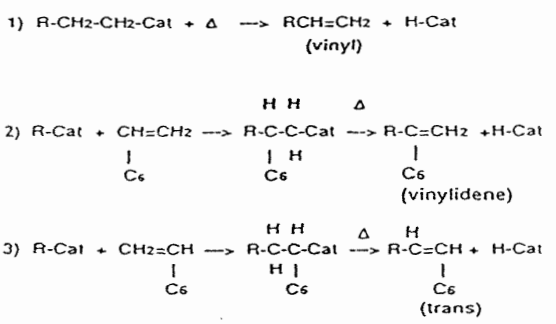


Figure A-2 POSSIBLE SOURCES OF LONG CHAIN BRANCHING

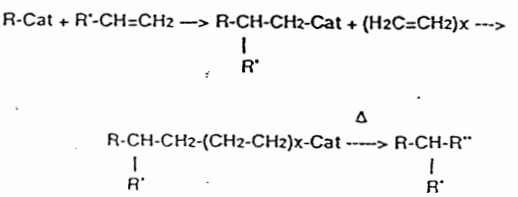


Figure A-3. BRANCHING OF HOMOPOLYMERS

POLYMER #	NMR, LCB/CHAIN	I10/I2
1	0.2	8.89
2	0.44	10.63
3	0.53	11.82
4	0.66	16.07