Title	UNPERTURBED DIMENSIONS, CONFORMATIONS AND STERIC ISOMERISMS OF POLYMER CHAINS(Dissertation_全文)
Author(s)	Miyamoto, Takeaki
Citation	Kyoto University (京都大学)
Issue Date	1970-01-23
URL	http://dx.doi.org/10.14989/doctor.r1558
Right	
Type	Thesis or Dissertation
Textversion	author

UNPERTURBED DIMENSIONS, CONFORMATIONS AND STERIC ISOMERISMS OF POLYMER CHAINS

By

Takeaki Miyamoto

Institute for Chemical Research
Kyoto University
Kyoto, Japan

May, 1969

CONTENTS

Chapter 1

Introduction

1.1 Main Purpose of the Present Dissertation

Prominent progress in polymer chemistry enables us at present to produce a wide variety of new polymeric substances,[1] and industrial applications of polymers are familiar in almost every aspect of existence. The purpose of studies on physical properties of polymers has been situated in making clear not only the solution and bulk properties but also the relationship between molecular structure and physical property. From the industrial and academic points of view, it has increasingly been required to know what a molecular structure and furthermore what a fine structure a polymer chain should have in order to exhibit as many of the desirable property as possible.

Much of information about the sizes and shapes of polymer molecules, structure and arrangement, effects of crystallinity, the nature and properties of polymer net-works, is now of quite general validity, However, still at present, we have no generalized recipe for obtaining a polymeric substance with arbitrarily required physical properties, even if much accumlation of our knowledges for this purpose has recently been achieved. This means that further efforts must be devoted to draw various relationships between molecular structure and physical property. Thus the more examination of the fundamental properties of polymers with well-defined chain structure, both in solution and in bulk, is of paramount importance to an understanding of the factors which decide ultimate use.

Along the line of such a requirement, this dissertation presents some findings of chemical and steric microstructures of stereoregular polymers, especially of polypropylene including oligomers and polymethyl methacrylate. Here, the term "chemical microstructure" represents the internal structure of isolated polymer chain which signifies not only the difference of chemical structure of monomer but also the difference of polymer chain resulting from the structural irregularities such as head-to-head and tail-to-tail additions, branching and cross-linking of the polymer chains (structural isomerism[2]), while the term "steric microstructure", the difference of steric configurations around the main-chain sites of steric isomerism in structurally regular polymer molecules and the sequence distribution of such configurations.

A special feature for the works included in this dissertation may consist in the fact that all conclusions for the chemical and steric structure of polymers are drawn here not only based on information deduced from assemblies of polymer chains --solid state -- but also on that from an isolated polymer chain -- dilute solution state. Thus in the following we will give a short survey of development in the study of polymer chains in solution.

1.2 Conformational Study of Polymer Chains in Solution[3,4,5]

The study in dilute polymer solution may be characterized by reducing the intermolecular interactions, because we can not eliminate them, differing from the case of general low molecules which can be brought to gas state. Thus we can draw out intrinsic properties of a polymer chain isolated in solution and quantitative information concerning thermodynamic and hydrodynamic interactions between chain segments or between chain segment and solvent molecule.

Since the interactions between chain segments diminish rapidly with increase in the distance, except for the cases where the Coulomb potential acts, they fall into two categories; short-range and long-range interactions acting between adjacent segments and between non-adjacent segments, respectively. The average chain dimension under the theta condition, at which the influence of long-range interactions is absent, may be called the "unperturbed dimension". Besides we use the characteristic ratio, $\langle R^2\rangle_0/nl^2$ and a parameter A as the index of the unperturbed dimension. $\langle R^2\rangle_0$ is the unperturbed mean square end-to-end distance and is given by

$$\langle R^2\rangle_0 = nl^2 \frac{(1 + \cos\theta)\ (1 + <\cos\varphi>)}{(1 - \cos\theta)\ (1 - <\cos\varphi>)} \qquad (1)$$

for the simplest case of the polymethylene chain. Here l is the bond length, n is the number of bonds, θ is the supplement of the bond angle, and φ is the internal rotation angle measured from the trans conformation. Further A is defined by

$$A^2 = \langle R^2\rangle_0/M \qquad (2)$$

where M is the molecular weight of polymer.

These quantities can be obtained directly from the light scattering measurement under the theta condition or indirectly from the viscosity measurement with the aid of existing theories for the intrinsic viscosity. This theoretical treatment will be described later in more detail. Eq. (1) shows the fact that the internal degree of freedom determined by rotation about a single bond of the chain is restricted. As a measure for any hindrance of internal rotation about single bond, a steric factor σ defined by the following equation is introduced generally for polymer chains:

$$\sigma = \langle R^2 \rangle_o / \langle R^2 \rangle_{of}$$

where $\langle R^2 \rangle_{of}$ is the mean square end-to-end distance of the chain for which the fixed valence angle but the completely free internal rotations are assumed. The σ-values have been calculated for various structural types of polymer chains.[5] Thus from the σ-value obtained for a polymer chain, we may anticipate the relationship between chain flexibility and molecular structure.

Extensive works for evaluating the σ-values with various structural types of polymers have been made to date, and this has allowed us to collect various knowledges of relationships between chain flexibility and chain structure. Further investigations have been carried out in order to correlate the chain flexibility to the bulk properties. As an intuitive example it is interesting to cite the case of polyvinylacetate:[6] the σ-value of polyvinylformal, the chain flexibility was enhanced with increasing the degree of acetalization, this being reflected directly in one of the bulk properties of the polymer, namely, elevation of the second order transition temperature.[7] As the above example indicates, any information deduced from isolated polymer chains in dilute solution has been ensured to be related directly to some bulk properties of polymer. Here we find clearly the importance of study on polymer solution property.

Further analogous successes may be found in the conformational study of biopolymers in solution.[8] Generally speaking, polymer chains exist assuming a wide variety of randomly coiled conformations in solution and in melt. However, some experiments with biopolymers such as polypeptides, nucleic acids, and the synthetic analog show that these polymers assume well defined helical conformations in solution. It is also one of the subjects of the present dissertation to discuss whether some regular chain conformations would be retained still in solution for some synthetic stereoregular vinylpolymers.

1.3 Choice of Sample Materials

In order to pursue the study along the line mentioned above, the choice of sample materials comes first into question. The requirement that a polymer should have a well-defined chain structure for the first step of the present study may be fulfilled to a certain extent with amorphous homopolymers. However, the discovery of techniques for synthesis of stereoregular polymers and various types of copolymers has given us a great deal of new attractive problem.[9] Thus it seems reasonable to choose such polymer species for the present request that one should treat polymeric substances that have the most accurate molecular structure, when characterized. For this reason, the author treats various types of propylene polymers including oligomers, which are the simplest stereoregular polymer, and at the same time for which typical three steric isomers are known, viz. atactic, isotactic, and syndiotactic polymers. Moreover, the so-called "stereoblock" polypropylenes will be chosen as sample material for this study. In the last Chapter of this dissertation, the author takes up different types of polymethyl methacrylate (PMMA); atactic, isotactic, and syndiotactic PMMA, because the tacticity of these polymers can be quantitatively determined by the nmr analysis, and all the samples are easily dissolved in many solvents at ordinary temperatures.

1.4 Introductory Remarks

As has been described in sec. 1.2, it is difficult to estimate the unperturbed dimensions of polymer chains if the theta condition for a given system can not be realized. In such cases, we are obliged to seek a suitable theory that permits one to eliminate the excluded volume effect. With such a theory one may estimate the unperturbed dimensions using the relationship between intrinsic viscosity and molecular weight found in good solvent. Thus Chapter 2 gives a short survey of theoretical development on the excluded volume effect in solution as well as the estimate of the unperturbed dimensions for linear and branched polymers from intrinsic viscosity data obtained in a good solvent. In addition, the present status of the ways to investigate the steric isomerism of polymers, such as high-resolution nuclear magnetic resonance (nmr) and thin layer chromatography (tlc) methods, are stated.

In Chapter 3 the unperturbed dimensions for propylene polymers with different steric isomerisms are compared with those of polyethylene. Two types of syndiotactic polypropylene have been prepared. Determination of molecular weights was made by the Archibald ultracentrifugal method and by light scattering. Intrinsic viscosities of these fractions were determined in different solvents. The results are analyzed on the basis of some recent equations for estimating the unperturbed dimensions. In connection with the results obtained a quantitative discussion is made on the correspondence of molecular conformations assumed in the solid state to those in solution.

The results in Chapter 3 may allow one to set forth a hypothesis that some regular chain conformations would be retained to a certain extent still in solution. In Chapter 4, in order to afford an indirect proof for the hypothesis, single crystals of syndiotactic polypropylene were attempted to prepare from its α-chloronaphthalene solution. Further experiments were carried out with poly-ε-caprolacton, in which molecular packing in the crystalline state is similar to that of polyethylene. In connection with these results, the rule for choosing a solvent appropriate to the single crystal preparation will be discussed.

In Chapter 5, the structural and steric isomerisms of propylene polymers are estimated on the basis of solution properties as well as infrared and high-resolution nmr spectra. Three general types of polypropylenes were prepared. The characterization of all samples was accomplished by equilibrium ultracentrifugation, light scattering, vapor-pressure osmometry, viscometry, and gel permeation chromatography. We first elucidate more clearly the structural and steric isomerisms of amorphous and stereoblock polypropylenes, and a discussion on the correlation between theta temperature and microtacticity will be given. Second, changes in the absorption bands at 1154, 974, and 997 cm^{-1} in the ir spectra are interpreted in terms of sequence length dependence of propylene chains. Finally, the high-resolution nmr spectra of different polypropylenes, including isotactic polymers of low-molecular weight, are investigated, and several notes in estimating the microstructure will be given.

In Chapter 6 application of thin layer chromatography (tlc) to studies on the steric isomerism of stereospecific polymethyl methacrylate (PMMA) is discussed. Various stereoregular PMMA were prepared, and the characterization of all samples was accomplished by viscometry and high-resolution nmr method. The separation characteristic of isotactic and syndiotactic PMMA as well as their mixture is explored by this method, and the amount of components separated from the mixture is determined quantitatively. This Chapter deals further with application of tlc to investigating the specific interactions between isotactic and syndiotactic PMMA chains. The problem is devided into two subjects, viz., the stereocomplex formation in dilute solution,[10] and the structure of crystallizable PMMA, which has been supposed first as a stereoblock PMMA.[11] The chromatographic behavior of the complexws and the so-called stereoblock polymers are observed. On the basis of the results obtained, the properties of the stereocomplexes and the structure of the so-called stereoblock polymers will be revealed.

References

(1) N. G. Gaylord and H. F. Mark, Linear and Stereoregular Addition Polymer, P. 319 Interscience Publ. Inc., New York, 1959.

(2) J. C. Woodbrey, in The Stereochemistry of Macromolecules, Vol. 3 (A. D. Ketley, ed.) Marcel Dekker, Inc., New York, 1968, Chap. 2.

(3) P. J. Flory, Principle of Polymer Chemistry, Cornell Univ. Press, 1953.

(4) M. V. Volkenstein, Configurational Statistics of Polymer Chains, Interscience Publ. Inc., New York, 1963.

(5) M. Kurata and W. H. Stockmayer, Fortschr. Hochpolymeren-Forsch, 3, 196 (1963).

(6) H. Matsuda and H. Inagaki, J. Macromol. Sci., A-2, 191 (1968).

(7) K. Fujino, K. Senshu, T. Horino, and H. Kawai, J. Colloid Sci., 17, 726 (1962).

(8) T. M. Birshtein and O. B. Ptitsyn, Conformations of Macromolecules, Interscience Publ. Inc., New York, 1966.

(9) Copolymerization, edited by G. E. Ham, Interscience Publ. Inc., New York, 1964.

(10) See, for example, H. Z. Liu and Kang-Jen Liu, Macromolecules, 1, 157 (1968).

(11) T. G Fox, B. S. Garret, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell, and J. D. Stroupe, J. Amer. Chem. Soc., 80, 1768 (1958).

Chapter 2

Theoretical and Experimental Background

2.1 Two Parameter Theories for Linear Polymers

2.1.1 Theory of excluded volume effect

As has been described briefly in Chapter 1, the mean square end-to-end distance of polymer chain is influenced by the so-called excluded volume effect. This effect on chain dimension is usually expressed in terms of the linear expansion factor α that is defined as the ratio of the root mean square end-to-end distance of a polymer chain in the presence and absence of this effect. Thus for estimating the unperturbed dimension, the factor α should be reduced to unity (the theta state), that is to say, the excluded volume effect should be eliminated.

Elimination of this effect may be easily done when a theta solvent for a given polymer is known. However, such is unusual, especially for chemical as well as steric copolymers. Therefore we are obliged to look for a suitable theory, on the basis of which the data obtained in good solvent can be deduced to those expected in theta state. Such theories should give us functional relationships between α and thermodynamic variable, such as temperature and solvent power. The thermodynamic variable is usually expressed with so-called the long-range interaction parameter between non-adjacent segments, B.

Flory[1] has first attempted to relate α to molecular constants of polymers and solvents and derived

$$\alpha^5 - \alpha^3 = 4/3\ z \tag{4}$$

where

$$z = 0.330\ BA^{-3}M^{1/2} \qquad (5)$$

This equation has been tested theoretically as well as experimentally. Several years ago Kurata-Stockmayer-Roig,[2] Ptitsyn,[3] and Fixman[4] have published equations different from the Flory equation. These are given by

$$\alpha^3 - \alpha = 4/3\ g(\alpha)z \qquad (6)$$

$$\alpha^2 = 0.786 + (1 + 9.36z)^{2/3}/4.86 \qquad (7)$$

$$\alpha^3 - 1 = 2z \qquad (8)$$

respectively. As has been demonstrated by Kurata and Stockmayer,[5] the α^3-type equations are in better agreement with the experimental data than is the Flory equation. At present there are still different objections to the Flory equation as well as to the other equations from different aspects.[6,7] What is now sure with respect to these theories may be that if two parameters, A and B, are given, then α is unique function of molecular weight irrespective of solution system. Thus the theories available to date are generally called the two parameter theory.

2.1.2 Estimate of unperturbed dimensions

To estimate two independent parameters A and B, using relationships between intrinsic viscosity in good solvent and molecular weight alone, a need for an appropriate equation describing the excluded volume effect upon the hydrodynamic radius of polymer chains is apparent. In order to apply the above equations (4), (6), (7), and (8) to viscosity data, we need to convert the expansion factor α_η for the hydrodynamic radius to that for the end-to-end distance α. For the purpose we adopt the exponential type of relation:

$$\alpha_\eta{}^3 = \alpha^{5/2} \tag{9}$$

which has first been suggested by Yamakawa and Kurata.[8] If α^3 is replaced, according to its definition, by the familiar Flory-Fox equation[9]

$$\alpha_\eta{}^3 = [\eta]/KM^{1/2} \tag{10}$$

with

$$K = \Phi_0 A^3 \tag{11}$$

where Φ_0 is the universal constant of Flory at theta point.[10]

We can obtain different viscosity equations corresponding to different possible combinations of these existing theoretical equations of α and α_η. One of the most available equations is the familiar Stockmayer-Fixman equation,[11] which yields

$$[\eta]/M^{1/2} = K + 0.330\ C_\eta \Phi_0 BM^{1/2} \tag{12}$$

Here the conversion from α to α_η is simply made by modifying the numerical factor in eq. (8) as $\alpha_\eta{}^3 = 1 + C_\eta z$. However, eq. (12) did not provide a complete fit to the experimental data over the entire range of molecular weight and temperature studied.[7,12,13] Especially at high values of molecular weight and temperature, the experimental points in the $[\eta]/M^{1/2}$ versus $M^{1/2}$ plot tend to deviate downward from the straight line predicted by eq. (12). This means, in turn, that the Stockmayer-Fixman method based on the combination of eq. (8) and eq. (10) still leads to an unreliable estimate of the unperturbed dimensions if it is applied to an extremely good solvent system. Extrapolation of eq. (12) to zero value of M from the region of high values results in overestimation of the unperturbed dimensions.[14] But eq. (12) will be used in the low α region for the sake of simplicity of treatment.

Recently, Inagaki, et al.[14] have proposed a tentative procedure based on combining the Ptitsyn equation (7) with eq. (9). If unity appearing in the second term in eq. (7) is neglected, the combination of these equations yields

$$([\eta]/M^{1/2})^{4/5} = 0.786\ K^{4/5} + 0.950\ K^{4/5}z^{*2/3}M^{1/3} \tag{13}$$

Here z* is defined by

$$z^* = 0.330\ BA^{-3} \tag{14}$$

The above equation offers a method for determining two independent parameters A and B from relationships between $[\eta]$ and M alone. However, this equation is expected to afford correct K values only for good solvent systems, in which

$$\alpha > 1.4 \quad \text{or} \quad [\eta]/KM^{1/2} > 2.2 \tag{15}$$

Thus eq. (13) corresponds to the asymptote of eq. (7) for larger values because of the neglection of unity in the second term.

2.2 Unperturbed Dimensions of Branched Polymers

As a measure for the effect of branching on the chain dimension, a ratio g_s defined by the following equation has been introduced:

$$g_s{}^2 = \langle S^2\rangle_b / \langle S^2\rangle_l \tag{16}$$

where $\langle S^2\rangle_b$ and $\langle S^2\rangle_l$ are the mean square statistical radii of a branched and linear polymer chain of the same molecular weight, respectively. The values of $\langle S^2 \rangle_b$ for various types of branched polymer chains have been calculated by Zimm and Stockmayer.[15] According to the calculations, the ratio decreases with increasing frequency of branching. On the other hand, g_η has been defined by

$$g_\eta^{\,3} = [\eta]_b/[\eta]_1 \qquad (17)$$

where $[\eta]_b$ and $[\eta]_1$ are the intrinsic viscosities for branched and linear polymer of the same molecular weight, respectively. It has been established that the intrinsic viscosity of branched polymer chains is smaller than that of linear polymer chains when compared at the same molecular weight level, that is to say, g_η is less than unity. Thus comparison of $[\eta]_b$ with $[\eta]_1$ should imply the effect of branching directly.

To determine the mode of branched polymer using the values of g_η , a need for an appropriate equation describing viscosity of branched polymer chains is apparent. If Flory-Fox viscosity equation[9] is assumed to be valid for branched polymer chains as well, g_η may be written as

$$g_\eta = g_s \qquad (18)$$

On the contrary to this, Zimm and Kilb[16] have found theoretically that g_η was related to g_s by

$$g_\eta^{\,3} = g_s \qquad (19)$$

for polymer chains of star-type. This relation has been tested by several authors[17-20] and proved to be in good agreement with some experimental results. However, no complete relation between g_η

and g_s have yet been proposed for other types of branched polymers.

Here, much care must be taken of the following two important points on the study of the branching effect. First, the branching effect upon intrinsic viscosity will be influenced to a certain extent by solvent used, and one had better carry out the experiments in the theta solvent.[19-20] The second is the effect of polydispersity. Generally it is often difficult to distinguish the effect of branching from that of polydispersity, and it is desirable to examine the effect of branching in the same molecular weight distribution level.[22]

Recently Benoit, et al.[23] have pointed out that the effect of branching might be investigated using the gel permeation chromatography (gpc) technique. The relationship between logarithm of molecular weight and elution volume, which is obtainable with gpc, is different for linear and branched polymer chains. Thus if one has once established this relationship for a homologous series of linear polymer the effect of branching of a given polymer sample with known molecular weight may be estimated by determining the elution volume on the chromatograph. In the present study these two methods for investigating the effect of branching will be adopted as stated later.

2.3 High-Resolution Nuclear Magnetic Resonance Spectra of Polymers

Narrowline or high-resolution nuclear magnetic resonance(nmr) spectra of many polymers in dilute solutions have been obtained during the last few years.[24, 25] A number of these spectra have been obtained unique information about localized fragments of molecular structure (microstructure) in polymer molecules. That is, this method is useful for determinations of stereochemical configuration and conformation of polymer in solution, and have been used for the quantitative analysis of tactic placements or triads (tacticity). With polymers such as polymethyl methacrylate and poly-α-methylstyrene, no appreciable spin-spin coupling occurs between the methylene and the methyl protons, but there are considerable changes depending on the stereoregularity.[26, 27] Therefore, the spectra are not complicated, and this method is effective. On the other hand, with polymers such as polypropylene, many protons interact with each other and the shift due to tacticity is small. Hence complicated spectra are obtained.[25] In this case, a useful method for simplifying spectra is that of deuterium substitution, and this has proved to be useful for the analysis of polypropylene.[28] A second useful method for simplifying spectra is to use higher values of the applied magnetic field H_0 and the frequency ν_0, which enhances the observed chemical-shift differences. Another method is the spin-decoupling experiments by double resonance.[29] However, those methods are not always effective. A way to analysis complicated spectra, especially those of polypropylene, will be discussed in the last part of Chapter 5.

2.4 Thin Layer Chromatography of Polymers

Longford and Vanghan[30] have probably introduced the thin layer chromatography (tlc) for separating high polymers of different chemical compositions. Very recently, extending this idea, Inagaki and co-workers[31] successfully applied the tlc to the determination of composition distribution curves of styrene-methacrylate copolymers without inferrence of polydispersity in molecular weight. Furthermore, they elucidate the effect of monomer arrangements in copolymer chain upon the chromatographic separation. In the last Chapter of the present dissertation, the author will apply this method to stereoregular polymers and will show that this method is useful for the determination of the steric isomerism of polymers.

References

(1) P. J. Flory, J. Chem. Phys., 17, 303 (1949).

(2) M. Kurata , W. H. Stockmayer, and A. Roig, ibid., 33, 151 (1960).

(3) O. B. Ptitsyn, Vysokomol. Soedin., 3, 1673 (1961).

(4) M. Fixman, J. Chem. Phys., 36, 3123 (1962).

(5) M. Kurata and W. H. Stockmayer, Forschr. Hochpolymeren-Forsch. 3, 196 (1963).

(6) G. C. Berry and T. G Fox, J. Amer. Chem. Soc., 86, 3540 (1964).

(7) H. Inagaki, H. Suzuki, M. Fujii, and T. Matsuo, J. Phys. Chem., 70, 1718 (1966).

(8) H. Yamakawa and M. Kurata, J. Phys. Soc. Japan, 13, 78 (1958).

(9) P. J. Flory and T. G Fox, J. Amer. Chem. Soc., 73, 1904 (1951).

(10) (a) P. L. Auer and C. S. Gardner, J. Chem. Phys., 23, 1545, 1546 (1955); B. H. Zimm, ibid., 24, 269 (1956); J. E. Hearst, ibid., 37, 2547 (1962); and C. W. Phun and M. Fixman, ibid., 42, 3838 (1965). The theoretical values of $10^{-3}\Phi_0$ (cgs) obtained by these authors are 2.87, 2.84, 2.82, and 2.68, respectively. By refining mathematical approximations introduced into those calculations, the Φ_0 value may be expected to be slightly smaller than 2.68; (b) Experimental determination of Φ made by Baumann shows that this value is ca. 2.4 as an average of different determinations: F. H. Baumann, J. Polymer Sci., B3, 106 (1965).

(11) W. H. Stockmayer and M. Fixman, J. Polymer Sci., C1, 137 (1963).

(12) H. Utiyama and M. Kurata, Rep. Progr. Polymer Physics Japan 7, 31 (1964).

(13) M. Ueda and S. Matsumoto, Report at the 13th Meeting of the Soc. Polymer Sci., Japan (1964); also M. Ueda, K. Kazitani, and S. Matsumoto, Report at the 13th Polymer Symp. Japan (1964); they gave the following empirical equation for viscosity data obtained with the system polyvinyl acetate and acetone at $30^{\circ}C$;
$[\eta]/M^{1/2} = 0.093 + 7.0\mathrm{x}10^{-4} M^{0.4}$

(14) H. Inagaki, H. Suzuki, and M. Kurata, J. Polymer Sci., C15, 409 (1966).

(15) B. H. Zimm and W. H. Stockmayer, J. Phys. Chem., 17, 1301 (1949).

(16) B. H. Zimm and R. W. Kilb, J. Polymer Sci., 37, 19 (1959).

(17) M. Cantow, G. Meyerhoff, and G. V. Schulz, Makromol. Chem., 49, 1 (1961).

(18) T. A. Orofino and F. Wenger, J. Phys. Chem., 67, 566 (1963).

(19) M. Morton, T. E. Helminiak, S. D. Gadkari, and F. Bueche, J. Polymer Sci., 57, 471 (1962).

(20) S. Gundiah, Makromol. Chem., 104, 196 (1967).

(21) G. C. Berry and T. A. Orofino, J. Chem. Phys., 40, 1614 (1964).

(22) W. W. Graessley and H. M. Mittelhauser, J. Polymer Sci., A2-5, 431 (1967).

(23) H. Benoit, Z. Grubisic, P. Rempp, D. Decker, and J. G. Zilliox, J. Chim. Physique, 11-12, 1507 (1966).

(24) F. A. Bovey and G. V. D. Tiers, Fortschr. Hochpolymeren-Forsch., 3, 139 (1963).

(25) J. C. Woodbrey, in The Stereochemistry of Macromolecules, Vol. 3 (A. D. Ketley, ed.) Marcel Dekker, Inc., New York, 1968, Chap. 2.

(26) F. A. Bovey, Pure and Applied Chem., 15, 349 (1967).

(27) K. C. Ramey and G. L. Statton, Makromol. Chem., 85, 287 (1965).

(28) S. Stehling, J. Polymer Sci., A2, 1815 (1964).

(29) J. D. Baldesschwieler and E, W. Randall, Chem. Rev., 63, 81 (1963).

(30) W. J. Langford and D. J. Vaughan, Nature, 184, 116 (1959).

(31) (a) H. Inagaki, H. Matsuda, and F. Kamiyama, Macromolecules, 1, 520 (1968); (b) F. Kamiyama, H. Matsuda, and H. Inagaki, Makromol. Chem., ~~in press.~~ 125, 286 (1969).

Chapter 3

The Unperturbed Dimensions of Polypropylene and Polyethylene

The mean dimension of the polymethylene chain has been discussed on the basis of various molecular conformation calculations for lower n-alkane homologs.[1,2] Thus the characteristic ratios, $\langle R^2 \rangle_0 / nl^2$, and the temperature coefficients $d\ln\langle R^2 \rangle_0 / dT$ observed for polyethylene have been interpreted fairly well in terms of the above calculations.[3,4] However, if the interdependent-rotation model[5] used for calculations is applied to stereoregular vinyl polymers bearing substituents R on alternate carbon atoms, $-(CH_2-CHR)_n-$, it follows that their characteristic ratios should be much larger than that of polyethylene.[6] This result is the contrary to the observations of some other workers.[7] This discrepancy between calculation and experiment might be partly attributed to uncertainties associated with the estimate of the unperturbed dimensions. There has been no sure method to making these estimates for this purpose since they were based on viscosity $[\eta]$ and molecular weight M alone,[8,9] and especially since the theta solvent could not be found for a given system.

As was mentioned in Sec. 2.2, however, Inagaki and co-workers[10] have proposed a tentative method (eq. 13) for estimating the unperturbed dimensions from viscosity data obtained for extremely good solvent systems, especially those in which the expansion factor α is larger than 1.4.

$$([\eta]/M^{1/2})^{4/5} = 0.786\ K^{4/5} + 0.950\ K^{4/5} z^{*2/3}\ M^{1/3} \qquad (13)$$

Moreover, they have been proved that the Stockmayer-Fixman method (eq. 12) for the same purpose[11] is applicable if $1 < \alpha < 1.4$.[10]

$$[\eta]/M^{1/2} = K + 0.330\ C_{\eta} \Phi_{0} B M^{1/2} \qquad (12)$$

Thus if, corresponding to the magnitude of α of a given system, one of these two methods is alternatively used, the characteristic ratios ($\langle R^2\rangle_0/nl^2$) may be determined irrespectively of thermodynamic properties of the solvent used.

The purpose of this Chapter is to visualize the effect of substituted methyl groups upon the unperturbed dimension of the polymethylene chain by applying the methods mentioned above to data of $[\eta]$ and M obtained by different authors for polypropylene fractions in various solvents. The unperturbed dimensions of atactic and isotactic polypropylenes are estimated by referring to the relationships between $[\eta]$ and M reported by Danusso, et al.,[12,13] Kinsinger and Hughes,[14,15] and Parrini, et al.,[16] respectively. That of the syndiotactic polypropylene is estimated by using our new viscosity data. Two types of syndiotactic propylene polymers are prepared at -78°C with a catalytic system proposed by Natta, et al.,[17] in toluene and in heptane, respectively. Thus the characteristic ratios $\langle R^2\rangle_0/nl^2$ of these polymers with different stereoregularities are discussed in comparison with those reported recently for polyethylene.

3.1 Preparation and Fractionation of Syndiotactic Polypropylenes

Syndiotactic propylene polymers were prepared using a catalytic system of vanadium tetrachloride-anisol-diethylalminum monochloride, which has been described by Natta, et al.[17] Two different series of polymerizates were obtained using toluene and heptane, respectively, as the solvent for polymerization. The catalytic solution was obtained by treating 10^{-3} mole of vanadium tetrachloride and 10^{-3} mole of anisol with 5×10^{-3} mole of diethylalminum monochloride in 200 ml of one of the solvents at room temperature for about 1 hr. The 3 moles of liquid propylene was introduced into the catalytic solution and the polymerization mixture was kept at -78°C. After 24 hrs, the mixture was poured into a large amount of methanol which was slightly acidified with hydrochloric acid, thus recovering the polypropylene as a precipitate. The precipitated polymer was pulverized in a blender and washed several times with the acidified methanol until the green color of the polymer disappeared.

A very small amount of the polymer prepared with toluene as solvent was insoluble in boiling diethyl ether, and the removal of this insoluble portion was made by means of extraction with boiling-diethyl-ether for 24 hrs. The portion soluble in ether was recovered and its intrinsic viscosity in decalin at 135°C was 204 ml/g. This fraction will hereafter be designated SP-T. On the other hand, the polymer prepared with heptane as solvent was almost completely dissolved in boiling-n-heptane except for a small portion which existed in a gel form. After removing this gel portion, the fraction easily soluble in boiling-n-heptane (SP-H) was further divided into two portions with boiling-diethyl-ether, i.e., into boiling-ether-soluble and -insolble portions (SP-HE and SP-HI). The $[\eta]$ values in decalin at 135°C were 64 and 78 ml/g, respectively, and the weight fractions of SP-HE and SP-HI were 0.35 and 0.65, respectively.

The polymer sample SP-T was fractionated into eight fractions by usual fractionation-precipitation techniques with a system of n-octane and n-propyl alcohol at 30°C. Using the same procedure, the polymer sample SP-HE was fractionated into six fractions. Results of the characterization of these fractions are seen in Table 3-1. On the other hand, because of the instability of the n-octane solution of SP-HI,

Table 3-1. Characterization of Syndiotactic Polypropylene Samples

Polymer code	IR-index	Mp, °C	$M_w\cdot10^{-3}$ and $A_2\cdot10^3$		[η], ml./g.			
			Archibald	L.S.	decalin 135°	heptane 30°	toluene 30°	isoamyl acetate 45°
SP-T *)	0.85	83~94			204			
SP-T_2	0.79		422 (0.32)	452 (0.64)	370	320	264	125
SP-T_3	0.75		209 (0.74)	228 (0.83)	$209._5$	185	155	87
SP-T_4	0.85		151 (0.93)	154 (0.95)	$154._5$	$142._3$	121	73
SP-T_5	0.80		118 (1.24)	122**) (0.99)	130	$120._7$	102	$64._5$
SP-T_6	0.81		88 (1.14)	94 (1.04)	99	$95._4$	84	56
SP-T_7	0.85		54 (1.41)	---	$72._8$	$71._0$	61	42
SP-HE*)	1.20	96 104			64			
SP-HE_{234}***)				83.3****)				
SP-HI*)	1.50	130 132			78			

*) Unfractionated Polymers.

**) M_w = 117 000 in isoamyl acetate.

***) Mixture of fractions SP-HE_2, SP-HE_3 and SP-HE_4.

****) Determined in isoamyl acetate.

a sand column fractionation technique using decalin and buthyl carbitol as the elution agent at the boiling point of toluene was applied to this sample. As will be described later, the fractions obtained from SP-HI had high stereoregularities, and one of these fractions was used for theta point determination in isoamyl acetate.

3.2 Physical Measurements

3.2.1 Infrared spectra

The 2-15 μ spectra were taken on a Shimadzu AR-275 II_3 spectrometer. Polypropylene films (thickness of 80 μ) for the measurement were prepared from trichloroethylene solution. According to Natta, et al.,[17] syndiotactic polypropylene shows a characteristic absorption band at 11.53μ (867 cm^{-1}). The spectra obtained for all of the present samples were found to have this characteristic band, as is illustrated in Figure 4-1. To indicate the syndiotacticity of sample, an infrared index first proposed by Natta[18] was used. This index A_s is given by

$$A_s = A_{11.53}/(1/2)\ (A_{2.32} + A_{2.35})$$

where the A's are the optical absorptions at 11.53, 2.32 and 2.35 μ. The base line for the 11.53 μ band was the straight line drawn tangentially between the absorption minima near 11.3 and 11.7 μ, while that for the 2.32 and 2.35 μ bands was the straight line drawn tangentially between the absorption minima near 2.2 and 2.7 μ. The infrared indices of our samples were found to range from 0.8 to 1.5. The results are given in Table 3-1 together with the other data. The samples used showed the same X-ray spectrum characteristic of syndiotactic polypropylene as was observed by Natta, et al.[17] (see Fig. 3-2).

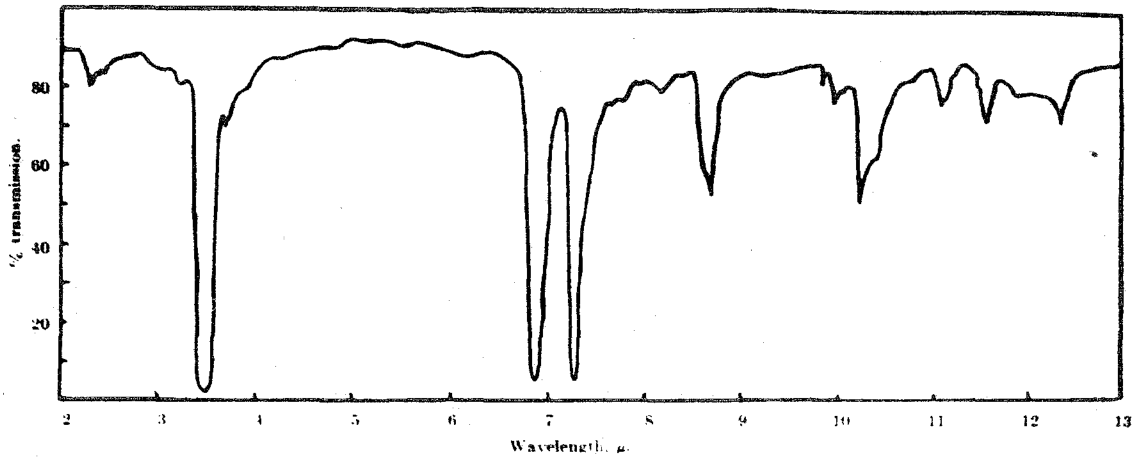


Fig. 3-1 IR-spectrum of syndiotactic polypropylene prepared in this Chapter.

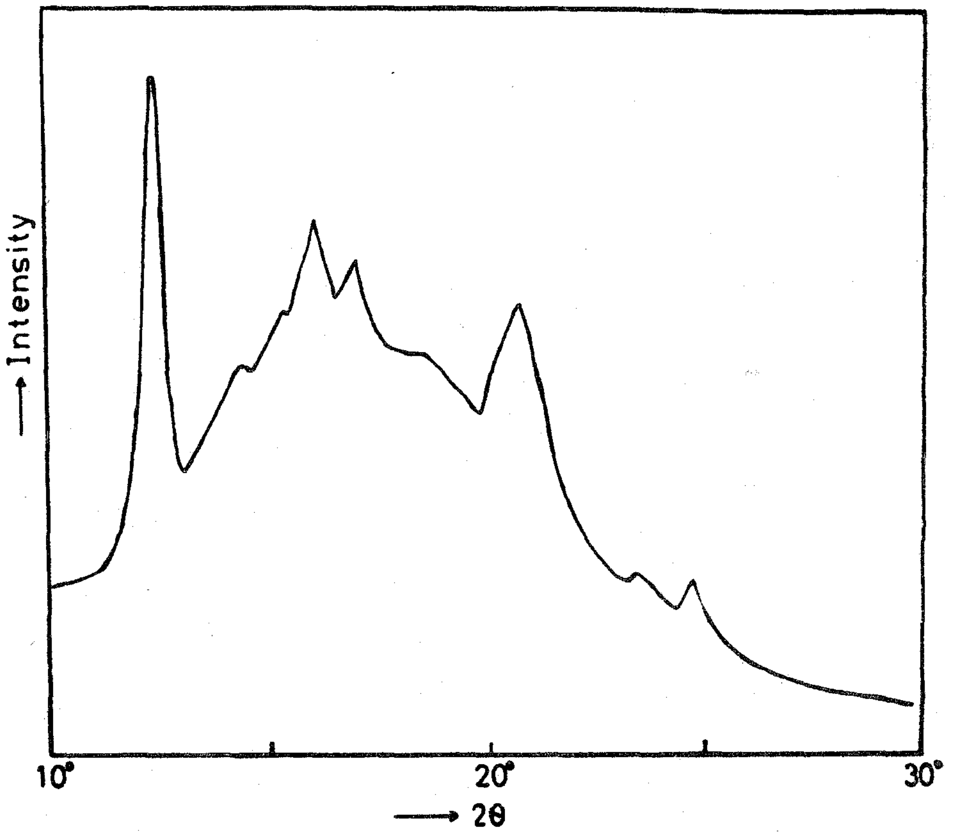


Fig. 3-2 X-ray diffraction spectrum of syndiotactic polypropylene corresponding to Fig. 3-1.

3.2.2 Melting point determinations

The melting point determinations were made only for the whole polymers with a Chiyoda polarization microscope equipped with a thermostage. The rate of temperature increase was adjusted to 0.25°C/min. Melting points observed for these samples were in a range between 83° and 132°C and parallel to the increases of the infrared indices (see Table 3-1).

3.2.3 Molecular weight determinations

All solution measurements were made in n-heptane unless otherwise stated. The Archibald ultracentrifugal procedure[19] was applied for the molecular weight determination of the fractions of the SP-T series. The measurements were carried out at 30±0.1°C using a Phywe analytical ultracentrifuge. Apparent molecular weights M_{app} obtained as a function of the initial concentration c_o were analyzed according to the following semi-empirical equation to yield the weight-average molecular weight M_w[20]:

$$\ln(1/M_{app}) = \ln(1/M_w) + 2A_2M_wc_o , \tag{20}$$

where A_2 is the osmotic second virial coefficient appearing in the well-known light-scattering equation. For the partial specific volume $\bar{v}$, we assumed that $\bar{v}$ was equal to the apparent specific volume $\bar{v}^*$, which was found for this system to be 1.127 ml/g at 30°C in the concentration range from 0 to 1g/dl. For the density of n-heptane, we used a literature value of 0.6753 g/ml at 30°C. The values of M_w and A_2 are included in Table 3-1. For unknown reasons, the A_2 value found for the hightest molecular weight sample SP-T_3 was abnormally low, and therefore we rechecked all of these data by light scattering.

Scattered light intensities were determined with a modified photometer of the Brice type (Shimadzu light scattering photometer)[21] equipped with a constant-temperature jacket.[22] The angular variation of the scattered intensity was determined at eleven different angles ranging from 30° to 150° using vertically polarized light of 436 mμ wave length. A cylindrical cell was used throughout the work. Calibration procedures of the apparatus are the same as reported in detail by Inagaki, et al.[9] Molecular weight determinations of all the samples were carried out in n-heptane at 30°C. To measure the theta temperature for some of the samples, isoamyl acetate was used as solvent. The solutions were clarified by filtration through grade "mittel" Ultracerafilter (Göttingen).

Refractive index increments were determined in a thermostated Shimadzu (Debye type) differential refractometer using 436 mμ. The value of the n-heptane solution at 30°C was found to be 0.107_7 ml/g.

The required values of Kc/R_0, where K is the well-known light scattering factor and R_0 the reduced intensity of the scattered light at zero angle, were obtained by the usual extrapolation according to Zimm.[23] The second virial coefficient A_2 was determined by the following equation,

$$Kc/R_0 = 1/M_w + 2A_2c \qquad (21)$$

The values of M_w and A_2 are given in Table 3-1. Except for the result of SP-T_2, these are in fairly good agreement with those obtained by the Archibald method, although M_w values obtained by light scattering are always higher by a few per cent. The double logarithmic plot between $[\eta]$ obtained in n-heptane at 30°C (see next section) and M_w determined by light scattering gives the equation

$$[\eta]_{30}(\mathrm{ml/g}) = 3.12 \times 10^{-2} M_w^{0.71}$$

In a preliminary experiment we found that isoamyl acetate which is known as a theta solvent for atactic polypropylene (Θ = 34°C)[11] could dissolve our syndiotactic samples as well. Thus the scattered-light intensities in isoamyl acetate were determined once more for three fractions, SP-T_5, SP-HE_{234}[24], and SP-HI_3 at various temperatures ranging from 45° to 70°C. The value of A_2 at each temperature was computed by above eq. (21). Subsequently, A_2 was plotted against T to find by extrapolation the theta temperature at which A_2 vanishes (see Fig. 3-3). Thus the theta temperatures for SP-T and SP-HE series were determined to be approximately 41° and 43.5°C, respectively. Details of the data obtained are given in Table 3-2. However, the theta point for SP-HI_3 could not be confirmed; the solution exhibited a transition into a turbid, gel-like state as soon as the temperature dropped below 70°C. For this higher crystalline polymer, therefore, we may only suppose that the theta point, if it exists, would be somewhat lower than 70°C. In any event, the close parallel correlation found between theta temperature and infrared index as a relative measure of syndiotacticity should be interesting. This finding will be discussed later.

3.2.4 Viscosity measurements

Viscosity measurements were made in a Ubbelohde viscometer with a flow time of 105 sec. for n-heptane at 30°C. The kinetic energy correction of $[\eta]$ was determined to be less than 0.2%. The sample of the highest molecular weight was examined in a variable-shear viscometer and was found to exhibit a Newtonian flow. The intrinsic viscosities of all of the fractions in decalin were determined at 135°C under a

Table 3-2. Light Scattering Data for Syndiotactic Polypropylene in Isoamyl Acetate

Polymer	$M_w \cdot 10^{-3}$	Temp., °C.	$A_2 \cdot 10^4$	Θ°C.
SP-T_5	117	46.5	0.8_0	41
		52.0	1.64	
		67.0	4.0	
SP-HE_{234}	83.5	52.0	1.37	43.5
		60.0	2.57	
		67.0	3.52	
SP-HI_3	---	---	---	70

Table 3-3. Temperature Dependence of Intrinsic Viscosity

Polymer	$[\eta]$			$(\partial \ln[\eta]/\partial T)_\theta \cdot 10^3$
	45.0°	46.5°	48.0°C.	
SP-T_2	124.0	125.5	128.3	11.3
SP-T_3	87.0	88.1	89.0	7.6
SP-T_5	66.2	67.0	67.2	5.5

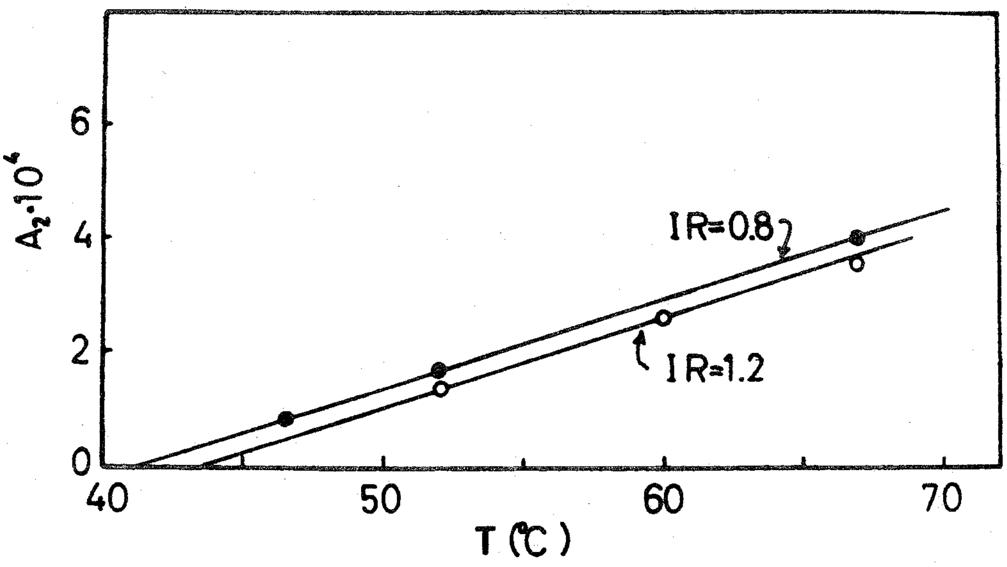


Fig. 3-3 Temperature dependences of A_2 for SP-T_5 and SP-HE_{234} studied by light scattering. The approximate estimates of theta temperatures are 41° and 43.5°C for the former and latter sample, respectively.

nitrogen atmosphere with 2,4-di-t-butyl-p-cresol added to the solution, in order to avoid the oxidative degradation of the polymers. In addition, the measurements in toluene at 30°C and isoamyl acetate at different temperatures near theta points relevant to each sample series were made on some selected fractions. The latter data will be used to derive the temperature coefficient of the unperturbed dimension and are listed in Table 3-3.

3.3 Unperturbed Dimensions and Stereospecificities

3.3.1 Atactic and isotactic polypropylene

Figure 3-4 shows plots of eq. (13) with relationships between intrinsic viscosity $[\eta]$ and number-average molecular weight M_n reported by Danusso and Moraglio for atactic polypropylene fractions.[12] The $[\eta]$ are determined in decalin at 135°C, and in cyclohexane, toluene, and benzene at 30°C, and the values of M_n by osmotic measurements. For the system in decalin the $[\eta]$-M_n and $[\eta]$-M_w data obtained by Kinsinger and Hughes[14] (half-filled and filled circles, respectively) are plotted simultaneously with those of Danusso and Moraglio (open circles). Disagreement between these two series of data is remarkable, especially in the region of the higher molecular weights. However, two data points for the lowest and the second from the lowest molecular weight obtained by the former authors fall on a line passing through those of the latter authors. Taking such a circumstance into consideration, an extrapolation of the plot to $M^{1/3} \rightarrow 0$ was made. The intercept on the ordinate was found to be 0.144, which yields $K = 12.0 \times 10^{-2}$ in accordance with eq. (13) (see Chapter 2). This K value is thus in

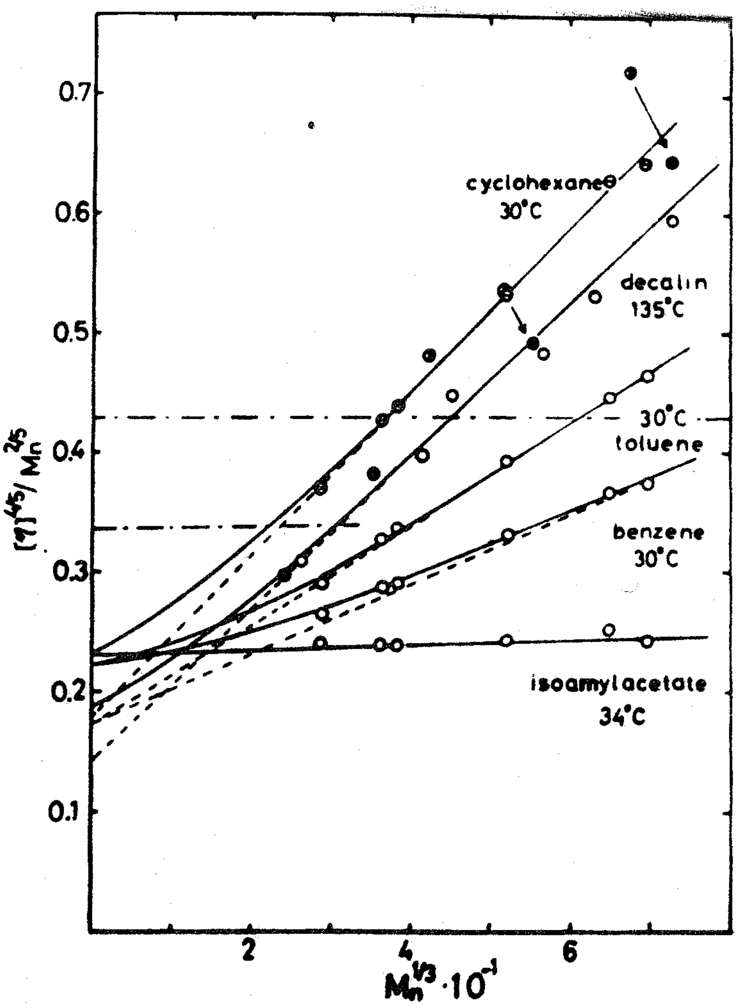


Fig. 3-4 Plots of eq.(13) with [η]-M_n relationshipd reported by various authors for atactic polypropylene in different solvents. The lower and upper chain lines indicate the limits of application of eq.(13) for the system in decalin at 135°C. and for the other solvent systems, respectively. For details, see Texst.

excellent agreement with that estimated by Kinsinger and Hughes using a theta solvent, diphenyl ether, at 153°C,[15] but remarkablely lower than the value of 16.8×10^{-2} obtained by Danusso and Moraglio using another theta solvent, isoamyl acetate, at 34°C.[12] This difference may be attributable to a negative temperature coefficient of the unperturbed dimension of this polymer. However, such an interpretation seems to be opposed to some observations of Kinsinger and Hughes made at other theta temperatures;[15] they have found higher K values than 16.8×10^{-2} at higher temperatures, e.g., 74 and 92°C (see Table 3-4). What we note will be the effect of molecular weight heterogeneity on the K value for the present treatment is made on the basis of number-average molecular weights. This effect may be corrected by introducing a factor q_n[25] defined by

$$q_n = [\eta]_\theta / K M_n^{1/2} = \Gamma(h + 1.5)/h\Gamma(h + 1) \qquad (22)$$

where $(h + 1)/h = M_w/M_n$ and Γ represents the Γ function. The last form results from the Schulz distribution. This correction is quite large if polymers are poorly fractionated, but this amounts only to 1.09 if $h = 4$. Moreover, our main interest consists not in the K value itself but in the quantity A, which is proportional only to $K^{1/3}$, as is seen in eq. (11). Thus differences in the characteristic ratios among polymers may be discussed without taking into consideration the average nature of the molecular weight.

In connection with the above problem, the K values estimated in other good solvents should be discussed. Chain lines drawn parallel to the abscissa in Figure 3-4 indicate the limit for the application of eq. (13), which is described by eq. (15) corresponding to $\alpha > 1.4$.

The lower chain line indicates the limit for decalin, while the upper indicates that for the other solvents. Data points below this limit should pass through a little higher point on the ordinate, which corresponds to $K^{4/5}$ rather than $0.786 \times K^{4/5}$. Thus below this limit, eq. (13) is the asymptote to eq. (7) and hence is inapplicable to data points for toluene and benzene, but is applicable for decalin and cyclohexane.[12] Therefore, for these series of data points we use the Stockmayer-Fixman equation (12). Figure 3-5 shows plots of eq. (12) with the data for toluene, benzene and isoamyl acetate. The data points for the highest and the second from the highest molecular weight with toluene as solvent derivate downward slightly from the most reasonable extrapolation line. However, such deviations should occur as expected from α values of these samples (see Figure 3-4). With the aid of the Stockmayer-Fixman plot we get nearly the same K value 15.3×10^{-2} for toluene and benzene.

To establish further the K values obtained above, we use the original equation of Ptitsyn.[26] This is

$$(\alpha^2 - 0.786)^{3/2} = 0.099 + 0.305BA^{-3}M^{1/2} \qquad (23)$$

where α is computed from

$$\alpha^2 = [\eta]^{4/5}/K^{4/5}M^{2/5} \qquad (24)$$

The above equation may permit the justification of whether a value of K assumed for calculation α was reasonable. If a wrong K value is assumed, the plot of eq. (23) should not pass through the theoretical value 0.099 on the ordinate.

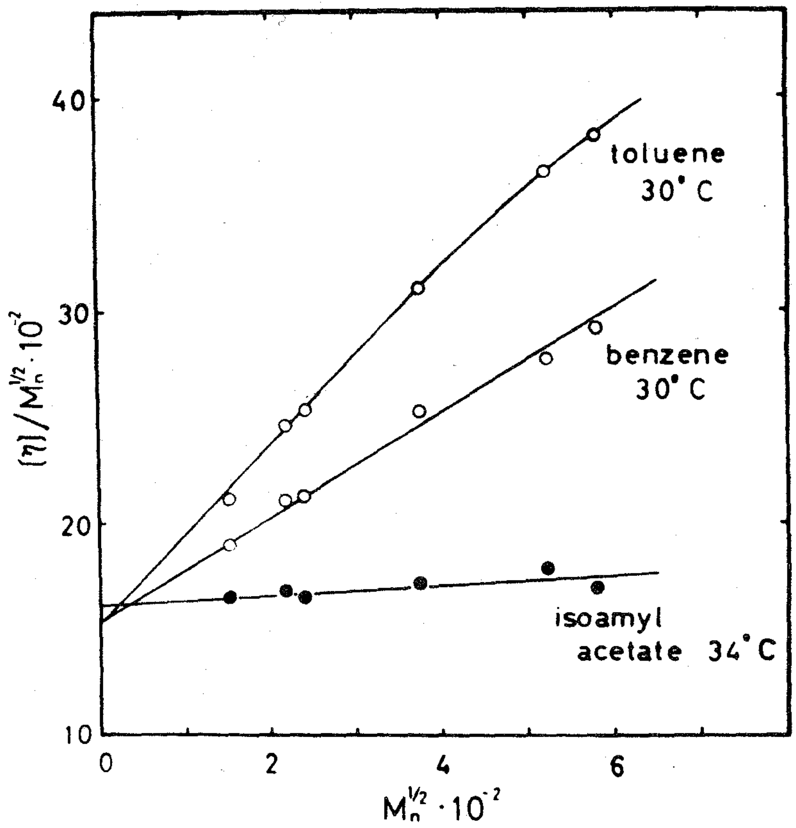


Fig. 3-5 Stockmayer-Fixman's plots with the same data as shown in Fig. 3-4.

For applying this procedure to the present problem, we assumed K values relevant to each system. Figure 3-6 shows plots of eq. (23). Straight lines for each system are obtained and meet at ca. 0.10 on the ordinate. This finding clearly indicates that the assumed K values were correct and, at the same time, that the unperturbed dimention of this polymer decreases with increasing temperature almost independent of solvent used. On the other hand, the B value for each system may be easily evaluated from the slope of each straight line. Using this B value and referring to eq. (13) we may draw the asymptote for each system. These asymptotes are shown in Figure 3-4 by dotted lines. Each dotted line appears to give a natural asymtote for each series of the data points. Thus we may concluded that the 10^2xK values 12.0 and 16.8 found at 135^o and 34^0C, respectively, are consistent with each other and a negative temperature coeffient of the unperturbed dimension is expected.

The same procedure for estimating the unperturbed dimension is applied to $[\eta]$ and M_w data reported by different authors for isotactic polypropylene in decalin,[14] tetralin at 135°C, and α-chloronaphthalene at 145°C.[16] These plots are demonstrated in Figure 3-7 together with the limit for application of this procedure indicated by chain line. According to Fig. 3-7, we see that all of the data points for decalin and tetralin lie beyond the chain line. Thus a direct extrapolation to $M_w^{1/3} \longrightarrow 0$ should be permissible to obtain correct K values. Dotted lines indicate such extrapolations for each system and appear to have a common intercept on the ordinate at 0.120, which leads to $K = 9.5_5 \times 10^{-2}$ irrespective of the solvent used. This $K \times 10^2$ value

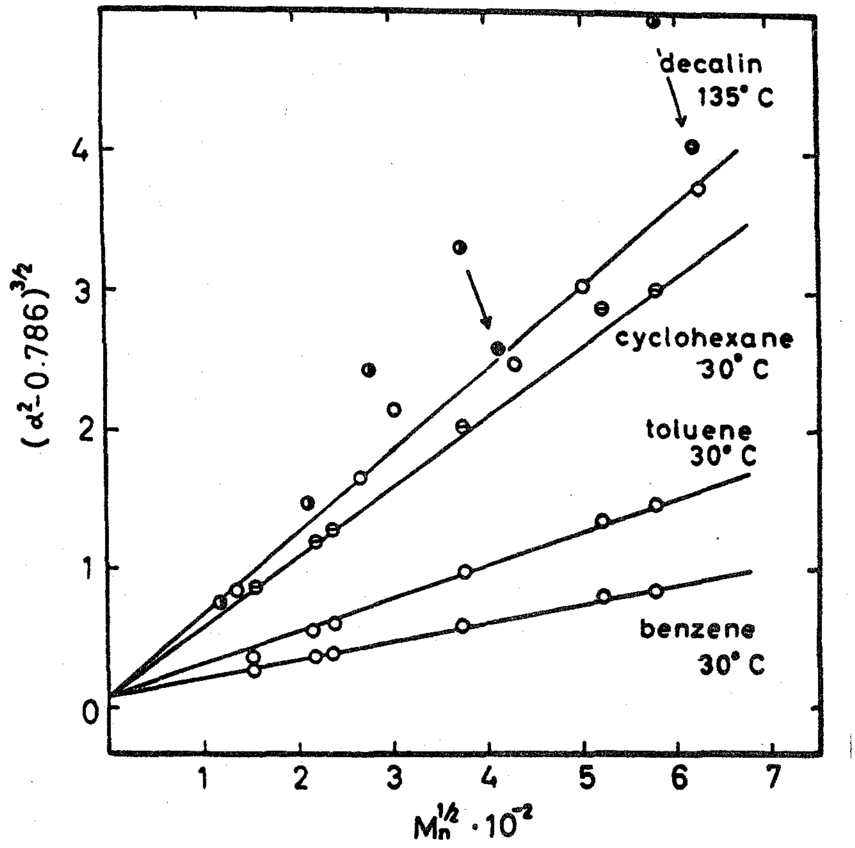


Fig. 3-6 Plots of the original Ptitsyn equation(23) with the same data shown in Fig. 3-4 for justifying the K values estimated according to eq. (13).

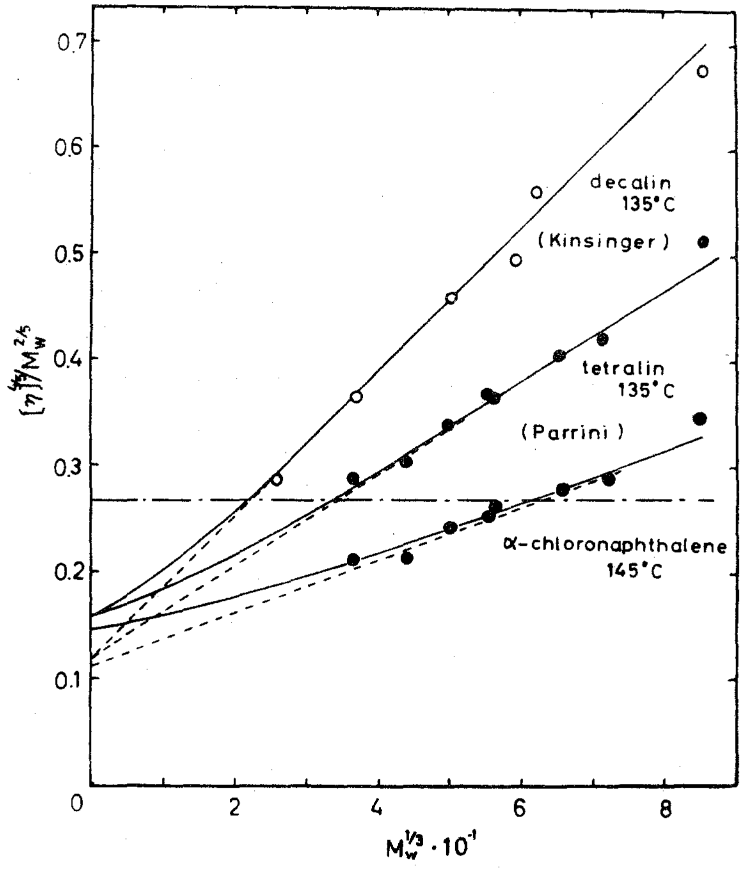


Fig. 3-7 Plots of eq.(13) with $[\eta]$-M_w relationships for isotactic polypropylene in different solvents. For details, see Text.

is considerably lower than the 13.2 estimated by Kinsinger and Hughes from theta point viscosity data in diphenyl ether at 145°C,[14] but in good agreement with 9.4 reported by Kotera, et al., for the same system as mentioned above.[7] In this connection it should be noted that if eq. (12) is applied to the same data shown in Fig. 3-7, higher K values, approximately 13×10^{-2} (11×10^{-2} for α-chloronaphthalene), are obtainable. However, taking into consideration the fact that the solvents used are extremely good for this polymer, these values may be overestimated. This is unavoidable associated with the application of eq. (12).

3.3.2 Syndiotactic polypropylene

For estimating the unperturbed dimension of syndiotactic polymer we use our own data of $[\eta]$ and M_w obtained in decalin (135°C), heptane and toluene (30°C), and isoamyl acetate (45°C). Figure 3-8 shows plots of eq. (13) for SP-T series having the infrared indices of ca. 0.8. As is indicated by two chain lines in the figure, only data points for decalin may be treated in accordance with eq. (13), while the others should be treated with eq. (12). Figure 3-9 shows the results of the latter treatment. From this figure we see that isoamyl acetate is a theta solvent for the syndiotactic polymer as well as for the atactic. K values estimated using eq. (12) and (13) alternatively are given in Table 3-4. Tests of these K values according to eq. (23) are shown in Figure 3-10. The mathematical requirement of eq. (23) seems to be fulfilled with these K values.

As pointed out previously, the unperturbed dimensions of propylene

Table 3-4. Polypropylene at the Ideal States (θ)

Configuration	Solvent	Temp.($^\circ$C.)	$K\cdot10^2$	$A\cdot10^{11}$ *)	$B\cdot10^{27}$	σ	$\langle R^2\rangle_0/nl^2$
Atactic	Isoamyl acetate[a)]	34(θ)	16.5	831	~ 0	1.75	6.12
	Cyclohexane[a)]	30	15.9	820	9.05	1.73	5.96
	Benzene[a)]	30	15.3	811	2.30	1.71	5.83
	Toluene[a)]	30	15.3	811	4.12	1.71	5.83
	1-Chloronaphthalene[b)]	74(θ)	18.2				
	Cyclohexanone[b)]	92(θ)	17.2				
	Decalin[a)]	135	12.0	748	8.11	1.57	4.96
Syndiotactic	Isoamyl acetate[c)]	45(θ)	17.2	843	~ 0	1.77	6.30
	Toluene[c)]	30	16.4	830	3.37	1.75	6.11
	Heptane[c)]	30	16.4	830	5.13	1.75	6.11
	Decalin[c)]	135	11.2	731	8.70	1.54	4.74
Isotactic	Tetralin[d)]	135	9.55	693	4.85	1.46	4.26
	Decalin[b)]	135	9.55	693	9.52	1.46	4.26
	α-Chloronaphthalene[d)]	145	8.95	678	1.84	1.43	4.07
	Diphenyl ether[b)]	145(θ)	13.2				

*) Calculated assuming $\Phi_0 = 2.87 \times 10^{23}$ c.g.s..

a) Data of Danusso and Moraglio[12,13)]; b) Those of Kinsinger and Hughes[14,15)]; c) the present work and d) those of Parrini et al.[16)].

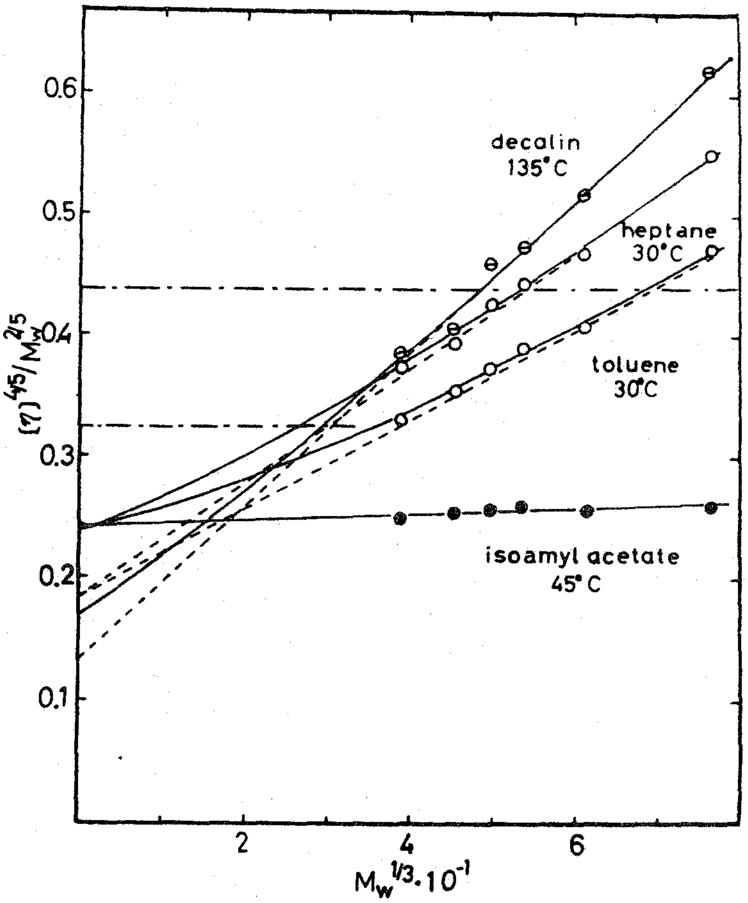


Fig. 3-8 Plots of eq.(13) with our own data for fractions of SP-T series with IR-index of ca. 0.8 in various solvents. Lower and upper chain line indicate the limits of application of eq.(13) for decalin and for the other solvents, respectively.

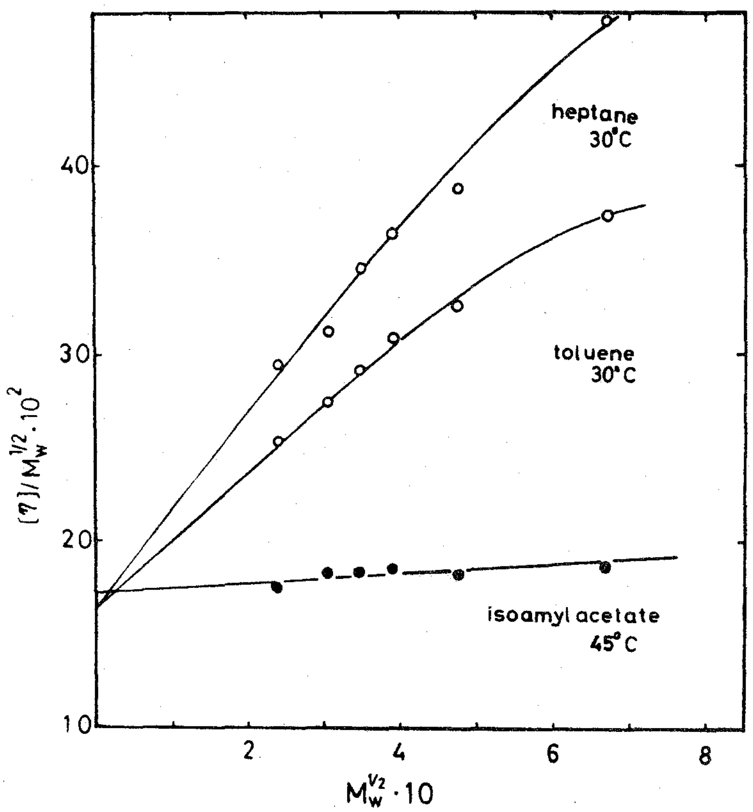


Fig. 3-9 Plots of eq.(12) with the same data as shown in Fig. 3-8.

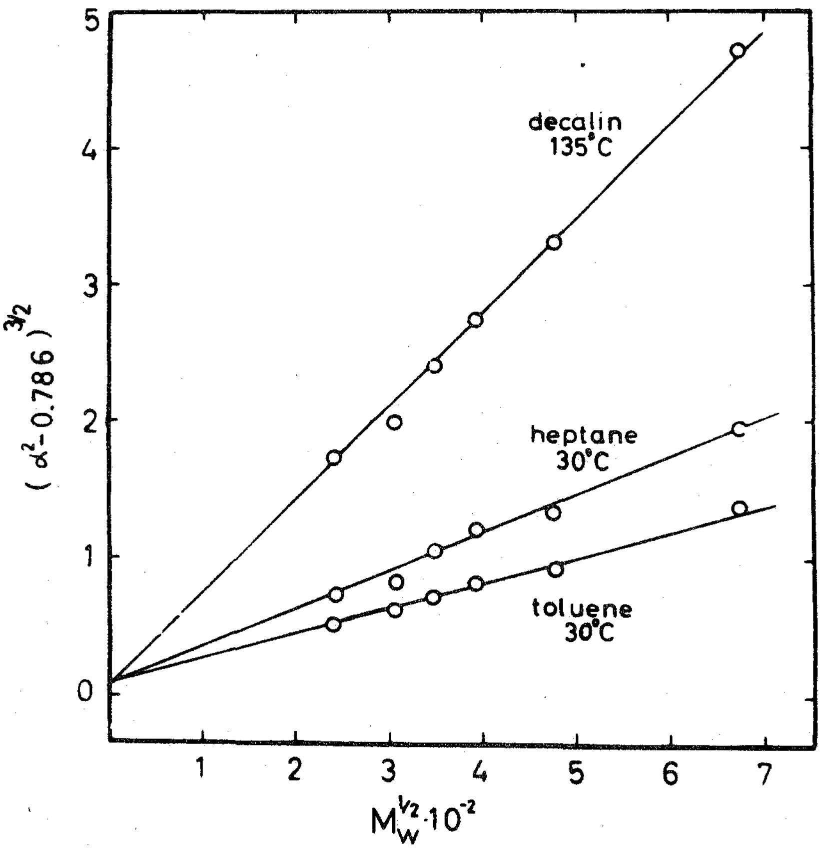


Fig. 3-10 Plots of eq.(23) for the same systems given in Fig. 3-8, using K values estimated according to eq.(13) and/or (12).

polymers are influenced much more by temperature than by the solvents used. Thus to discuss the dependence of the K value on stereospecificity, we choose the data obtained in decalin at 135°C. The values of $10^2 \times K$ for the atactic and syndiotactic samples are nearly the same, i.e., 12.0 and 11.2, respectively, whereas they differ considerably from 9.6 found for the isotactic. However, this finding supports previous observations that the unperturbed dimension generally depends little on stereoregularity.[15,27,28] Especially, the fact that the unperturbed dimensions of propylene polymers are almost independent of stereospecificity may be well interpreted in terms of the theoretical prediction made by Flory, et al., taking the existence of heterotactic units in the polymer chain into consideration.[6] In addition, the characteristic ratios evaluated experimentally converge at about 6.0. This also is in agreement with calculations by Flory, et al.[6] (see Table 3-4).

In connection with the above finding, it is interesting to note the following facts. The atactic and syndiotactic polymers have a common theta solvent, isoamyl acetate. The theta temperature of the latter polymer increases proportionately to its stereoregularity, changing from 34°C (or somewhat lower) for the former to ca. 70°C (or somewhat lower) for the latter with an infrared index of 1.5 (see Table 3-2).

In accordance with the conclusion drawn by Kinsinger and Wessling,[27a] these observations imply that the atactic and syndiotactic polypropylene may be identified as a family in which only the microsyndiotacticity differs from the one to the other. Such an idea may be well supported by the finding of Woodbrey that a polypropylene sample, which has been regarded as atactic because of the absence of its optical absorption at 867 cm^{-1}, could be predominantly syndiotactic from the viewpoint of nmr study.[29b] This problem will be discussed later in terms of the microtacticity along the single main chain.

3.3.3 Temperature coefficient of syndiotactic polypropylene

In this section, the temperature coefficient of syndiotactic polypropylene $d\ln\langle R^2\rangle_0/dT$ is discussed. This coefficient affords the important knowledge of the conformational study of a given polymer chain as well as the absolute value of unperturbed dimension does. Especially, for isotactic polypropylene, its temperature coefficient had not been known, until very recently Nakajima and Saijo reported the value of -4.09×10^{-3} deg.$^{-1}$.[29d]

Starting from the Kurata-Yamakawa perturbation theory of intrinsic viscosity,[30] Inagaki, et al. arrived at

$$(d\ln[\eta]/dT)_\theta = (d\ln\langle R^2\rangle_0^{3/2}/dT) + KM^{1/2} \qquad (25)$$

where K is a constant independent of T and M and the subscript 0 means that the quantities referred to are those at the theta point.[9] Thus the temperature coefficients evaluated with eq. (25) should differ from those with other methods by a change due to temperature variation of appearing in eq. (11). Since $\ln[\eta]$ changes linearly with T in the vicinity of the theta point,[9] the value of its temperature derivative at θ is obtainable with good accuracy.

In Figure 3-2, values of $(d\ln[\eta]/dT)_\theta$ obtained with the system syndiotactic-polypropylene-isoamyl acetate are plotted against $M_w^{1/2}$ (see Table 3-3). Extrapolation of this plot to $M_w^{1/2} \rightarrow 0$ yields

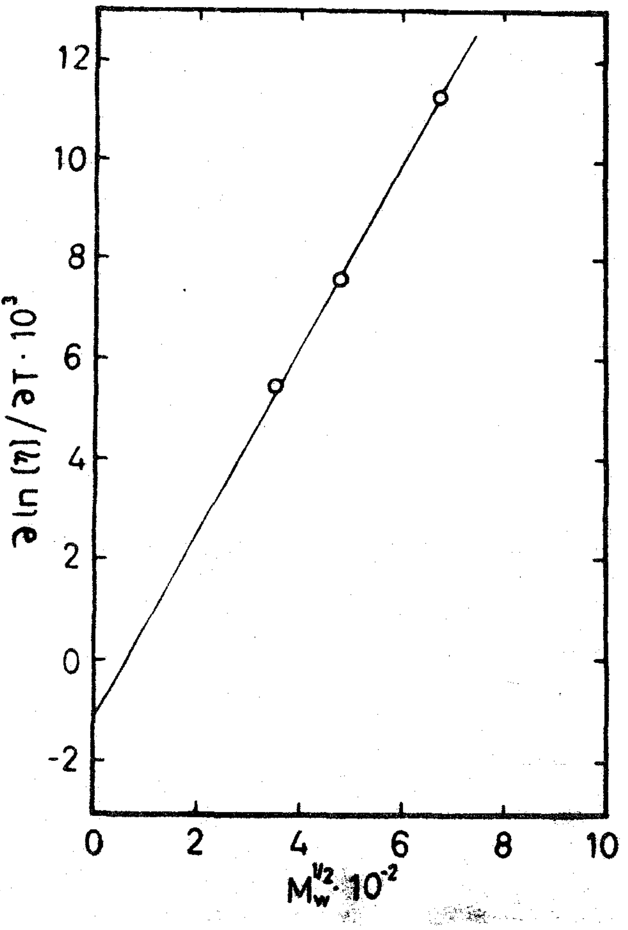


Fig. 3-11 Plots of eq.(25) with data obtained for syndiotactic polypropylene in isoamyl acetate.

$-(d\ln[\eta]/dT)_\theta = 1.1 \times 10^{-3}$ deg.$^{-1}$, which corresponds to

$$-(d\ln\langle R^2\rangle_0/dT)_\Theta = 0.7 \times 10^{-3} \text{ deg.}^{-1}$$

Because of the lack of experimental data this value is somewhat inaccurate and might be inadequate for direct comparison with those of the other polymers. However, the fact that this value lies between those for polyethylene and polyisobutylene[3] might be explained in terms of the effect of the methyl group on the steric hindrance of bond rotations. Moreover, the negative sign of this coefficient informs us of an important factor for understanding the role of the internal rotations of side groups with regard to those round the main chain.

3.3.4 Comparison of polypropylene with polyethylene

Recently, a number of authors have been engaged in establishing $[\eta]$-M relationships for polyethylene in different solvents. Thus K values reported by different authors now give an identical value within experimental error.[4,31] As an example, Figure 3-12 shows a plot of eq. (13) with Chiang's data of $[\eta]$ and M_w for the system polyethylene-decalin at 135°C.[4a] A reasonable extrapolation of this plot to $M^{1/3} \rightarrow 0$ affords 30.6×10^{-2} for its K value, which is almost identical with the value of 30.0×10^{-2} estimated using eq. (12). These $10^2 \times$ K values are also in excellent agreement with the values of 29.5 and 31.6 obtained in diphenyl ether at its theta point (161.4°C)[4a] and in dodecanol-1 at its theta point (138°C)[4b], respectively. In connection to this finding, it should be noted that poly(butene-1) chain has a positive sign of the temperature coefficient of $\langle R^2\rangle_0$ while polyethylene and polypropylene the negative sign.

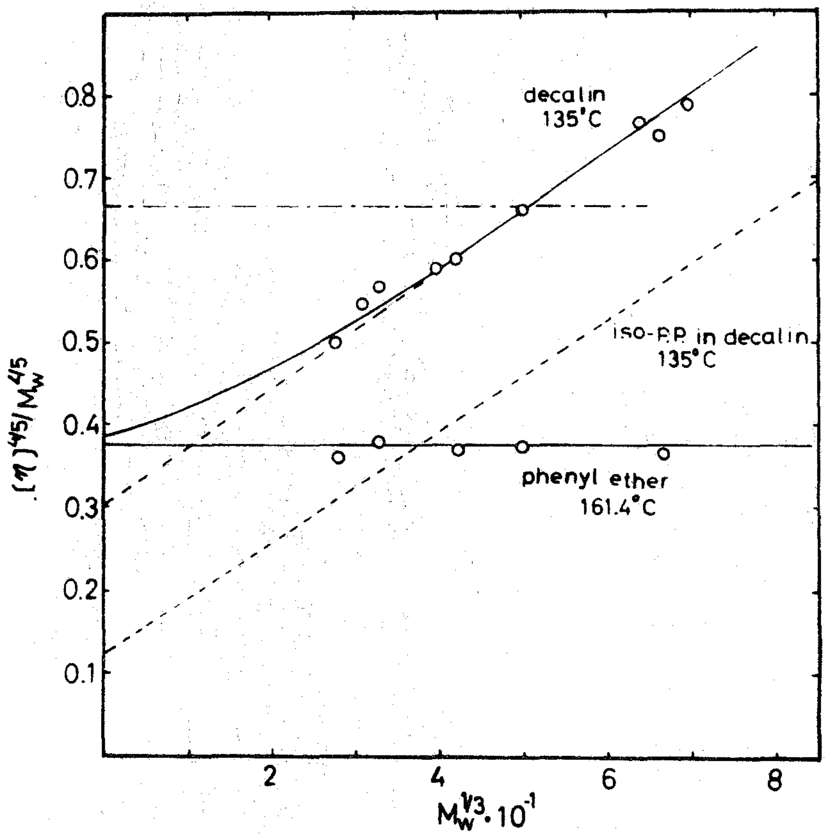


Fig. 3-12 Plots of eq.(13) with [η]-M_w relationships obtained by Chiang for polyethylene in decalin and phenyl ether (Θ-solvent). The same plot for isotactic polypropylene in decalin at 135°C is given for comparison by dotted line.

Now we compare the characteristic ratios or the steric factors σ for polyethylene with those for polypropylene. The characteristic ratio is related to σ by

$$\langle R^2\rangle_0/nl^2 = \sigma^2(1 + \cos\Theta)(1 - \cos\Theta)^{-1} \tag{26}$$

For the purpose of eliminating the effects of temperature and solvent upon the unperturbed dimension, we may conveniently use K values obtained in a common solvent at a common temperature. Fortunately, we have such data, those for decalin at 135°C. The available data to date, summarized in Table 3-5, indicate clearly that the characteristic ratios or the σ values for polypropylene, irrespective of its stereospecificity, never exceed that of polyethylene. This result presents a sharp contrast to that of the calculation of Allegra, et al.,[32] and also with that of Flory, et al., in which the interdependent-rotation model[5] was applied to strictly stereoregular poly-α-olefin.[6]

In spite of this discrepancy between calculation and experiment, the order of magnitudes found for the σ values is fortuitously consistent with the fact that in the crystalline state, polyethylene chains take the most extended conformation tttt........, while syndiotactic and isotactic polypropylene chains take the more contracted conformations ttgg.... and tgtg....., respectively.[33] Here t denotes the trance form and g the gauche form. A similar interpretation has been presented by Kotera.[7] Thus a simple question arises as to how far the chain conformations preferred in crystalline state are retained still in solution. There exist several cases, e.g., for polyethylene,[3,4], polyisobutylene,[34] and polyethylene oxide,[35], in which calculation achieved good agreement with experiments made on solutions. This would be an answer to the question just raised above. However, the solvent effect on the unperturbed dimension, hence

Table 3-5

Summary of the Characteristic Ratios and the Steric Factors Obtained for Polypropylene in Decalin at 135°C. and Comparison with Polyethylene.

Polymer	Configuration	σ		$\langle R^2\rangle_0/ nl^2$	
		(a)	(b)	(a)	(b)
Polypropylene	Atactic	1.57	1.67	4.96	5.60
	Syndiotactic	1.54	1.64	4.74	5.36
	Isotactic	1.46	1.55	4.26	4.81
Polyethylene		1.75	1.86	6.14	6.94

a) Calculated assuming $\Phi_0 = 2.87 \times 10^{-23}$.

b) Calculated assuming $\Phi_0 = 2.4 \times 10^{-23}$.

on the chain conformation, has only been studied very little from experimental as well as theoretical viewpoints,[36] although a formulation of this effect was proposed.[37] Perhaps owing to the average torque induced by solvent molecules upon the internal rotations,[37] original conformations of polymer chains would only partly be retained fluctuating about their preferred positions. Thus an original conformation could be modified to another one after the polymer is isolated in solution.[36] In fact, Tadokoro, et al. observed by infrared studies that syndiotactic polypropylene dissolved in CS_2 indicated the absorption bands at 831, 964, and 1131 cm^{-1} characteristic of the planar zigzag more distinctly than the solid did, whereas the band at 867 cm^{-1} characteristic of the original helical conformation almost disappeared.[38a] Very recently, analogous findings have been observed by them as a result of infrared study in solution on other polymers.[38b]

On the other hand, there is little doubt that, for instance, the planar zigzag is the minimum energy conformation for an isolated polyethylene chain. Thus we think of a polyethylene chain with all the linkages fluctuating around their favorable positions. This picture differs somewhat from the usual one that a small fraction of the linkages departs from the trans position and a number of "planar zigzag" is connected by gauche linkages. In general, the pattern of the conformation fluctuation may be related to the nature of nonbonded interactions between neighboring substituents, or between substituents and chain atoms. In isotactic chains of $-(CH_2-CHR)_n-$type, where R means any alkyl group, the conformation fluctuation could be affected dominantly by the molecular volume of R, since the repulsions between nonbonded atoms are not symmetrical about the 120° position. Upon increasing the volume of R the conformation fluctuation would tend to be diminished, bringing the chain to a more extended form. Taking the experimental result of Tadokoro, et al.,[38] into consideration, however, the pattern of the fluctuation in polyethylene chains should not be noticeably different from that in polypropylene chains, and the original conformations of these polymer chains could be retained in solution to nearly the same extent. This situation may allow one to compare the σ values of these polymers solely on the basis of the original conformations. However, this trend no more holds for isotactic poly-(pentene-1) probably because of its bulky side group; the σ value is found to be far larger than that of polyethylene (> 2.0).[39] At present, we believe that the σ value may be described essentially in terms of a balance between the following two factors; the type of the original conformation and the degree of the conformation fluctuation or the retention of the conformation. Thus to achieve good agreement between calculated and observed unperturbed dimensions, one might have to invoke whole profiles of potential curves of internal rotations, in addition to energy difference between rotational isomerisms. Possibly the calculated unperturbed dimensions are much larger than the observed because of the approximate nature of the potential functions employed. It may be worthwhile to notice that the agreements between calculation and experiment reported to date have been limited to chain polymers having either no substituents[2,3,33,34] or two equal substituents[32] and to polyamide chains.[35]

Last to be mentioned here is the σ value of atactic polypropylene. This σ value has been computed on the basis of the number-average molecular weight, and this must be corrected for the polydispersity to compare directly with the other data. Since this correction factor will amount to only a few per cent, it is probable that the atactic polymer has a σ value close to that of the syndiotactic polymer. On the other hand, no finite figure has been given to the atactic polymer extracted with ether from the n-heptane-soluble fraction obtained in the isotactic polymerization.[40] However, the magitude of this σ value implies that the atactic polypropylene is very similar to the syndiotactic with respect to its stereochemical structure. The problem on the stereochemical structure of polypropylene is discussed in detail in Chapter 5.

References

(1) C. A. J. Hoeve, J. Chem Phys., **35**, 1266 (1961).

(2) K. Nagai and T. Ishikawa, Ibid., **37**, 496 (1962).

(3) (a) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, J. Amer. Chem. Soc., **83**, 1015 (1961); (b) P. J. Flory, A. Ciferri, and R. Chiang, Ibid., **83**, 1023 (1961).

(4) (a) R. Chiag, J. Phys. Chem., **69**, 1645 (1965); (b) C. J. Stacy and R. L. Arnett, Ibid., **69**, 3109 (1965).

(5) (a) T. M. Birshtein and O. B. Ptitsyn, Zh. Tekhn. Fiz., **29**, 1048 (1959); (b) S. J. Lifson, J. Chem. Phys., **30**, 964 (1959); (c) K. Nagai, Ibid., **31**, 1169 (1959); (d) C. A. J. Hoeve, Ibid., **32**, 888 (1960); (e) P. J. Flory and R. L. Jernigan, Ibid., **42**, 3509 (1965).

(6) (a) P. J. Flory, J. E. Mark, and A. Abe, J. Polymer Sci., **B3**, 973 (1965); (b) A. Abe, R. L. Jernigen, and P. J. Flory, J. Amer. Chem. Soc., **88**, 631 (1966); (c) P. J. Flory, J. E. Mark, and A. Abe, J. Amer. Chem. Soc., **88**, 639 (1966).

(7) A. Kotera, Report at the 13th Meeting of the Soc. of Polymer Sci. Japan, Kyoto, June, 1965.

(8) G. C. Berry and T G. Fox, J. Amer. Chem. Soc., **86**, 3540 (1964).

(9) H. Inagaki, H. Suzuki, M. Fujii, and T. Matsuo, J. Phys. Chem., **70**, 1718 (1966).

(10) H. Inagaki, H. Suzuki, and M. Kurata, J. Polymer Sci., **C15**, 409 (1966).

(11) W. H. Stockmayer and M. Fixman, Ibid., **C1**, 137 (1963).

(12) F. Danosso and G. Moraglio, Rend. Accad. Nazl. Lincei, [8] **25**, 509 (1958).

(13) F. Danusso and G. Moraglio, Makromol. Chem., 28, 250 (1958).

(14) J. B. Kinsinger and R. E. Hughes, J. Phys. Chem., 63, 2002 (1959).

(15) J. B. Kinsinger and R. E. Hughes, Ibid., 67, 1922 (1963).

(16) P. Parrini, F. Sebastiano, and G. Messina, Makromol. Chem., 38, 27 (1960).

(17) G. Natta, I. Pasquon, and A. Zambelli, J. Amer. Chem. Soc., 84, 1488 (1962).

(18) (a) G. Natta, Irish Patent Application 430/60 (filed June 1960); (b) E-J- Addink and J. Beintema, Polymer, 2, 185 (1961); (c) M. Okamoto, K. Miyamichi, and O. Ishizuka, Chem. High Polymers Japan, 21, 218 (1964).

(19) H. Fujita, H. Inagaki, T. Kotaka, and H. Uchiyama, J. Phys. Chem., 66, 4 (1962).

(20) (a) H. Inagaki, Makromol. Chem., 64, 196 (1964); (b) H. Inagaki and S. Kawai, Ibid., 79, 42 (1964).

(21) H. Inagaki and T. Oyama, J. Chem. Soc. Japan, 78, 676 (1957).

(22) T. Matsuo and H. Inagaki, Makromol. Chem., 55, 150 (1962).

(23) B. H. Zimm, J. Chem. Phys., 16, 1099 (1948).

(24) See footnote c of Table 4-1.

(25) M. Kurata and W. H. Stockmayer, Fortschr. Hochpolymer. Forsch., 3, 196 (1963).

(26) O. B. Ptitsyn, Vysokomolekul. Soedin., 3, 1673 (1961).

(27) (a) W. R. Krigbaum, D. K. Carpenter, and S. Newman, J. Phys. Chem., 62, 1586 (1958); (b) W. R. Krigbaum, J. E. Kurz, and P. Smith, Ibid., 65, 1984 (1961); (c) I. Sakurada, A. Nakajima, O. Yoshizaki, and K. Makamae, Kolloid-Z., 186, 41 (1962); (d) G. V. Schulz, W. Wunderlich, and R, Kirste, Makromol. Chem., 75, 22 (1964).

(28) V. Crescenzi, in The Stereochemistry of Macromolecules, Vol. 3 (A. D. Ketley, ed.) Marcel Dekker, Inc., New York, 1968 , Chap. 6.

(29) (a) J. B. Kinsinger and R. A. Wessling, J. Amer. Chem. Soc., 81, 2908 (1959); (b) J. C. Woodbrey, Polymer Letters, 2, 315 (1964); (c) I. J. Grant and I. M. Ward, Polymer, 6, 223 (1965); (d) A. Nakajima and A. Saijyo, J. Polymer Sci., A2-6, 735 (1968).

(30) (a) M. Kurata and H. Yamakawa, J. Chem. Phys., 29, 311 (1958); (b) M. Kurata, H. Yamakawa, and H. Utiyama, Makromol. Chem., 34, 139 (1959).

(31) L. H. Tung, J. Polymer Sci., 24, 333 (1957).

(32) G. Allegra, P. Gains, and P. Corradini, Makromol. Chem., 61, 225 (1963).

(33) (a) C. W. Bunn and D. R. Holmes, Discussion Faraday Soc., 25, 95 (1958); (b) S. Mizushima and T. Shimanouchi, J. Amer. Chem. Soc., 86, 3521 (1964).

(34) M. V. Volkenstein, Configurational Statistics of Polymer Chains, (translated by S. N. Timasheff and M. J. Timasheff) Interscience Publishers, Inc., New York, 1963, Chap. 6.

(35) J. E. Mark and P. J. Flory, J. Amer. Chem. Soc., 87, 1415 (1965).

(36) The solvent effect on the unperturbed dimension has been studied somewhat systematically by Elias, et al., Makromol. Chem., 89, 12, 228 (1965) and by Abe and Fujita, J. Phys. Chem., 69, 3263 (1965).

(37) S. Lifson and I. Oppenheim, J. Chem.Phys., 33, 109 (1960).

(38) (a) H. Tadokoro, M. Kobayashi, S. Kobayashi, K. Yasufuku, and K. Mori, Report at the 13th Polymer Symp. Japan , 1964;

Rep. Progr. Polymer Physics Japan, 9, 181 (1966); (b) M. Kobayashi, K. Tsumura, and H. Tadokoro, J. Polymer Sci., A2-6, 1493 (1968).

(39) (a) G. Moraglio and J. Brezzinski, J. Polymer Sci., B2, 1105 (1964); (b) J. E. Mark and P. J. Flory, J. Am. Chem. Soc., 87, 1423 (1965).

(40) See Chapter 5.

Chapter 4

Single Crystal Growth of Polymer Chains from Dilute Solution

The purpose of this Chapter does not consist in the discussion on the morphology of single crystals, but it is a matter to afford an indirect proof for our hypothesis of molecular conformation of polymer chains in solution.

The fact that the stereoregular chain polymers in solid state assume proper conformations relevant to each but behave as random coils in solution has been well confirmed. It is of interest to elucidate the correlation between these two extremely different states of polymer chains, in other words, to study whether a chain conformation assumed in solid be retained still in solution. On the basis of the results obtained in the preceding Chapter, a hypothesis for the retention of chain conformations in solution has been proposed. In the experimantal part an indirect evidence for our hypothesis is presented by investigating dilute-solution-grown single crystals of syndiotactic polypropylene and poly-ε-caprolacton.

4.1 Hypothesis for the Retention of Chain Conformation in Solution

The available data to date are summarized again in Table 4-1. The result indicates clearly that the σ values for polypropylenes, irrespective of its stereoregularity, never exceed those for polyethylene. That is to say, the characteristic ratios $\langle R^2\rangle_0/nl^2$ of these polymers are arranged as followed:

$$\text{Polyethylene} > \left.\begin{array}{l}\text{atactic}\\ \text{syndiotactic}\end{array}\right\} \text{Polypropylene} > \text{isotactic Polypropylene}$$

Table 4-1

Summary of the Characteristic Ratios and the Steric Factors Obtained for Polypropylene in Decalin at 135°C and Comparison with Polyethylene.

Polymer	Configuration	σ		$\langle R^2 \rangle_0 / nl^2$	
		(a)	(b)	(a)	(b)
Poly-propylene	Atactic	1.57	1.67	4.96	5.60
	Syndiotactic	1.54	1.64	4.74	5.36
	Isotactic	1.46	1.55	4.26	4.81
Poly-ethylene		1.75	1.86	6.14	6.94

a) Calculated assuming $\Phi_0 = 2.87 \times 10^{-23}$.

b) Calculated assuming $\Phi_0 = 2.4 \times 10^{-23}$.

This order of magnitude is in conflict not only with the present conception that the methyl side group effect on the internal rotation[1] but also with the conformational calculations of Allegra,et al.[2] and Flory, et al.[3] On the other hand, however, this seems to be consistent with the well established fact in crystalline state, as discussed in the last part of the preceding Chapter. This may allow one to set forth a hypothesis that any chain conformation be retained to a certain extent still in solution.

No general evidence for this hypothesis has yet been adduced to date, except in the case of polypeptides; this hypothesis appears rather to be irreconcilable to the experimental result on the lower alkanes that the energy of the gauche state for a C-C of polymethylene chain is ca. 0.6 Kcal per mole.[4] However, we do not know if the same situation of the energy be valid for the higher alkanes, especially those bearing any side group.[5] In addition, we have several cases, in which conformational calculation achieved in good agreement with experiment made on solution.[6]

Several years ago, Ohshika pointed out that on the basis of infrared study, the helical nature of isotactic polypropylene could be retained in solution.[7] Analogous discussions have been made by Takeda, et al. as a result of infrared study on isotactic polystyrene[8] and by Nukada, et al. as a result of high-resolution nmr study on isotactic and syndiotactic polypropylene.[9] Recently, Tadokoro, et al. reported that syndiotactic polypropylene in CS_2 solution exhibited some ir bands characteristic of the planar zigzag conformation, differing from the 8_1 helix[10a], but this is in good agreement with the finding in solid.[11] More recently, analogous findings have been observed by them from infrared spectra of polymer solutions on several polymers.[10b] These observations may permit to recognize the retention of comformation in solution.

4.2 Single Crystal Growth of Isotactic Polypropylene

Among various solution-grown polymer single crystals, those of polyethylene are specific in respect to the fact that they can be easily obtainable without any special precaution (solvent, concentration, polymolecularity of sample, thermal condition, etc.). Such a feature of polyethylene may mainly be attributed to its simplest chemical structure (conformation). In the case of poly-α-olefins, however, the growth of the primary nucleus up to a single crystal would proceed only under the condition that the conformation within a short range along the chain is retained in solution; the extent of the retention will depend on the stereoregularity and the nature of nonbonded interactions between neighboring substituents, or between substituents and chain atoms. In general, it may be conceivable that in the isolated state of the polymer chain, the original conformation would fluctuate about the preferred positions, probably due to the solvent effect.[12] The conformation fluctuation may be supposed to perturbed the growth of primary nuclei.

It is well known that the solution-grown single crystals of isotactic polypropylene had not been obtained in spite of much efforts,[13] until Morrow, et al.[14] and subsequently Kojima[15] achieved the success. In contrast to this histry, one has experienced no serious difficulty in preparing solution-grown single crystals of poly-(butene-1).[16] This may be interpreted in terms of difference in the conformation fluctuation between these polymers; the bulkiness of the methyl group is less sufficient to limit the fluctuation than that of the ethyl group. The fact that the σ value of poly-(butene-1) is far higher than that of polypropylene may be explained by the same reason.

Comparing with polymer chains taking any helical form, those taking the planar zigzag form will much easily afford solution-grown single crystals (compare polyvinyl alcohol with polyacrylontril in the sense of single crystal formation). Single crystals of polyvinyl chloride, polytetrahydrofuran[17], poly-ε-caprolacton[23] should be easily obtainable, if an appropriate solvent were found. Indeed, Single crystals of polyvinyl chloride[18] and poly-ε-caprolacton (see next experimental section) have been obtained after that. On the basis of infrared studies[10] and from correspondence of our hypothesis, we may expect that single crystals of syndiotactic polypropylene from dilute solution should be more easily obtainable than those of isotactic polypropylene, since syndiotactic polypropylene would assume simpler conformation in solution than isotactic polypropylene.

4.3 Experimental Results

4.3.1 Syndiotactic polypropylene

To prove this presumption, single crystals of syndiotactic polypropylene were attempted to prepared from its α-chloronaphthalene solution. By Morrow, et al., the crystallizations were successfully performed utilizing sharp fractions ($M_w/M_n < 1.05$) of a high isotactic polypropylene and very dilute concentrations (0.001 - 0.004% by weight) of α-chloronaphthalene solution. In contrast with the careful experimental condition of Morrow, et al., an unfractionated sample with a considerable low tacticity (ir-index = 1.60) and M_w of 7 x 10^4 was used. The $[\eta]$ value in decalin at 135°C was 78 ml/g. α-chloronaphthalene that behaves as theta solvent for them (Θ = 80 - 90°C), was used as solvent. The range of experimental concentration was 0.005 - 0.01% by weight, which are common as those for polyethylene but about tentimes higher than those of isotactic polypropylene. The sample were dissolved in α-chloronaphthalene at 140°C under a nitrogen atmosphere. Then, the solution was cooled down to room temperature (1.0°C/hr.). It was confirmed by vicosity measurement that no decrease of molecular weight occurred during the procedure.

Figure 4-1 shows an electron micrograph of a group of needle-like single crystals, which are always observed in crystals grown from 0.01% α-chloronaphthalene solution. The corresponding electron diffraction pattern is given in Figure 4-2. A preliminary analysis of the above diffraction pattern indicates that it cannot be interpreted in terms of a rhombic system, which will be characteristic of the spatial arrangement of the 8_1 helices.[10] Single crystal aggregates result from their solution with increase of concentration and show a ring-form electron diffraction pattern, as illustrated in Figure 4-3. Cooling down of the isoamyl acetate solution resulted in only aggregates of crystals which show no diffraction pattern. This observation suggests an important rule for choosing a solvent appropriate to the single crystal preparation. A theta solvent will be preferred, but its theta point should be

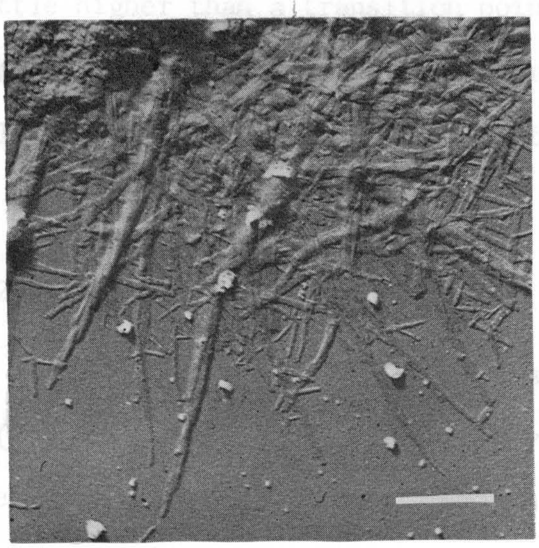


Fig. 4-1 Representative single crystal of syndiotactic polypropylene (IR-index = 1.60; M_w = 70000) grown from α-chloronaphthalene solution.

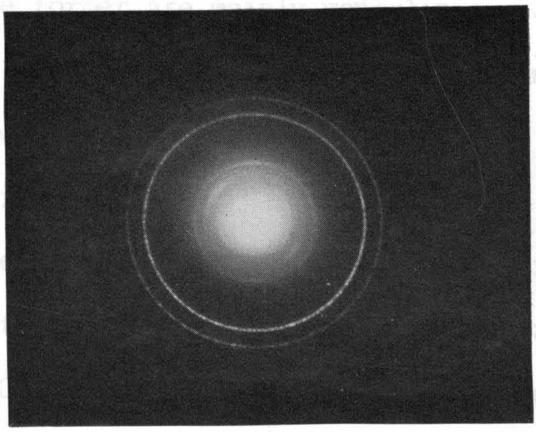


Fig. 4-2 An electron diffraction pattern of single crystal shown in Fig. 4-1.

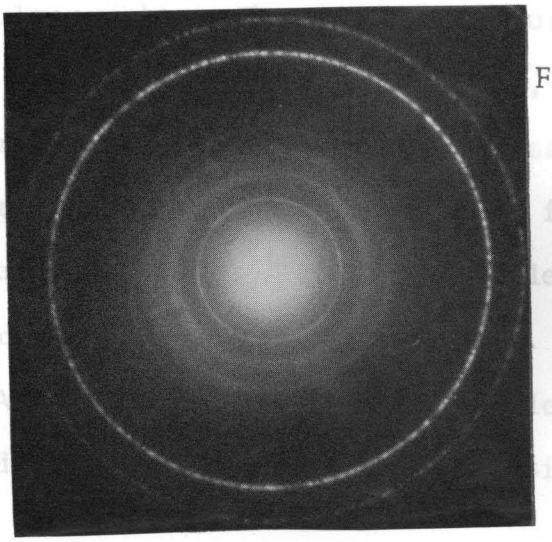


Fig. 4-3 A ring-form electron diffraction pattern observed from single crystal aggregates.

a little higher than a transition point of an isolated polymer chain, at which the chain will begin to move freely (theta temperatures of α-chloronaphthalene and isoamyl acetate for this polymer are ca. 80 - 90°C and ~ 60°C, respectively).

4.3.2 Poly-ε-caprolacton

The crystal structure of linear aliphatic polyester, $-(\mathrm{CO}-(\mathrm{CH}_2)_n-\mathrm{CO}\cdot\mathrm{O}(\mathrm{CH}_2)_m-\mathrm{O})-$, have been published by several authors.[19,20] With increasing n or m number, the molecular packing in the crystalline state becomes similar to that of polyethylene, although the unit cells of the former are mainly monoclinic. Single crystals of polyesters with large n and m from dilute solution, therefore, should be obtainable without any difficulty as well as those of polyethylene, according to our hypothesis.[21,22,23]

However, linear aliphatic polyesters with high molecular weights cannot be obtained from condensation polymerization.

On the other hand, poly-ε-caprolacton obtained from ring-opening polymerization of ε-caprolacton, $\underline{\lceil(\mathrm{CH}_2)_5\text{-CO-O}\rceil}$, may have high molecular weights. The crystal structure has been determined using X-ray diffraction analysis by Tadokoro, et al.[24] The unit cell is orthorhbic. The unit cell dimensions are a=7.47 Å , b=4.98 Å , c (fiber axis)=17.05 Å, showing that the fiber repeat comprises two monomer units. The skeleton of the molecular chain has a planar zigzag conformation with twofold helical axis.

According to our hypothesis, single crystals of poly-ε-caprolacton from dilute solution also should be easily obtainable. In this section the results of experimental test of our hypothesis are shown by preparing solution-grown single crystals of poly-ε-caprolacton. An unfractionated sample ($[\eta] = 195$ ml/g in toluene at 30°C and M_w = ca. 2.5×10^5) was used.[25] The sample was dissolved in isoamyl acetate and 2-ethoxy ethanol at 70°C, respectively, and each solution cooled down to room temperature (1.0°C/hr.). Figure 4-4 shows an electron micrograph of a group of lamellar single crystals grown from 0.03% isoamyl acetate solution. Figure 4-5 shows electron micrographs of those grown from 0.03% 2-ethoxy ethanol solution and the corresponding electron diffraction patterns.

On the basis of the above various observation we feel justified to conclude that an indirect evidence for the retention of conformation in solution has been adduced. At the same time we suggested some general rule for the growth of single crystals from dilute solution. The ability of polymer chains to single crystal growth, above all, is dependent on the simplicity*) of their conformations and how far their conformations were retained in solution.

---

*) The term "simplicity" means that planar zigzag form is simpler than helical form.

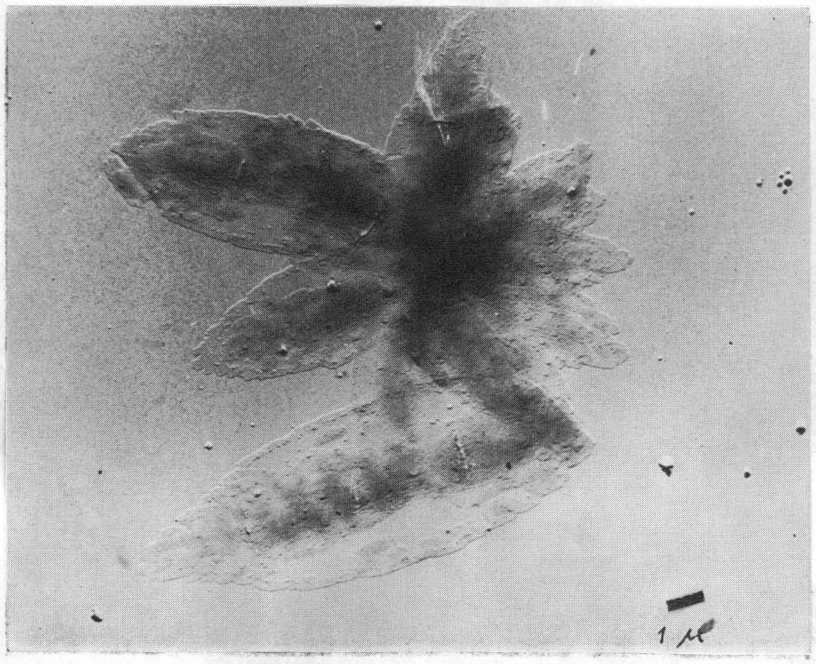


Fig. 4-4 Representative single crystal of poly-ε-caprolacton grown from isoamyl acetate solution.

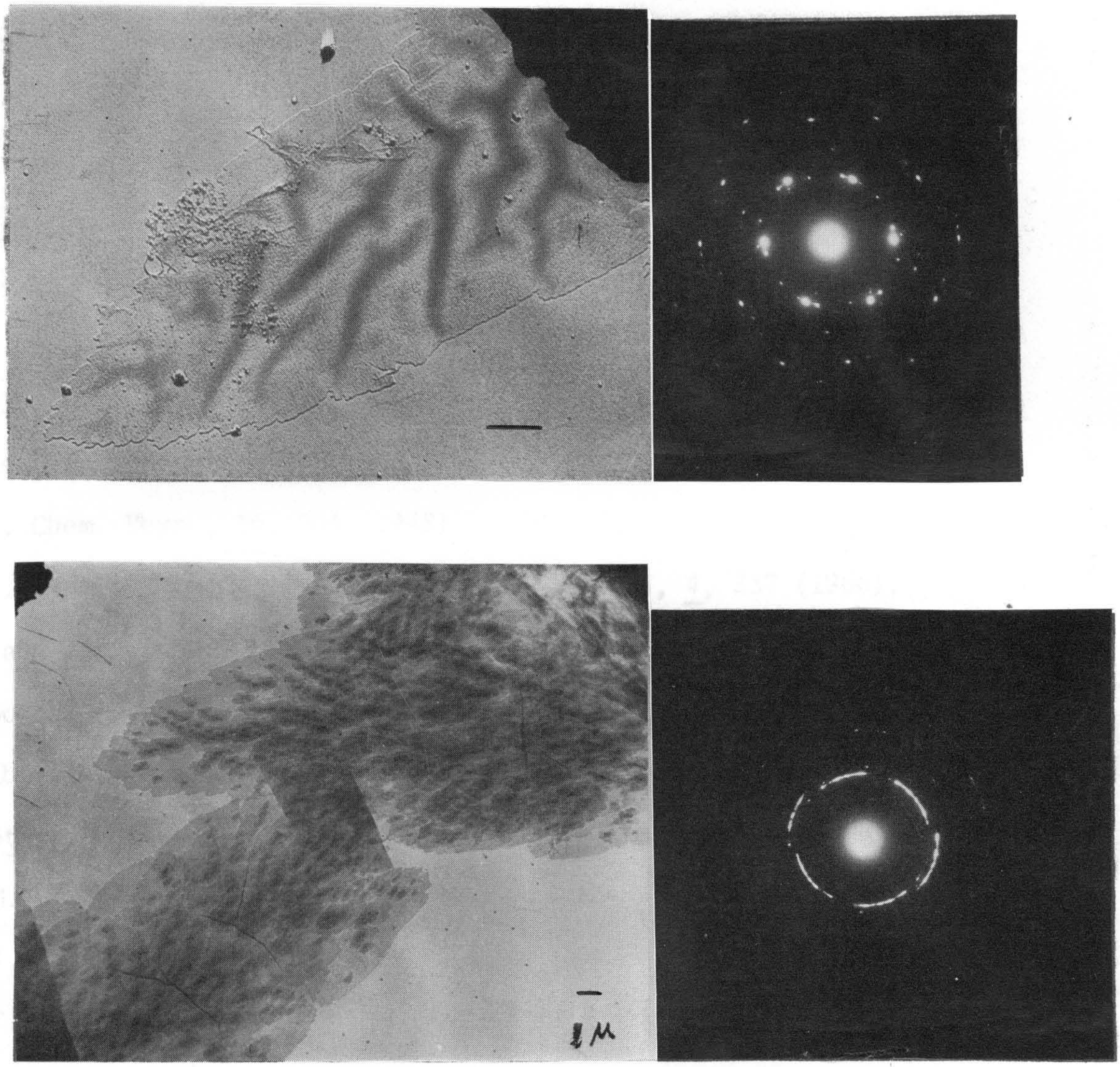


Fig. 4-5 Representative single crystals of poly-ε-caprolacton grown from 2-ethoxyethanol solution and the corresponding electron diffraction patterns.

References

(1) M. Kurata and W. H. Stockmayer, Fortschr, Hochpolymeren-Forsch. 3, 196 (1963).

(2) G. Allegra, P. Ganis, and P. Corradini, Makromol. Chem., 61, 225 (1963).

(3) P. J. Flory, J. E. Mark, and A. Abe, J. Polymer Sci., B3, 973 (1965); J. Amer. Chem. Soc., 88, 639 (1966).

(4) see, for example, G. J. Szasz, N. Sheppard, and D. H. Rank, J. Chem. Phys., 16, 704 (1948).

(5) R. A. Scott and H. A. Scheraga, Biopolymers, 4, 237 (1966).

(6) (a) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, J. Amer. Chem Soc., 83, 1015 (1961); (b) P. J. Flory, A. Ciferri, and R. Chiang, ibid., 83, 1023 (1961); (c) M. V. Volkenstein, Configurational Statistics of Polymer Chains, translated by S. N. Timasheff and M. J. Timasheff, Interscience Publ. Inc., New York, 1963.; (d) J. E. Mark and P. J. Flory, J. Amer. Chem. Soc., 87, 1415 (1965).

(7) T. Ohshika, J. Chem. Soc. Japan (Ind. Chem. Sec.), 63, 1265 (1960).

(8) S. Ohnishi and K. Nukada, J. Polymer Sci., B3, 179, 1001 (1965).

(9) S. Ochiai, K. Iimura, and M. Takeda, Report at the 19th Meeting of the Chem. Soc. Japan (1966); M. Takeda, K. Iimura, and S. Ochiai, J. Polymer Sci., B4, 155 (1966).

(10) (a) H. Tadokoro, M. Kobayashi, S. Kobayashi, K. Yasufuku, and K. Mori, Report at the 13th Polymer Symp. Japan (1964); (b) Rep. Progr. Polymer Physics Japan, 9, 181 (1966);(c) M. Kobayashi, K. Tsumura, and H. Tadokoro, J. Polymer Sci., A-2 6, 1493 (1968).

(11) G. Natta, M Peraldo, and G. Allegra, Makromol. Chem., 75, 215 (1964).

(12) S. Lifson and I. Oppenheim, J. Chem. Phys., 33, 109 (1960).

(13) (a) V. A. Kargin, N. F. Bakeev, L. Li-Shen, and T. S. Ochapovskaya, Vysokomol. Soedin., 2, 1280 (1960); (b) B. G. Ranby, F. F. Morehead, and N. M. Walter, J. Polymer Sci., 44, 349 (1960); (c) S. Minami and M. Takayanagi, Rep. Progr. Polymer Physics Japan, 7, 241 (1964).

(14) D. R. Morrow, J. A. Sauer, and A. Woodward, J. Polymer Sci., B3, 463 (1965); Prof. K. Kobayashi, Kobunshi no Bussei, Chapt. 11, Kagaku-Dozin, Tokyo (1962).

(15) M. Kojima, J. Polymer Sci., 5, 597 (1967); ibid., 5, 615 (1967); Polymer Letters, 5, 245 (1967).

(16) H. Yasuda and M. Takayanagi, Rep. Progr. Polymer Physics Japan 7, 245 (1964).

(17) K. Imada, T. Miyakawa, Y. Chatani, H. Tadokoro, and S. Murahashi, Makromol. Chem., 83, 113 (1965); M. Cesari, G. Perego, and A. Mazzei, Ibid., 83, 196 (1965).

(18) R. W. Smith and C. E. Wilkes, Polymer Letters, 5, 433 (1967).

(19) C. S. Fuller and C. J. Frosch, J. Phys. Chem., 43, 323 (1939).

(20) A. Turner-Jones and C. W. Bunn, Acta Cryst., 15, 105 (1962).

(21) Yu. Y. Mnyukh, E. M. Belavtseva, and A. T. Kitaigorodskii, Proc. Acad. Sci. (USSR), Phys. Chem. (Eng. Transl.), 133, 739 (1960).

(22) N. Hirai, N. Toyama, Y. Ogawa, and A. Yonamine, Report at the 18th Meeting of the Chem. Soc. Japan (1965).

(23) K. Tanaka, T. Kanamoto, and H. Nagai, Intern. Sym. on Macromol. Chem. Tokyo, 1966, Reprint No. 4.5.04.

(24) Y. Okita, Y. Chatani, H. Tadokoro, and Y. Yamashita, Report at the 16th Meeting of the Soc. Polymer Sci. Japan (1967).

(25) T. Yagi, T. Miyamoto, and H. Inagaki, Report at the 17th Polymer Symp. Japan (1968).

Chapter 5

The Structural and Steric Isomerism of Polypropylenes

A number of studies for characterizing the microstructure of polypropylene and propylene copolymers have been published during the last decade.[1-4] These works have been concerned mainly with the characterization of isotactic polymer, and little attention has been paid to atactic and so-called stereoblock polymer. Recently, Natta and co-workers[5] have emphasized that an "atactic" α-olefin polymer should be distinguished clearly from an "amorphous" α-olefin polymer. For instance,we have two general types of amorphous polypropylenes. One type is the ethyl-ether soluble portion of polypropylene prepared by a structurally regular polymerization technique (in this case, one giving regular head-to-tail addition), and the other type is obtained by cationic polymerization technique.[6,7] Investigations by high-resolution nuclear magnetic resonance (nmr) show that the tactic placement or tactic dyad contents of samples of the first type of polypropylene are predominantly syndiotactic.[8-10] The infrared (ir) spectra for the latter type of polypropylene lack two absorption bands at 1154 and 974 cm^{-1},which are characteristic of structurally regular ("head-to-tail") polypropylene.[6,11-13] The ir spectra of cationically prepared polymers have been interpreted in terms of various aspects of molecular structure. However, there is no sufficient experimental evidence for the complete elucidation of the microstructures (the structural and steric isomerisms) of polypropylenes, especially of the amorphous and stereoblock polymers. In addition, we feel that the methods for the microstructure analysis themselves have not been fully developed.

The purpose of this Chapter is to elucidate more clearly the microstructure of amorphous and stereoblock polypropylenes prepared with different catalytic systems. We have examined solution properties, the ir and the high-resolution nmr spectra. First, the microstructures of these samples are assessed from some solution properties, such as the relation between intrinsic viscosity $[\eta]$ and molecular weight M, and the theta temperatures, and also on the basis of the gel permeation chromatogram (gpc). The comparisons of cationic polymers with other polypropylenes are made at a common molecular-weight level. Then, we investigated the molecular-weight dependence of ir spectra and high-resolution nmr spectra for samples of low molecular weight. Information on the tactic sequence length of a highly isotactic polypropylene was obtained by means of a thermal degradation technique.

5.1 Preparation of Polypropylene

5.1.1 Stereoblock polymers

Different stereoblock samples were prepared by successive extraction[14] with acetone, ethyl ether, n-pentane, n-hexane, and n-heptane at the boiling points from a commercial product (Tokuyama Soda Co., Ltd, Tokuyama), which did not contained stabilizers. The fractions soluble in acetone, ethyl ether, n-pentane, and n-hexane were designated as SCA, SCE, SBP, and SBH, respectively. The sample SCE was further fractionated into seven fractions by a customary precipitation-fractionation technique with the system cyclohexane and n-propyl alcohol at 30°C (SCE_2, SCE_3,....., SCE_6 indicate the middle fractions). The sample SBP was also fractionated into ten fractions with the system cyclohexane and acetone at 30°C (SBP_2, SBP_3,....., SBP_8 indicate the middle fractions). All samples and fractions obtained were purified by twofold precipitation from toluene solution into methanol, followed by vacuum drying at about 60°C. Results of the characterization of these fractions are shown in Table 5-1. Sample SP-HI, prepared previously, was used as a standard syndiotactic polypropylene.

5.1.2 Cationically prepared polymers

A sample was prepared at -78°C with a cationic $AlCl_3$-C_2H_5Cl catalytic system. The polymer product was designated as NC. The sample was purified by twofold precipitation from benzene solution into methanol, followed by repeated freeze-drying from benzene solution. Results of characterization of this polymer are also shown in Table 5-1. The ir and the nmr spectra of sample NC are shown in Figures 5-1 and 5-2, respectively. The ir spectrum of NC is different from that of structurally regular polypropylenes; that is, the former sample has no absorption bands at 1154 and 974 cm^{-1} which are characteristic of the latter type of polymer. This observation is in good agreement with those reported by several authors.[6,7,15,16]

5.1.3 Low-molecular-weight isotactic polymers

Low-molecular-weight isotactic samples (ID series) were obtained by thermal degradation of a highly isotactic polymer IPP (the ratio of absorbances at 997 and 974 cm^{-1} was approximately unity), which was a portion insoluble in boiling-n-heptane and had a melting point of 176°C. Before degradation the sample was purified by precipitation from hot decalin solution into methanol, followed by vacuum drying at 60°C. After degradation was carried out at 400°C for 50 hrs. under vacuum (10^{-2}mm Hg), the product IDA was further subjected to successive extraction with acetone, ethyl ether, n-pentane, n-hexane and n-heptane at 25°C. The product IDB prepared under the same conditions as above but in the shorter degradation

Table 5-1

Characterization of Oligopropylene Samples

Polymer designation	Molecular weight x 10^{-3}		$[\eta]$, ml/g, cyclohexane, 30°C	M_p, °C	IR index
	M_w a)	M_n			A_{997}/A_{974}
SBP_2	64.0	...	115	90	0.69
SBP_3	33.0	18.2	64	90	0.64
SBP_4	24.0	12.0	42.5	90	0.60
SBP_5	10.8	8.6	25.5	95	0.63
SBP_6	7.6	4.9	15.7	98	0.66
SBP_7	5.0	3.3	12.9	98	0.66
SBP_8	2.0	1.7_3	7.9	98	0.63
SCA	...	1.1_5	5.5		0
NC	2.3_7	1.5_o	4.0_5		

a) Determined by light scattering for SBP_2 and by equilibrium ultracentrifugation for the other samplws.

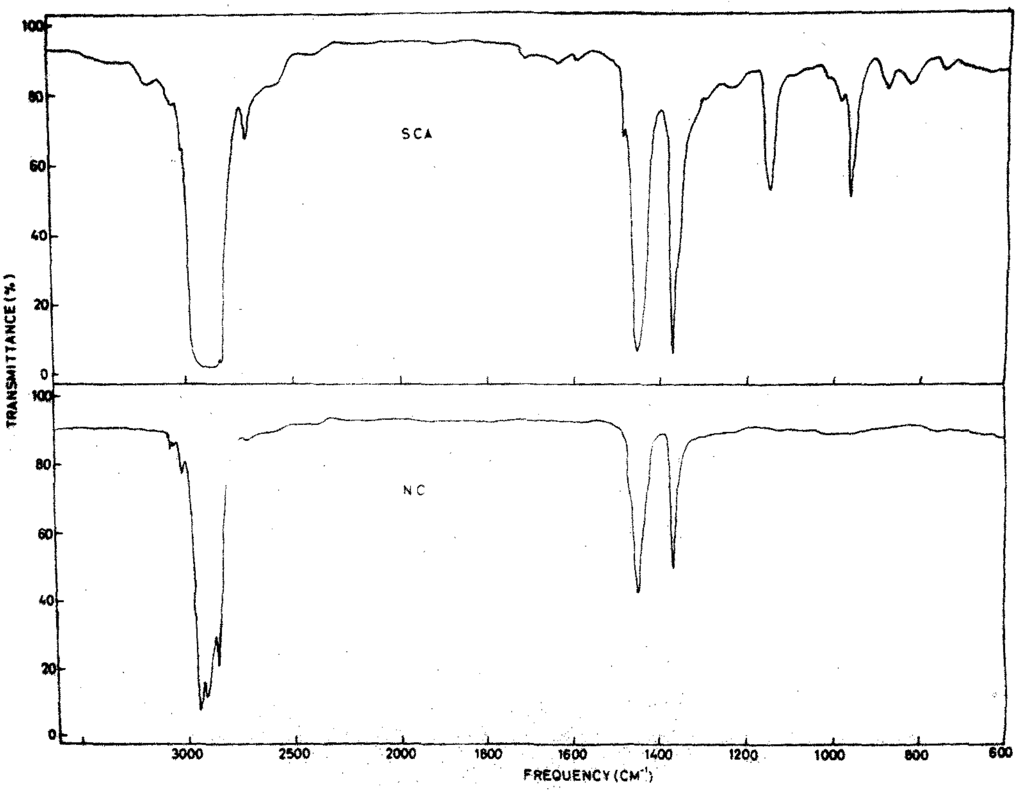


Fig. 5-1 IR-spectra of acetone extract from polypropylene prepared with a stereospecific catalyst, SCA, and of cationically prepared polypropylene, NC.

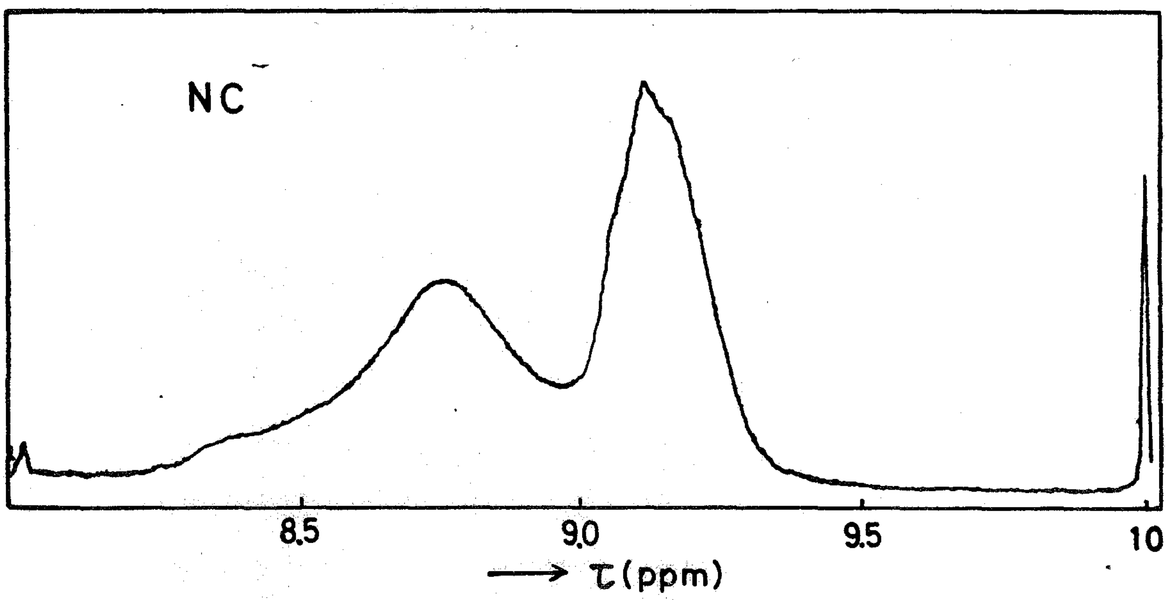


Fig. 5-2 The complete 100 Mc./sec. nmr spectrum of cationically prepared polypropylene in 10% tetrachloroethylene at 97°C.

time of 30 hrs., was fractionated by successive extraction with ethyl ether, n-pentane, and n-hexane at each their respective boiling points. The hydrogenation of unsaturated end-groups was applied to each fraction with Adam's catalyst in dioxane solution at 40°C.[17] Five samples with different molecular weight from IDA and three samples from IDB were obtained, which were designated as IDA$_1$,....., LDA$_5$ and IDB$_1$,....., IDB$_3$, respectively. Figure 5-3 shows the ir spectrum of IDA$_4$ before hydrogenation. Figure 5-4 shows ir spectra of four fractions of different molecular weights from the IDA series after hydrogenation. As can be seen in Fig. 5-4, the two absorption bands at 1645 and 887 cm^{-1}, which are assigned to the C=C stretching and out-of-plane C-H bending of vinylidene groups, respectively, vanish completely after hydrogenation. As will be described later, $[\eta]$ and M for IDB$_1$ are in good agreement with the $[\eta]$-M relationship established for SBP fractions. The thermal scission of the chain yield an unsaturated and an n-propyl end-group without any other detectable structural or steric isomerization. This same result has been described by Natta and co-workers.[18] After hydrogenation, it can be regarded that the degrared samples mutually differ only in their molecular weights. Results of the characterization of these fractions are shown in Tables 5-2 and 5-3.

5.2 Molecular Characterization

5.2.1 Molecular weight determinations

Samples fractionated from a whole polymer having an extremely broad molecular weight distribution have been still polymolecularities, and it is desirable to use the basis of weight-average-molecular-weight in order to compare $[\eta]$-M relationships with each other. However, application of the light scattering method is not sure when samples have low molecular weights,

Table 5-2

Characterization of Degraded and Atactic Samples

Polymer designation	Molecular weight[a)]		$[\eta]$, ml/g, cyclohexane, 30°C
	M_n	M_w	
IDB_1	1100	1170	5.5
IDB_3	...	2100	8.0
SCE_2	...	5500	13.1
SCE_6	...	40000[b)]	79.0

a) M_n and M_w were determined by vapor-pressure osmometer and by equilibrium ultracentrifugation, respectively.

b) Value estimated from $[\eta]$ data by use of $[\eta] = 0.683 \times 10^{-2} M_w^{0.88}$

Table 5-3

Characterization of Degraded Samples by Vapor-Presure Osmometry and Freezing Point Depression

Polymer designation	M_n	
	VPO	FPD
IDA_1	...	200
IDA_2	...	305
IDA_3	480	490
IDA_4	660	680
IDA_5	770	800

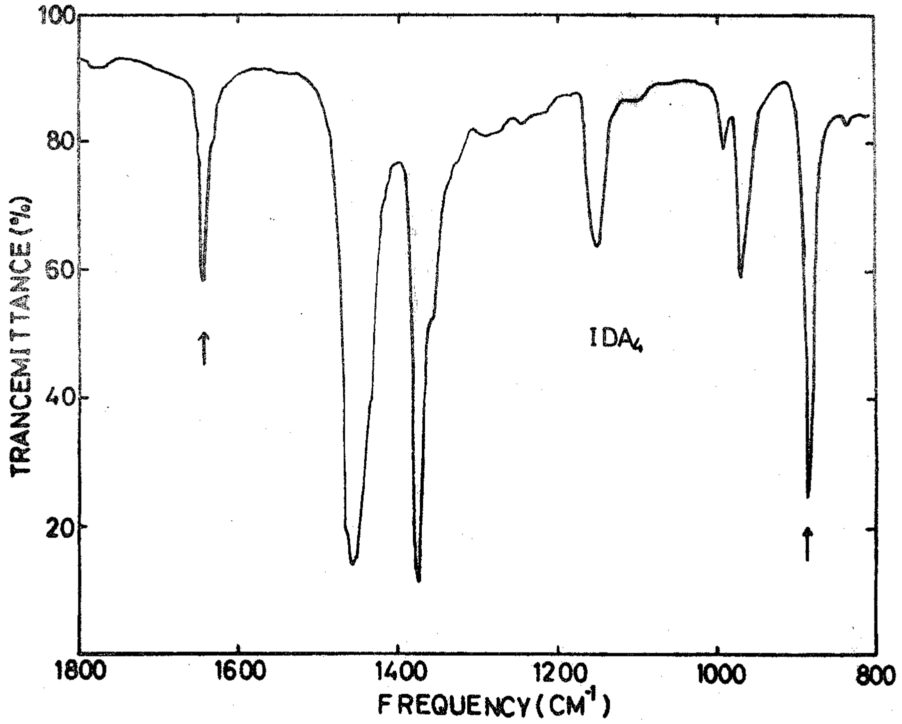


Fig. 5-3 IR-spectrum of degraded polymer fragment IDA$_4$ before hydrogenation.

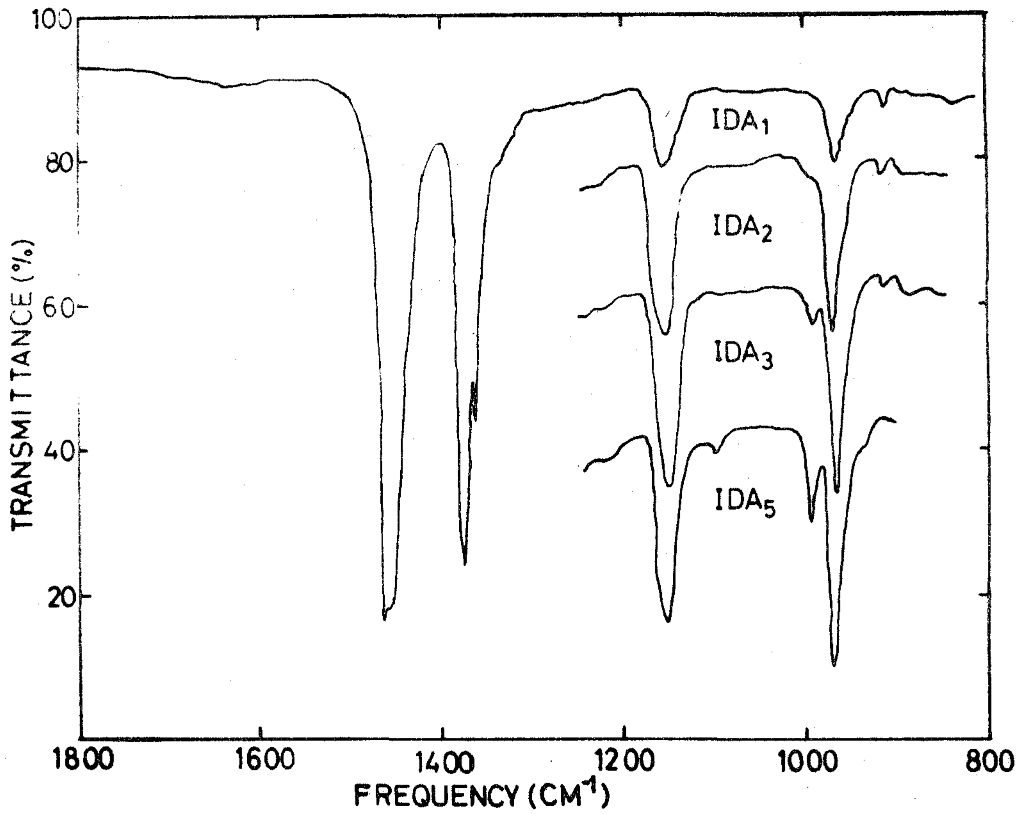


Fig. 5-4 IR-spectra of low-molecular-weight, isotactic polypropylene after hydrogenation.

and the equilibrium ultracentrifugal method[19,20] has been adopted for the present purpose.

The measurements were carried out in heptane at 30±0.1°C by using a Spinco Model E ultracentrifuge equipped with schlieren optics. An Yphantis eight-channel cell[20] was used. The rotor speed was varied from 17,250 to 19,750 rpm, depending on the molecular weight. The observation was made at two phase plate angles, 75° and 80°. One of the equilibrium patterns is shown in Figure 5-5. Schlieren diagrams were read on a "universal contour" projector (Nippon Kogaku Co., Tokyo) within an accuracy of ca. $\pm 10^{-2}$ mm, which corresponds roughly to $\pm 10^{-3}$mm on the photographic plate. Apparent molecular weights M_{app} were caliculated as a function of initial concentration c_o as[19]

$$M_{app} = \frac{RT}{\bar{r}\ c_o\ (1-\bar{v}\rho)\omega^2} \left(\frac{dc}{dr}\right)_{r=\bar{r}}$$

where $\bar{r} = (r_a + r_b)/2$ is the mean distance from the center of rotation, r_a and r_b denoting the meniscus and bottom positions, respectively; ω is the angular velocity (rad.sec^{-1}); $\bar{v}$ is the partial specific volume of solute; ρ is the density of solvent; R is the gas constant; and T is the absolute temperature. The value $\bar{v}$ = 1.127 (ml/g) which has been obtained for syndiotactic polypropylene (see Sec.3.2.3), was used for all samples. The refractive index increment for sample SBP_2 was found to be 0.1105 (ml/g) in heptane at 30°C for 436 mμ. Values of M_w were caliculated from M_{app} according to the equation[20,21],

$$1/M_{app} = (1/M_w) + 2A_2' c_o$$

where A_2' is the light-scattering second virial coefficient of the system. Values of M_w are given in Table 5-1.

Center of rotor ←

Fig. 5-5 A typical equilibrium pattern observed with schlieren optics.

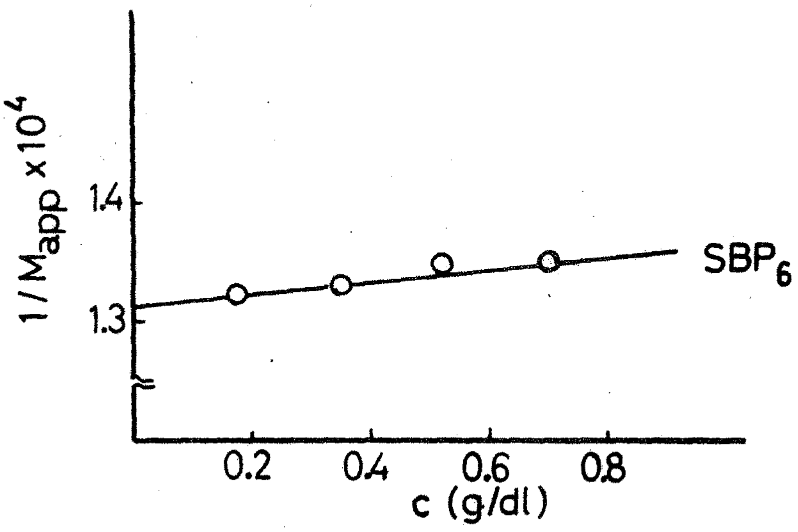


Fig. 5-5' A typical example of plots of $1/M_{app}$ against concentration in heptane at 30°C.

The number-average molecular weights M_n were determined at 37°C by using a vapor-pressure osmometer (Mechrolab Model 301). The quantity measured by this apparatus is the steady-state temperature difference established when a drop of solution and one of solvent are exposed to the solvent vapor, with heat exchange that occurs only through the vapor. Thus the principle of the measurement is that this temperature difference, which is indicated by a dial reading ΔR, is proportional to the difference in vapor pressure of the two drops. A calibration plot of values of ΔR read after 5 min. as a function of solute molarities m of benzil (molecular weight = 210.1) was established for benzene as solvent. A straight line relationship was obtained between ΔR and m (see Figure 5-6). For the polymer samples we first evaluated apparent molecular weights M_{app} given by $(\Delta R/c)^{-1}$ at each concentration c (g/ml). Reciprocal values of M_{app} were plotted against c. Straight line was obtained in all cases, and the resultant plots were extrapolated to zero concentration to determine M_n as intercepts on the ordinate. Figure 5-7 shows a typical plot of apparent molecular weight against concentration. Values of M_n are listed in Table 5-1.

Figures 5-8 and 5-9, respectively, show~~s~~ the double logarithmic plots of $[\eta]$ vs. M_w and of $[\eta]$ vs. M_n established for the linear SBP fractions. In the low-molecular-weight region $(< 10^4)$, these relations may be represented by

$$[\eta] = 1.40 \times 10^{-3}\, M_w^{0.50}$$

$$[\eta] = 1.32 \times 10^{-3}\, M_n^{0.56}$$

The exponents of M are approximately equal to 0.5. This result is in good agreement with the theoretical prediction that the excluded volume effect should vanish in the low-molecular-weight region.[22]

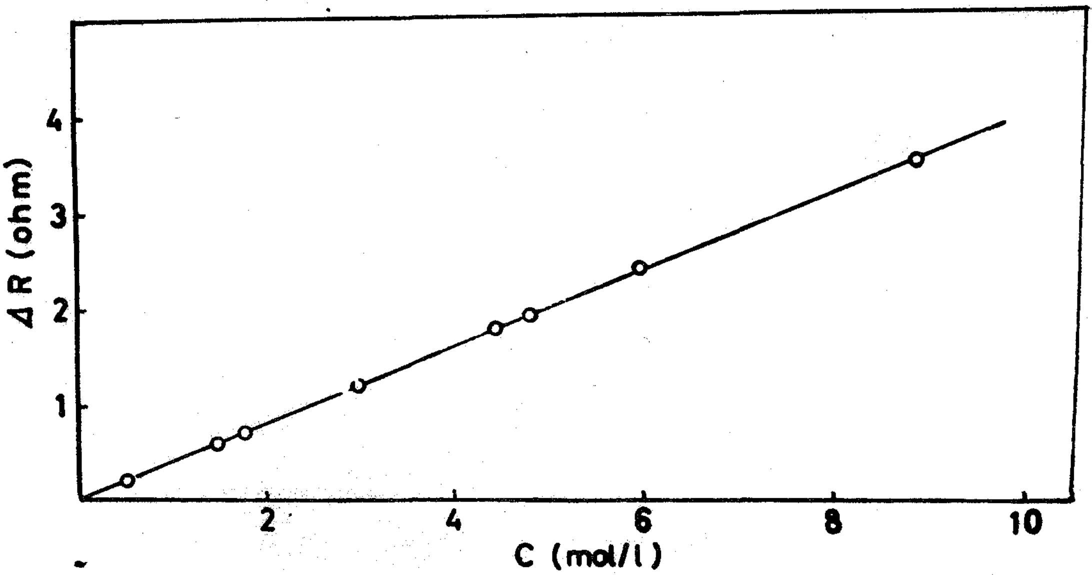


Fig. 5-6 Calibration graph for vapor-pressure osmometer (Mechrolab Model 301). Benzil in benzene at 37°C.

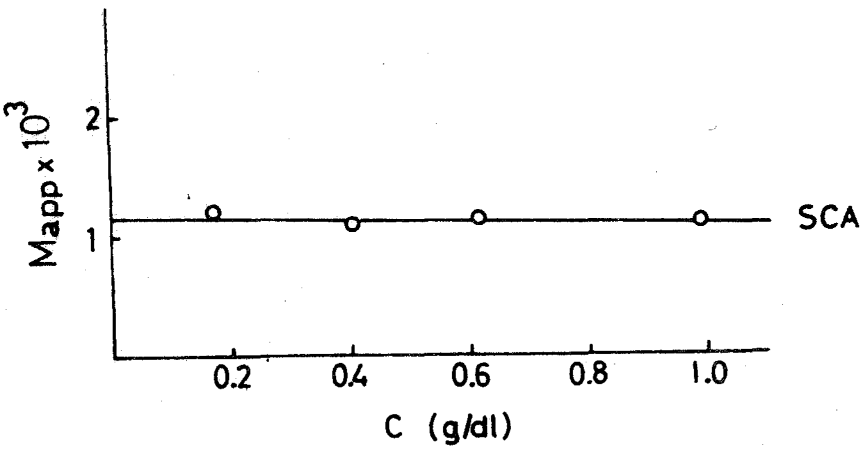


Fig. 5-7 A typical example of plots of apparent molecular weight against concentration at 37°C.

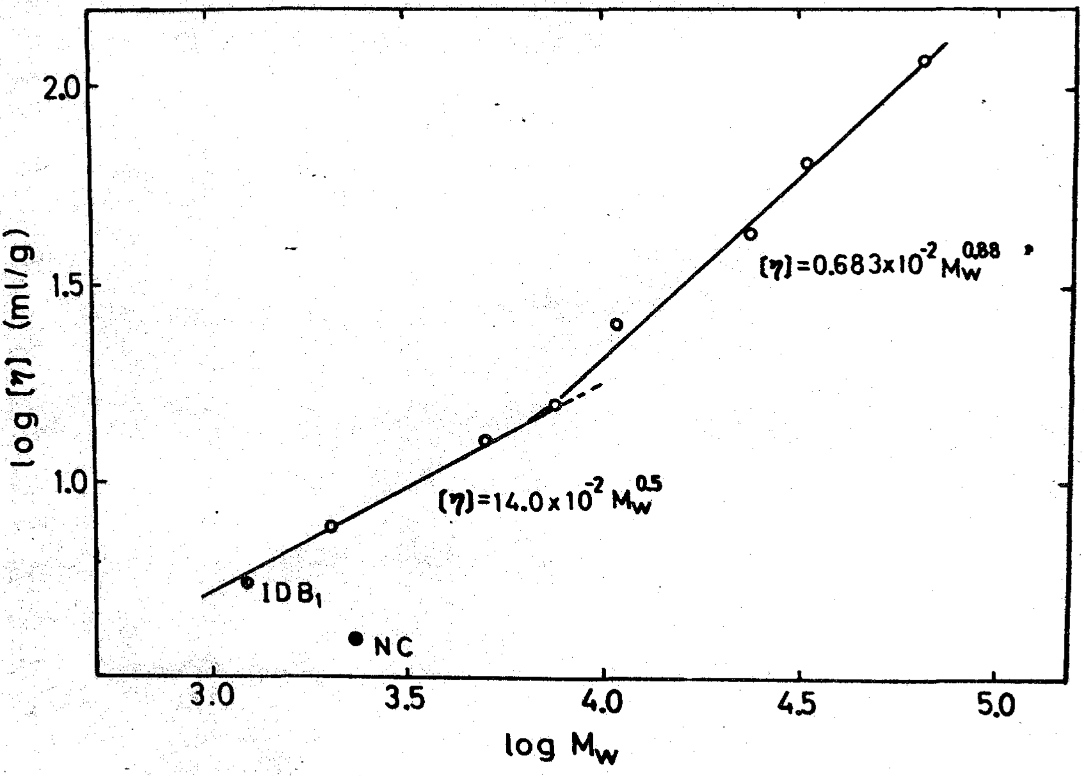


Fig. 5-8 Plots of log $[\eta]$ vs. log M_w for SBP fractions ○, NC ●, and IDB_1 ◐ in cyclohexane at 30°C.

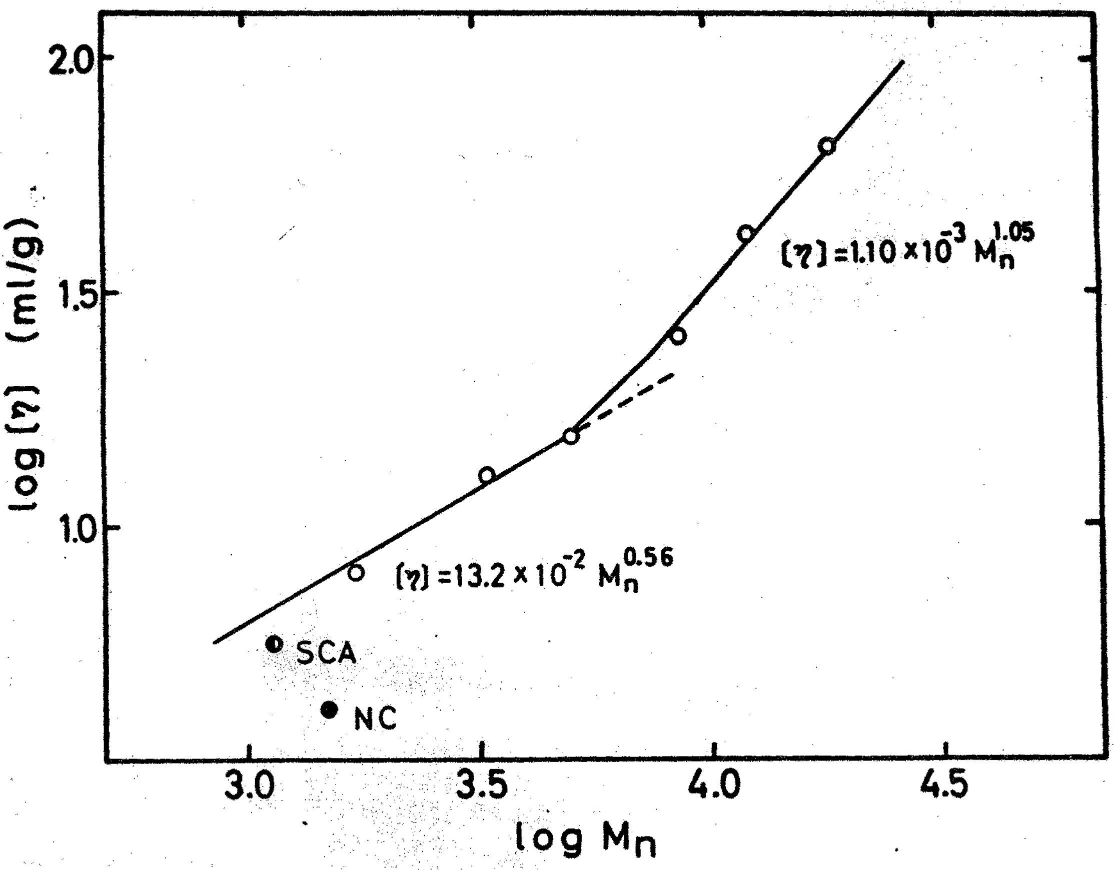


Fig. 5-9 Plots of log[η] vs. log M_n for SBP fractions ○, NC ●, and SCA ◐ in cyclohexane at 30^0C.

As vapor-pressure osmometry is very sensitive to impurities in solution, it is very difficult to determine accurately molecular weights over ca. 10^4, and M_n obtained for two high molecular weight fractions, 18,200 and 12,000, would be underestimated. The fact that the exponent α in the Mark-Houwink-Sakurada equation, $[\eta] = K M^{\alpha}$, takes the value near unity in the high-molecular-weight region ($> 10^4$) may be due to such an underestimate of M_n (see Fig. 5-9).

5.2.2 Determination of theta temperatures

In a preliminary experiment we found that isoamyl acetate, which has been known as a theta solvent for atactic[23] and syndiotactic polypropylene, dissolved stereoblock polypropylene unless its isotacticity exceeds 40%; if a stereoblock sample has higher isotacticity than this limit, the polymer becomes insoluble in this solvent because of its crystallinity. The theta temperature for SBP_2 fraction was determined by light-scattering measurements as the temperature at which the light-scattering second virial coefficient A_2' vanished (see Fig. 5-10). The theta temperature for SBP_2 fraction was determined to be approximately 38°C. Details are given in Table 5-4.

Light scattering measurements were carried out in a Shimadzu (modified Brice type) light scattering photometer equipped with a constant temperature jacket (± 0.1°C). The calibration and use of the light scattering photometer were described in Chapter 3.

5.2.3 Gel permeation chromatography

The measurements were carried out at 30°C by using a Shimadzu gel permeation chromatograph Model 1A. The solvent was tetrahydrofuran. Solution and solvent flow rate were ca. 1 ml/min., i.e. each sample was

Table 5-4

Light-Scattering Data for Stereoblock Polypropylene in Isoamyl Acetate

Polymer designation	$M_w \times 10^{-4}$	Temp., °C	$A_2 \times 10^4$	Θ, °C
SBP_2	64.0	48.5	3.4	38.0
		53.5	5.8	
		58.5	7.0	
Atactic	....	....	...	34.0[a)]

a) Data of Danusso, et al. (22)

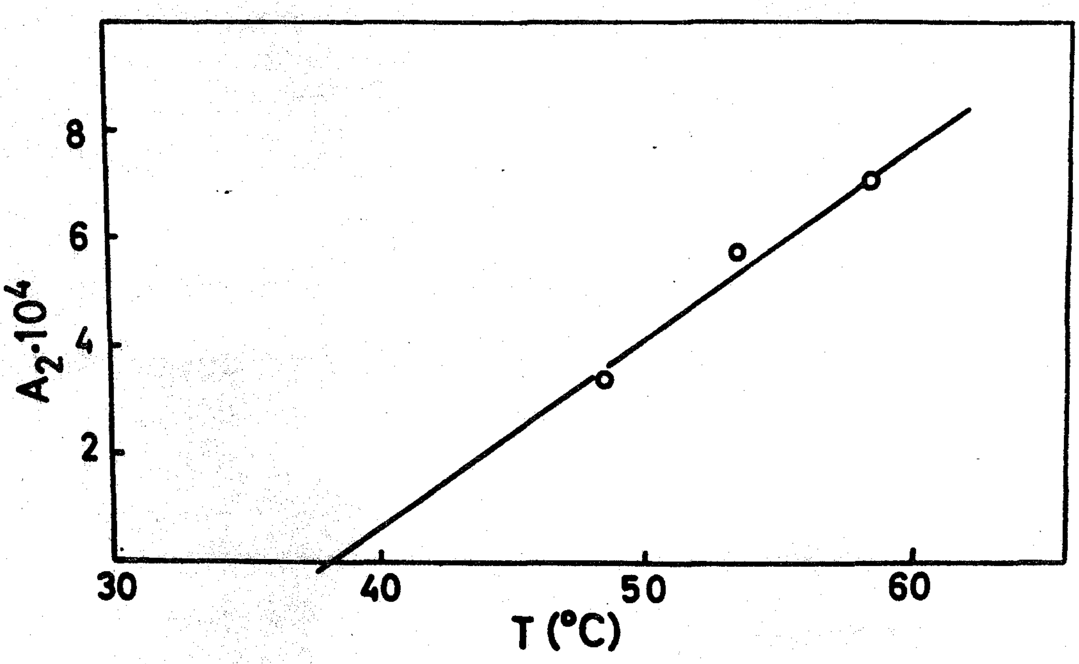


Fig. 5-10 Temperature dependence of A_2' in isoamyl acetate for fraction SBP_2 studied by light-scattering. The theta temperature is ca. 38.0°C.

injected for 2 min., yielding approximately a 2 ml sample (concentration of 6 g/l). Molecules are separated by their varied ability to permeate a porous crosslinked polystyrene gel[24]. Elution is in inverse order of molecular size as small molecules find more available volume and penetrate the gel more fully than larger molecules. Consequently, the largest molecules elute first, followed by progressively smaller molecules. Eluted polymer molecules in solution are detected in a differential refractometer through which solvent and solution streams flow and refractive index differences are recorded. The refractive index difference between solution and solvent is proportional to solute concentration. Three columns having 2×10^3, 10^2, and 10 Å permeability limits were used. For each sample the elution volume V_e was taken to be the position of the maximum of the peak in counts. One count is equivalent to 5 ml of eluent. Figure 5-11 shows the calibration curve established for SBP fractions.

5.2.4 Viscosity measurements

Viscosity measurements were made in Ubbelohde viscometers with various flow times ranging from 190 to 1,200 sec. for cyclohexane at 30°C; the choice was made depending on the molecular weights of samples. The kinetic energy correction was determined to be less than 0.2%. Solvent used was carefully purified and dried in accordance with standard procedures.

5.2.5 Infrared spectra

All quantitative spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer. Solid-phase spectra were obtained from films (thickness of 80μ) prepared from trichloroethylene solution. Some other spectra were obtained with films prepared by first casting a solution onto a rock-salt surface, followed by evaporation of the solvent. In addition, two

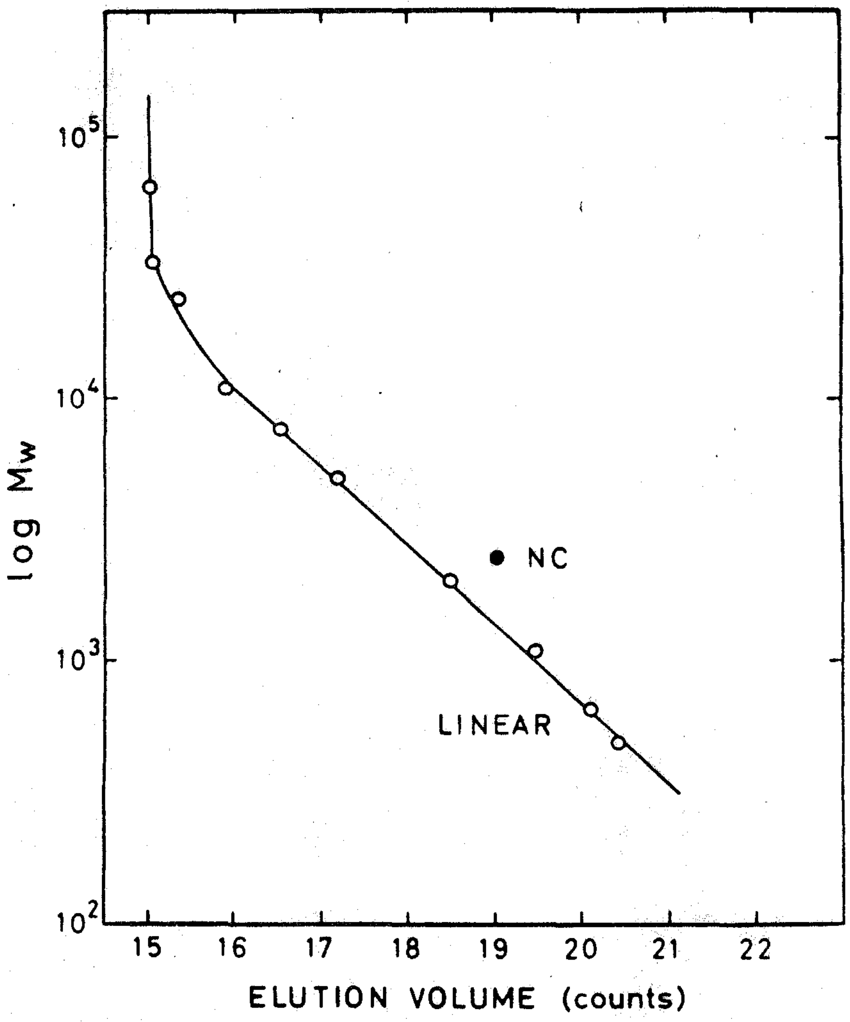


Fig. 5-11 GPC calibration curve for low-molecular-weight polypropylenes in tetrahydrofuran.

ir spectra for samples IDA_4 and IDA_5 were obtained by using a Nippon Bunko Model DS-4029 spectrophotometer equipped with a low-temperature attachment (see Fig. 5-12).

5.2.6 High-resolution NMR spectra

High-resolution nmr spectra were obtained with a Varian HR-100 spectrometer. All the spectra were obtained from 10-20 (W/V) solution in tetrachloroethylene at 97°C. The samples were degassed and tetramethylsilane was added as an internal standard. The methylene and the methyl proton resonance region of the nmr spectra obtained for IPP, SPP, SCE_2, SCE_6, SBP_5 and SBH are illustrated in Figs. 13 and 14, respectively. Figures 15 and 16 show the methylene and the methyl proton resonance regions, respectively, of spectra of the ID series.

5.3 Structural Isomerism of Sample NC

Data on $[\eta]$ vs. M_w and $[\eta]$ vs. M_n obtained for sample NC are shown as filled circles in Figs. 5-8 an 5-9. Each point is located far below the straight line constructed for SBP fractions for both M_w and M_n. From theoretical[25] as well as experimental standpoints,[26] this result confirms the fact that the chain of sample NC is branched because of structural isomerization during polymerization. This finding gives additional evidence for the interpretations proposed by several authors from different experiments.[6,11-13]

A gpc calibration curve (log M vs. elution volume V_e) was first established with SBP fractions and used for assigning the V_e value for sample NC, as Fig. 5-11 illustrates. When the molecular weight of NC is read off from the calibration curve by referring to the experimental value of V_e, the result is too low molecular weight in comparison with that obtained independently by ultracentrifugation (see the filled circle shown

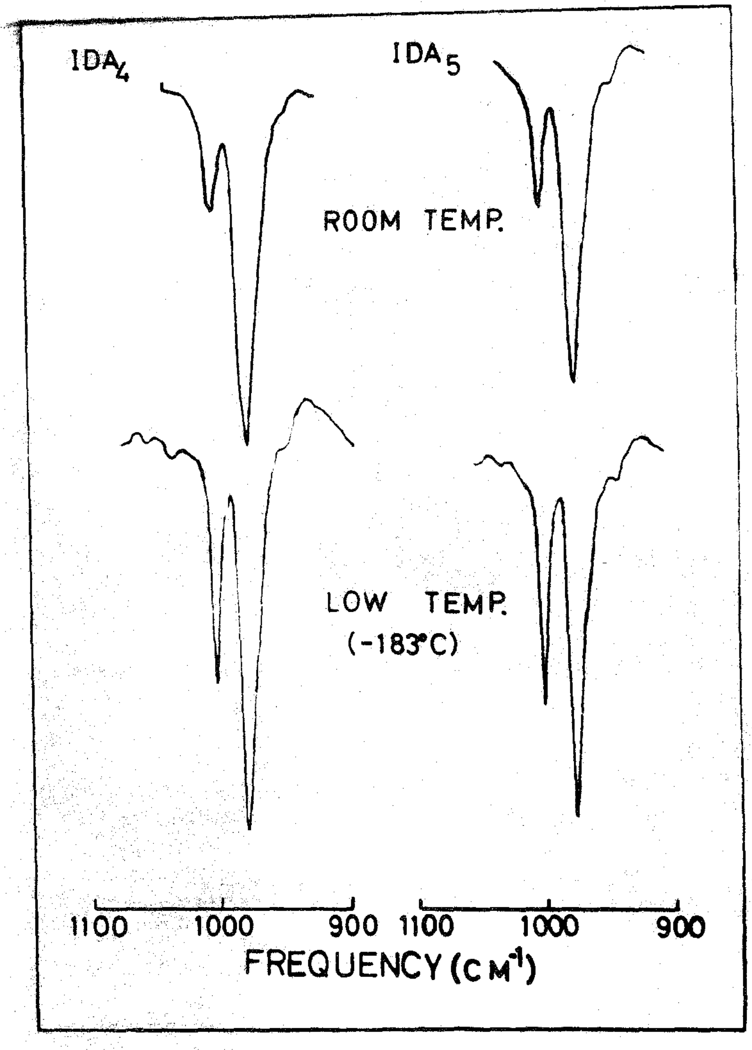


Fig. 5-12 IR spectra of the 900 cm^{-1} to 1100 cm^{-1} region of low-molecular-weight, isotactic polypropylenes, IDA_4 and IDA_5, taken at room temperature and at -183°C.

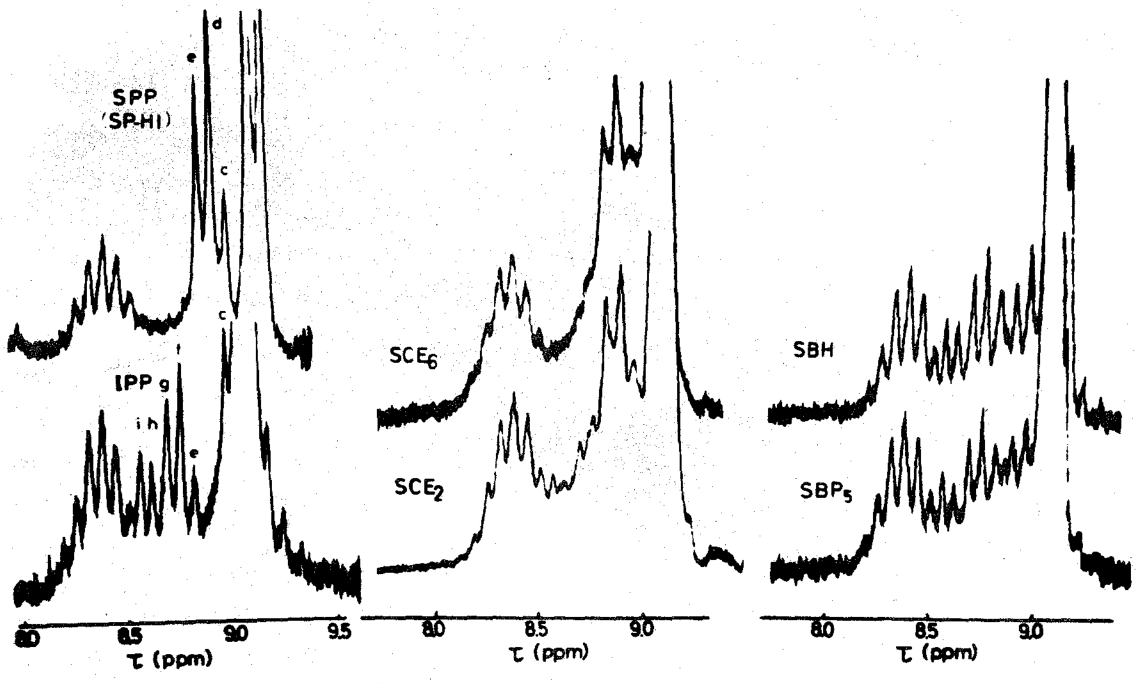


Fig. 5-13 Methylene proton resonance region of 100 Mc/sec. nmr spectra of isotactic (IPP), syndiotactic (SPP), atactic (SCE), and stereoblock (SB) polypropylenes.

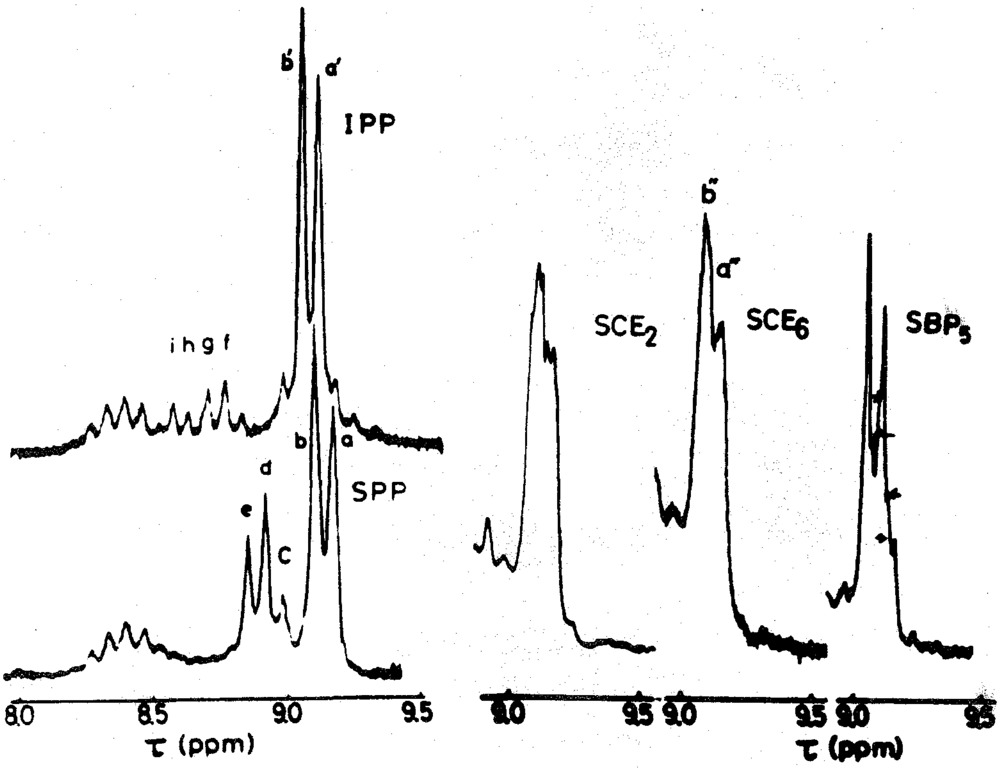


Fig. 5-14 Methyl proton resonance region of 100 Mc/sec. nmr spectra of the samples indicated in Fig. 5-13.

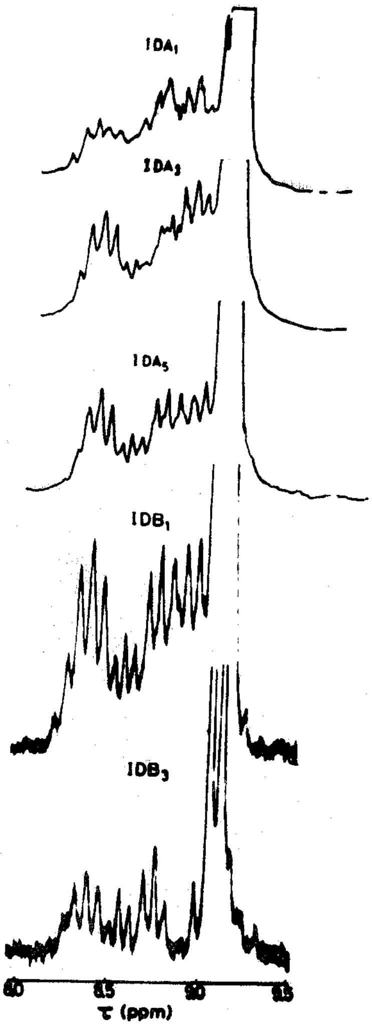


Fig. 5-15 Methylene proton resonance region of 100 Mc/sec. nmr spectra of low-molecular-weight, isotactic polypropylenes.

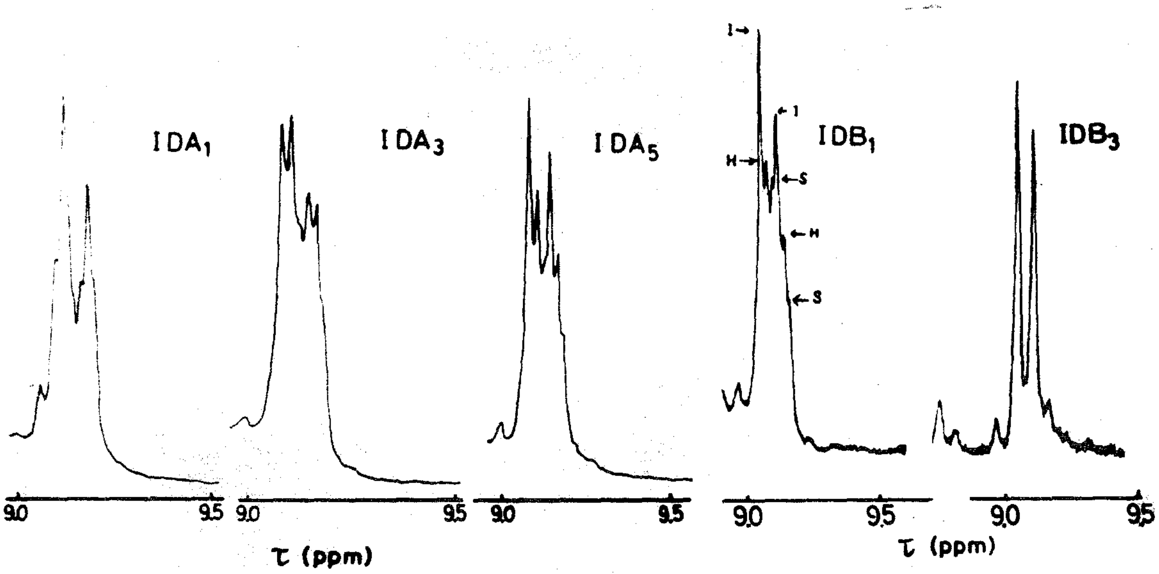


Fig. 5-16 Methyl proton resonance region of 100 Mc/sec. nmr spectra of the samples indicated in Fig. 5-15.

in Fig. 5-11). This finding implies, on the basis of the theory of gpc,[27] that the hydrodynamic radius for sample NC is much smaller than that expected for a linear chain of the same molecular weight. This result supports the conclusion deduced above.

Additional support for the above conclusions may be obtained by comparing the 100 Mc/sec. nmr spectra of samples NC and IDB_1 (see Figs. 2 and 15). The latter spectrum illustrates the high resolving power of the spectrometer used. In spite of the high resolution, sample NC gives a spectrum of apparent very broad envelopes of many lines, as ~~constructed~~ contrasted with that of sample IDB_1. Sample IDB_1 has a low molecular weight (M_w= 1,170) which is comparable with that of NC. Thus, the broadened character of the spectrum of sample NC cannot be attributed, for example, to a terminal group effect. Since exact assignments for each apparent broad envelope in Fig. 5-2 are lacking, the characteristic features are, for present purposes, interpreted in terms of many different proton environments in the different structural isomers that would be produced as a result of the hydride ion transfer mechanism.[6,28]

5.4 Theta Temperature and Microtacticity

The pattern of the microtacticity may be compared with that of the monomer arrangement appearing in a copolymer chain of unlike monomer units; any copolymer chain having the same overall monomeric composition can be different in the length distribution of monomeric units. The structure of stereoblock polymers is simpler than that of copolymers, because the repeating units are chemically the same and only its steric configuration is locally different. The theta temperature of copolymer depends not only on the difference in its composition but also on the difference in its sequence length of the same monomeric units along the chain.[29,30]

As already described in Sec. 3.2.3, the theta temperature of a stereoblock polymer may expected to depend both on its overall tacticity and sequence length distribution of steric configuration (microtacticity).

Table 5-5 summarizes our theta-temperature data, together with those of some other authors, for isoamyl acetate solutions of several polypropylenes with different ir indices. As one might expect, a close correlation is found between these two values. It should be noted that the two samples having almost identical ir indices (cf. atactic polymer and sample I-A_3 in Table 5-5) have different theta temperatures. This result implies that the theta temperature in isoamyl acetate is more sensitive to the characteristic tactic helical contents ("helicities") and tactic sequence distribution of the main chains of polypropylenes which are not highly tactic than are the ir indices. Thus, some differences in steric isomerism that may not be detected by ir spectroscopy can be reflected in theta temperature. By comparing theta temperature with ir spectra and other data, one can elucidate the steric isomerism of stereoblock polypropylenes with relatively low tactic content, including the essentially atactic polymers.

5.5 The Infrared Absorption Bands at 1154 and 974 cm^{-1}

Figure 5-4 shows that the absorption intensities at 1154 and 974 cm^{-1} decrease with decreasing molecular weight of the sample. This finding seems to be related to the fact (as Lomonte[34] pointed out) that the 1154 cm^{-1} band can be used satisfactorily for the determination of propylene content in block copolymers of propylene and ethylene, whereas this is not the case for random copolymers. On the basis of Lomonte's fiding and ours, we may draw a conclusion that, in addition to the existence of sequences of alternating CH_2 and $CH(CH_3)$ groups, a con-

Table 5-5

Theta temperatures for Polypropylenes in Isoamyl Acetate

Polymer designation	Infrared index iso.[a)]	syn.[b)]	M_p, °C	$M_w \times 10^{-3}$	Θ, °C	Ref.
SP-HI_3		1.50	*ca.* 130	....	65 70	(3)
SP-HE		1.20	*ca.* 100	83.5	43.5	(3)
SP-T_5		0.8	*ca.* 86	117.0	41.0	(3)
Atactic	0	0	—	....	34.0	(23)
SBP_2	0.69		*ca.* 90	64.0	38.0	this work
I-A_3	0.20		...	193	40.6	(31)

a) "isotacticity" given by A_{997}/A_{974} (32,33)

b) "syndiotacticity" given by $2A_{867}/A_{4310} + A_{4255})$ (3)

siderably long sequence is required for the appearance of the 1154 and 974 cm^{-1} bands. Inspection of spectra in Fig. 5-4 gives additional information on the observation that ir spectra of cationically prepared polymers have no absorbances at 1154 and 974 cm^{-1}. The molecular weight of sample NC is higher than that of sample IDA$_5$. Since thermal degradation of isotactic polypropylene produces no detectable structural or steric isomerism, expected for unsaturated terminal groups,[18] the ir spectroscopic features of cationically prepared polymer may be interpreted in terms of the primary structure rather than of molecular weight; head-to-tail additions do not occur without side reactions and regular "head-to-tail" sequences are too short to exhibit the absorptions at 1154 and 974 cm^{-1}.

Further discussion of the absorption at 997 cm^{-1} is warranted. This band is due to helical conformers highly populated by sequences of isotactic placements, particularly in the solid state. As can be seen from Fig. 5-4, the absorption intensity of this band appears to decrease with decreasing isotactic sequence length. The band finally disappears as the sequence length becomes less than about ten monomeric units (IDA$_3$). The absorption intensity at 997 cm^{-1} is not necessarily directly proportional to the isotactic placement or dyad content but to the isotactic helical content or isotactic "helicity" of these samples*) This implies

---

*) Since isotactic "helicity" in the solid state can in many instances of invariant stereoblock character vary regularly with isotactic crystallinity, the intensity of the 997 cm^{-1} band may in these cases be closely associated with isotactic crystallinity.[1c,11,32,33]

that polypropylene chain cannot assume the helical conformation unless the polymer chain has sequences containing of over ten isotactically connected monomer units. This conclusion also follows from the ir spectra at low temperature. Figure 5-12 shows the ir spectra for IDA_4 and IDA_5 at -183°C. In these spectra the absorbance ratio A_{997}/A_{974} is increased approximately to twice the value at room temperature; the ratios are increased from 0.27 and 0.37 to 0.58 and 0.67 for IDA_4 and IDA_5, respectively. On the other hand, the absorbance at 997 cm^{-1} in the spectrum for IDA_2, whose degree of polymerization is ca.7, can hardly be seen, even at -183°C. The isotactic chains can assume the helical form only if the number of isotactically connected monomer units in a chain is over ten.

5.6 High-Resolution NMR Spectra and Microtacticity of Polypropylene

5.6.1 Methylene proton resonance

The high-resolution nmr spectra of isotactic and syndiotactic polypropylenes differ significantly from each other in the methylene proton resonance region (Fig. 5-13). The problem of the analysis of nmr spectra of polypropylenes has received the attention of several authors.[1b,4,8-10] The method is applicable, at least in principle, to determining the difference in stereoregularity of polypropylene chains. Woodbrey[8,9] and Tincher[10] have determined quantitatively the relative tactic placement or dyad content of specific polypropylenes on the basis of the methylene proton resonances. Both their results have shown that ethyl-soluble portions of samples of structurally regular polypropylenes are predominantly syndiotactic. According to Zambelli and co-workers,[4a] the relative amounts of tactic dyads can be determined with high accuracy from the spectra of methylene protons, particularly for highly isotactic polypropylenes.

It is worthwhile to compare the spectrum of the standard syndiotactic sample SP-HI in the methylene proton resonance region with that for the atactic sample SCE_6. These spectra are shown in Fig. 5-13. One finds that both spectra quite similar with respect to three absorption lines at 8.95, 8.89 and 8.81 ppm, except that the lines for the atactic polymer are apparently broader. Such an apparent similarity in the nmr spectra appears irreconcilable with other physical data[3,35] indicating that the chain dimensions of SP-HI in solution, its melting point and infrared index are different from those of SCE_6. In order to understand this apparent inconsistency, one might expect to observe isotactic dyads or meso units (m) in sample SCE_6 which, on the basis of all other experiments, appears to have low tactic purity. The evidence for the presence of m units are the two groups of relatively weak lines indicated by the arrows on the spectrum of SCE_6 in Fig. 5-13. In addition, the "broader line widths" in the spectrum of SCE_6, contrasted to those in the spectrum of SP-HI, are additional evidence for the substantial amounts of m units in SCE_6 by the following two reasons. First, there is an important effect which makes the direct appearance of the methylene proton resonances of m units relatively much less pronounced than those of syndiotactic dyads or racemic units (r).[1b] The protons of each m-unit methylene group are heterosteric, magnetically nonequivalent and undergo both geminal and vicinal spin coupling. In contrast, the protons of most r-unit methylene groups are homosteric, all of a given type (of tactic tetrad) are virtually magnetically equivalent, and undergo only vicinal spin coupling. Thus, the m-unit methylene proton resonances are much more complicated and, relatively, much less pronounced in their appearance than the r-unit methylene proton resonances. Secondly, these resonances appear as envelopes of many rather closely spaced, unresolvable narrow lines which arise from the fact that the central methylene protons of tactic tetrads of monomer units have chemical-shift differences of about 0.045 ppm, as has been clearly established.[4e] These small chemical-shift differences, in combination with effects of spin coupling and the presence of substantial amounts of most of the possible type of tactic tetrads, give rise to the marked apparent broadening. Thus, the 100 Mc/sec. methylene proton resonances of atactic, or approximately atactic, polypropylenes are "barely" useful for characterizations of steric isomerism, provided one means quantitative determinations of tactic dyad or tetrad contents. On the other hand, it seems clear that the spectra of such polypropylenes offer some rather unique and direct qualitative information concerning the steric isomerism in the chains.

The methylene proton resonances of stereoblock polypropylenes SBP_5 and SBH show usual nmr spectra based on a linear combination of the corresponding resonances observed for pure isotactic and syndiotactic polypropylene (see also Fig. 5-13). In these cases, the relative tactic placement or dyad content can be determined with considerably high accuracy.[4a]

5.6.2 Methyl proton resonance

Figure 5-14 shows the methyl proton resonance region of the nmr spectra of the sample indicated in Fig. 5-13. The more intense doublets (with lines at τ = 9.11 and 9.01 ppm for IPP and 9.16 and 9.09 ppm for SPP) are due to central methyl protons of tactic triads; the central methyl protons of heterotactic triads have a chemical shift intermediate to those of the corresponding protons in isotactic and synditactic triads.[8,9]

The methyl proton resonances of SCE_6 in Fig. 6-14 shows only a doublet with broader components than those observed for the polymers of highly tactic purities, e.g. SPP and IPP. The centers of the doublet component envelopes observed for SCE_6 (designated a" and b") correspond to the line positions of central methyl proton resonances of heterotactic triads. Thus, each relatively broad component of the doublet observed for SCE_6 is an envelope of the overlapping components of doublets arising from isotactic, syndiotactic and heterotactic triads of monomer units; the heterotactic triads are present in substantial, and possibly predominating concentration. The spectrum of stereoblock polymer SBP_5 shows the presence of three resolvable doublets. The above observations show that the main chains of polypropylenes such as SBP and SBH consist mainly of relatively long tactic sequences, whereas those of SCE consist of very short tactic sequences due to the nearly random distribution of tactic placements or dyads along the chains. Such results yield, of course, direct information about the number-average closed tactic sequence lengths.

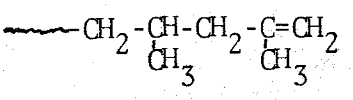
5.7 NMR Spectra of Thermally Degraded, Isotactic Polypropylenes

Figures 5-15 an -16 show, respectively, the methylene and the methyl proton resonance regions, of the ID series of polymers. The spectrum of IDB_3 is almost identical to that of the pure isotactic polymer IPP. However, when the molecular weight of the thermally degraded polymer decreases to about 2,000, the spectra become virtually identical with those of the stereoblock polymers. The changes in these spectra suggest that the isotacticity may decrease as the thermal degradation decreases the molecular weight. One might expect that such changes in spectra can be attributed to the following two factors.

(i) The original isotactic polymer sample contains a substantial degree of stereoirregularity, and the fractionation of the degraded whole polymer occurs not only on a molecular-weight basis but also according to stereoregularity.

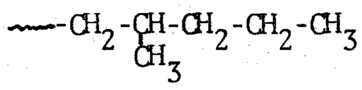
(ii) The number of end-groups increases as a result of thermal degradation, and the end-groups give rise to the observed effects on the spectra.

As to the first factor, the starting material was essentially pure isotactic, as is indicated by all the methods we adopted for tacticity determinations. Thus, we concentrate on the second factor. First, it is reasonable to assume that thermal degradation takes place randomly along the main chain. Then the degraded polymer fragments will differ only in their molecular weights. As the products resulting from thermal degradation, one has


$\sim CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{C}=CH_2$

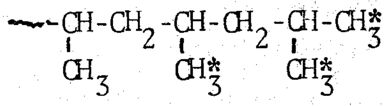
vinyliden end-group

and

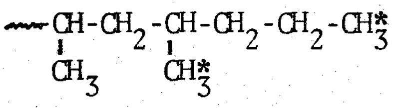

$\sim CH_2-\underset{CH_3}{CH}-CH_2-CH_2-CH_3$

n-propyl end-group

These considerations are the same as those reported by Natta and co-workers[18] and have been supported indirectly by our result on the $[\eta]$ vs. M relation. By hydrogenation, each end-group is converted into


$\sim \underset{CH_3}{CH}-CH_2-\underset{CH_3^*}{CH}-CH_2-\underset{CH_3^*}{CH}-CH_3^*$

and


$\sim \underset{CH_3}{CH}-CH_2-\underset{CH_3^*}{CH}-CH_2-CH_2-CH_3^*$

Here, the methyl protons marked by the asterisk have chemical shifts that differ from those of other methyl protons because they exsist at, or near, chain end. The average number of such "irregular" methyl terminal groups is five per degraded polymer fragment. The ratio of "irregular" to "regular" methyl groups increases as the average degree of polymerization decreases upon thermal degradation and hydrogenation. Changes in the spectra in Fig. 5-16, which accompany changes in molecular weight, appear to result from the effects of the "irregular" methyl groups on the nmr spectra. The critical point at which the influence of the "irregular" methyl protons in question appears in the spectra corresponds to a molecular weight of ca. 2,000. Similar argument appl~~y~~ies to the effects of "irregular, terminal" methylene protons on the methylene proton resonances.

If the average length of chains having the same steric configuration is quite short, the spectrum become~~s~~ more complex; the apparent widths of the resonance lines becomes greater because of the many proton resonances from groups with different magnetic environments.

References

(1) (a) P. Corradini, in *The Stereochemistry of Macromolecules*, Vol. 3 (A. D. Ketley, ed.) Marcel Dekker, Inc., New York, 1968, Chap. 1.; (b) J. C. Woodbrey, Ibid, Chap. 2.; (c) T. Miyazawa, Ibid., Chap. 3.; (d) V. Crescenzi, Ibid., Chap. 6.

(2) (a) G. Schnell, Ber. Bunsenges. Phys. Chem., 70, 297 (1966); (b) L. E. Nielsen, J. Appl. Polymer Sci., 2, 351 (1959); (c) S. Newman, J. Polymer Sci., 47, 111 (1960); (d) R. L. Miller, J. Polymer Sci., 57, 975 (1962).

(3) H. Inagaki, T. Miyamoto and S. Ohta, J. Phys. Chem., 70, 3420 (1966).

(4) (a) A. Zambelli, A. L. Segre, M. Farina, and G. Natta, Makromol. Chem., 110, 1 (1967); (b) E. Lombardi, A. L. Segre, A. Zambelli, A. Marinangeli, and G. Natta, J. Polymer Sci., C16, 2539 (1967); (c) A. Zambelli, M. G. Giongo and G. Natta, Makromol. Chem., 112, 183 (1968); (d) A. Segre, Macromolecules, 1, 93 (1968); (e) A. Zambelli and A. Segre, Polymer Letters, B6, 473 (1968).

(5) G. Natta, A. Valvassori, F. Ciampelli, and G. Mazzanti, J. Polymer Sci., A3, 1 (1965).

(6) A. D. Ketley and M. C. Harvey, J. Org. Chem., 26, 4649 (1961).

(7) E. H. Immergut, G. Kollmanan and A. Malatesta, J. Polymer Sci., 51, S57 (1961).

(8) J. C. Woodbrey, Polymer Letters, 2, 315 (1964).

(9) J. C. Woodbrey and Q. A. Trementozzi, J. Polymer Sci., C8, 113 (1965).

(10) W. C. Tincher, Makromol. Chem., 85, 34 (1965).

(11) T. Miyazawa, Polymer Letters, 2, 847 (1964).

(12) J. L. Koenig and A. Van Roggen, J. Appl. Polymer Sci., 9, 357 (1965).

(13) M. Peraldo, G. Natta and A. Zambelli, Makromol. Chem., 89, 273 (1965).

(14) G. Natta, et al., Chim. Ind. (Milan), 39, No 4, 275 (1957).

(15) C. Y. Liang and W. R. Watt, J. Polymer Sci., 51, S14 (1961).

(16) V. L. Folt, J. J. Shipman and S. Krimm, J. Polymer Sci., 61, S17 (1962).

(17) R. Adams, V. Voorhees and R. L. Shriner, in Organic Syntheses, Col. Vol. 1, 2nd Ed., p. 463 (1948).

(18) G. Natta, I. Pasquon, A. Zambelli and G. Gatti, Makromol. Chem., 70, 191 (1964).

(19) H. Fujita, Mathematical Theory of Sedimentation Analysis, Academic Press, New York, 1962.

(20) (a) D. A. Yphantis, Ann. New York Acad. Sci., 88, 586 (1960); (b) D. A. Yphantis, Biochemistry, 3, 297 (1964).

(21) K. E. Van Holde and R. L. Baldwin, J. Phys. Chem., 62, 734 (1958).

(22) P. J. Flory, Makromol. Chem., 98, 128 (1966).

(23) F. Danusso and G. Moraglio, Rend. Accad. Nazl. Lincei, [8] 25, 509 (1958)

(24) J. C. Moore, J. Polymer Sci., A2, 835 (1964).

(25) B. H. Zimm and W. H. Stockmayer, J. Phys. Chem., 17, 1301 (1949).

(26) See, for example, S. Gundiah, Makromol. Chem., 104, 196 (1967).

(27) (a) H. Benoit, Z. Grubisic, P. Rempp, D. Decker and J. O. Zilliox, J. Chim. Phys., 11-12, 1507 (1966); (b) Z. Grubisic, P. Rempp and H. Benoit, Polymer Letters, 5, 753 (1967).

(28) (a) C. M. Fontana, R. J. Herold, E. J. Kinney and R. C. Miller, Ind. Eng. Chem., 44, 2955 (1952); (b) C. M. Fontana, J. Phys. Chem., 63, 1167 (1959).

(29) T. Kotaka, H. Ohnuma and Y. Murakami, J. Phys. Chem., 70, 4099 (1966).

(30) Y. Murakami, Dissertation, Kyoto University (1968).

(31) T. Oyama, T. Takamizawa and Y. Kamihara, Report at the 16th meeting of the Polymer Science Society, Tokyo, Japan, 1967.

(32) J. P. Luongo, J. Appl. Polymer Sci., 3, 302 (1960).

(33) P. G. Schmidt, J. Polymer Sci., A1, 2317 (1963).

(34) J. N. Lomonte, Polymer Letters, 1, 645 (1963).

(35) H. Inagaki and T. Miyamoto, Makromol. Chem., 97, 267 (1966).

Chapter 6

Application of Thin Layer Chromatography to Stereoregular Polymers

Very recently application of thin layer chromatography (tlc) to studies on the chemical structure of copolymers has been discussed by Inagaki and co-workers.[1,2] In the first paper[1] they reported that the tlc combined with the concentration gradient development makes it possible to separate styrene-methyl acrylate copolymers according to the chemical composition without interference of polydispersity in molecular weight. The second paper[2] dealt with the effect of monomer arrangements in copolymer chain upon the chromatographic separation. Block, random and alternating copolymers of styrene and methyl methacrylate were subjected to the concentration gradient development with chloroform and ethyl acetate. It was found that first the random polymer, and belatedly the alternating polymer were developed, while the block polymer remained on the starting line. This result has been well elucidated in terms of the difference in adsorption forces onto stationary phase which are associated with three types of dyads in copolymer chain, viz. A-A, A-B and B-B. This success in interpreting the observation implied that not the overall chemical nature but only a fraction of much localized pieces (segments) of a copolymer chain would be responsible for the adsorption and the desorption at interfaces. For this reason we have expected that stereoregular polymers could be separated with respect to their steric isomerism if an appropriate development condition were found. In fact a preliminary tlc experiment on isotactic and atactic methyl methacrylate polymer

(PMMA) seemed to predict such a possibility.[1]

The first purpose of this Chapter is to utilize tlc to explore the separation characteristic of isotactic and syndiotactic PMMA as well as their mixture and investigate whether the amount of components separated from the mixture is determined quantitatively. Second is applications of tlc to investigating specific interactions between isotactic and syndiotactic PMMA chains. The problem treated here is further devided into two subjects, viz., the stereocomplex formation in dilute solution,[3-6] and the steric structure of crystallizable PMMA, which has been supposed first as a stereoblock PMMA.[7] For the first subject, stereocomplexes were formed in dilute solution in different mixing ratios of isotactic and syndiotactic PMMA, and the chromatographic behavior of the complexes was observed. For the second subject, tlc method was utilized to separate the so-called "stereoblock" polymer into components without chemical modification to the polymeric acid, as such was made by Liquori, et al.[8]

6.1 Preparation of Stereoregular Polymethyl Methacrylates

6.1.1 Isotactic polymers

Isotactic PMMA was obtained as described by Crescenzi, et al.[9] using phenylmagnesium bromide as initiator at 25°C in toluene. The product was fractionated into seven fractions by the usual precipitation-fractionation technique with the system acetone and methanol at 40°C. The middle fractions are coded iMA-2, iMA-3,.........., iMA-6. All samples and fractions obtained were purified by twofold precipitation from acetone solution into methanol, followed by vacuum drying at about 60°C.

6.1.2 Syndiotactic polymers

A syndiotactic sample was prepared by photopolymerization in bulk using ultraviolet light at -50°C in the presence of benzoin as photosensitizer.[10] The system acetone and methanol was employed to fractionate the product into nine fractions. The middle fractions are coded sMA-2, sMA-3,....., sMA-8. Purification of whole polymer and fractions was made by the procedure similar to that of isotactic polymers.

6.1.3 Atactic polymers

A monodisperse PMMA designated AMA was obtained through the kindness of Dr. H. Ohnuma of this Institute. This sample was prepared in tetrahydrofuran at -78°C with sodium biphenyl initiator in an all-glass vacuum apparatus.[11] Another atactic sample PMA was prepared by photopolymerization in toluene using ultraviolet light at 25°C in the presence of benzoin as photosensitizer.[10]

6.1.4 Stereoblock polymers

Two polymerization runs of MMA in toluene at -50°C using diphenylmagnesium and n-butylmagnesium chloride, respectively,[11] were carried out to gain so-called "stereoblock" polymers.[7] After extracting the products with acetone at boiling point, the insoluble portions were designated DPM and BMC, respectively.

Results of molecular characterization of these fractionated and unfractionated samples are summarized in Table 6-1. The nmr spectra of whole polymers are shown in Figure 6-1.

Table 6-1 Characterization of Sample Polymers Used

Sample Code	$[\eta]_{25^{o}}$ (dl./g) in chloroform	$M_v \times 10^{-5}$	IR index[a] A	Tacticity I	Tacticity H	Tacticity S
iMA-3	1.49_0	3.64	0	1.0	0	0
iMA-4	0.71_5	1.65	0	1.0	0	0
sMA-2	0.98_6	2.46	1.0	0.04	0.16	0.80
sMA-3	0.77_5	1.82	1.0	——	——	——
AMA	——	3.43[b]	0.70	0.07	0.40	0.53
PMA	1.28_7	3.25	0.76	0.07	0.33	0.60
DPM	0.84_2	2.02	0.60	0.39	0.11	0.50
BMC	1.05_0	2.66	0.57	0.32	0.11	0.57

a) Ratio of absorbance at 9.45μ to that at 7.25μ.

b) Number-average molecular weight determined by osmometry.

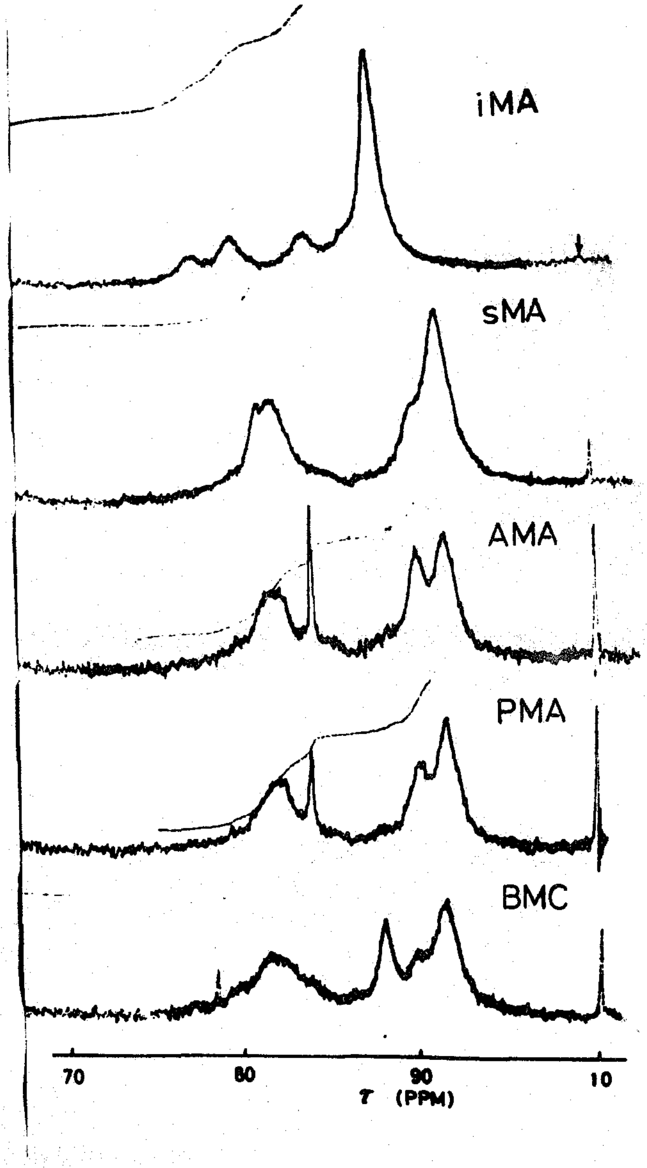


Fig. 6-1 The 60 Mc/sec. nmr spectra of isotactic (iMA), syndiotactic (sMA), atactic (AMA and PMA), and stereoblock (BMC) polymethyl methacrylates.

6.2 Physical Measurements

6.2.1 Viscosity measurements

Viscosity measurements were made in Ubbelohde viscometers with various flow times ranging from 120 to 240 sec. for chloroform at 25°C. Viscosity average molecular weights of samples were calculated by using a relation,

$$[\eta] = 4.8 \times 10^{-5} M_w^{0.8}$$

which has been established for conventional PMMA.[12,13]

6.2.2 Infrared spectra

The 2-15 μ spectra were taken by a Perkin-Elmer Model 521 spectrophotometer. The infrared index A, given by the ratio of absorbances at 7.25 and 9.45 μ, was used as a measure of tacticity. The value of A was determined by the method described by Baumann, et al.[14]

6.2.3 High-resolution nmr spectra

High-resolution nmr spectra were taken by a Varian A-60 spectrometer. All the spectra were obtained from 5-10% (W/V) solution in $CDCl_3$ at 30°C. Tetramethylsilane was used as an internal standard. The tacticity of polymers was determined by referring to the method developed by Bovey and Tiers.[15] The results indicated that the tacticities of isotactic and syndiotactic PMMA were respectively almost 100% and at least 90%.

6.3 Thin Layer Chromatography

6.3.1 Stationary phase

One part of silica gel, Silica-gel G (E. Merk AG., Darmstadt), containing approx. 13 gypsum, was slurried with two parts of distilled water, and applied as the stationary phase onto thick glass plates (20×10 or 10×10 cm^2). The thickness of the layer was adjusted to 0.25 mm, using a commercially available device. Immediately before use, the gel layer was activated by heating the plate at 110°C for one hour.

6.3.2 Development procedure

Stock solutions for tlc tests were prepared by dissolving 40 mg of each sample in 10 ml chloroform. With the aid of a microsyringe a spot of each solution, containing *ca.* 10 μg of polymer, was formed on the layer. The position of each spot, i.e. the starting points, was 2.0 cm from one edge of the glass. The plate was dried for several minutes and placed into a desicator containing the developing solvent at room temperature. After the solvent front had risen 10 cm from the starting point, the plate was removed from the container and kept in an oven at *ca.* 60°C to prevent further ascent of the solvent front. Then, a 1% methanol solution of iodine was sprayed unto the gel, marking the position of the polymer as brown spots. Because this color faded after 20-30 minutes, the chromatograms were photographed on high-contrast film.

6.3.3 Configuration dependence of the blackness of film

To determine the amount of polymer developed on chromatogram, the photographic procedure similar to that described by Inagaki, et al.[1], was applied. Chloroform solutions of iMA and of sMA with identical concentration of 4.0 g/l were prepared. By means of a microsyringe four spots for each solution, which contain 4, 8, 16 and 32 μg of polymer, were formed on the thin layer having thickness of 0.25 mm. Care was taken to keep the area of every spot constant (3 mm in diameter). After the solvent had been evaporated, the spots were stained and photographed. The blackness integrated over the area of each spot was measured by a densitometer equipped a slit whose length (4 mm) was longer enough than the diameter of spot. Plots of the blackness against the polymer amount are demonstrated in Figure 6-2. The result shows that the blackness is proportional to the polymer amount within a limited range (ca. 180 $\mu g/cm^2$) and varies prominently according to the configuration of polymer; iodine molecules have a higher affinity to the isotactic polymer by a factor of 1.3_2 than to the syndiotactic polymer.

6.4 Separation of Stereoregular PMMA with Respect to Their Steric Isomerism

For PMMA samples with different steric isomerisms, tlc developments were made first by using single solvents, chloroform, ethyl acetate, 2-butanone and acetone as developing agents. Values of rate of flow R_f thus obtained are given in Table 6-2. From the table it is seen that only ethyl acetate exhibits the ability of giving different R_f values to the isotactic, and the syndiotactic or atactic polymer; the isotactic polymer remains on the starting line, while the syndiotactic and atactic polymers reach the proximity of solvent front. However, the result obtained suggests that a mixture of ethyl acetate with 2-butanone or acetone will be useful to separate stereoregular PMMA composed of considerable amounts of heterotactic sequences. In addition, it is interesting to note that chloroform, which behaves as good solvent for PMMA with any steric isomerism, cannot develop the

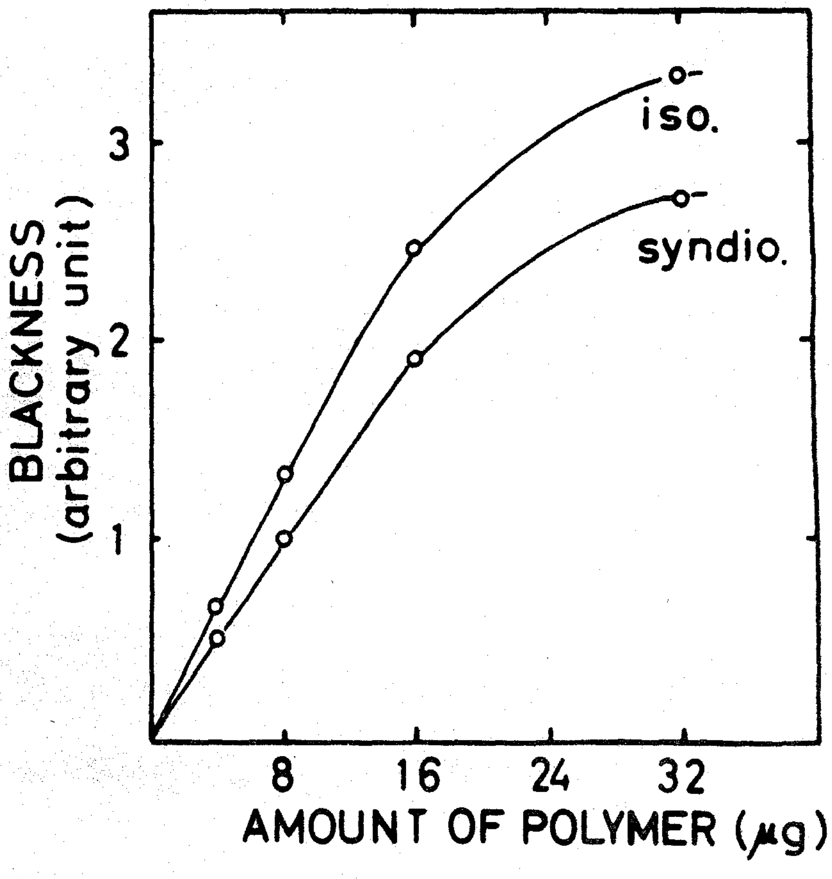


Fig. 6-2 Relation between the blackness on photographic film and the amount of polymer. For the details, see text.

Table 6-2 Results of Chromatographic Developments with Single Solvents

Developer	Dielectric const.	R_f		
		iMA-3	sMA-2	AMA
Chloroform	4.62	0	0	0
Ethyl Acetate	6.02	0.1	0.90	>0.9
2-Butanone	18.5	0.90	0.90	>0.9
Acetone	21.3	>0.9	>0.9	>0.9

polymers. This is indicative of the fact that in the chromatographic separation, the adsorbate-adsorbent interaction is more dominant than the adsorbate-solvent interaction, as has been pointed out previously.[1,2]

On the basis of the above experience a 1:2 mixture of iMA-3 and sMA-2 was subjected to the development with ethyl acetate. A chromatogram was gained which consists of two separated spots, as is shown in Figure 6-3. To determine whether this chromatogram is related to different migration rates of polymers with different steric isomerisms, further test was made. The same polymer mixture was developed on the stationary phase whose thickness is _ca._ 1 mm. Two spots again appeared separately, after the chromatogram was stained with a 1% methanol solution of iodine. The thin layer, on which each spot was located, was scraped off the glass plate and treated with acetone to extract adsorbed polymer. The stereoregularity of these extracts was assessed on the basis of nmr spectra. Thus it was confirmed that the upper and lower spot should be assigned to the syndiotactic and isotactic component, respectively.

The analytical method established in section 6.3.3 has been applied to the determination of the relative amounts of two components separated from the 1:2 mixture of isotactic and syndiotactic polymer. For this purpose the chromatogram obtained was photographed, and the area and the blackness of the upper and lower spot, which have been assigned to the syndiotactic and isotactic component, respectively, were determined. In consideration of the correction to the area of spot and the factor of 1.32 relating the blackness of syndiotactic polymer with that of isotactic polymer, the final result of the relative amounts

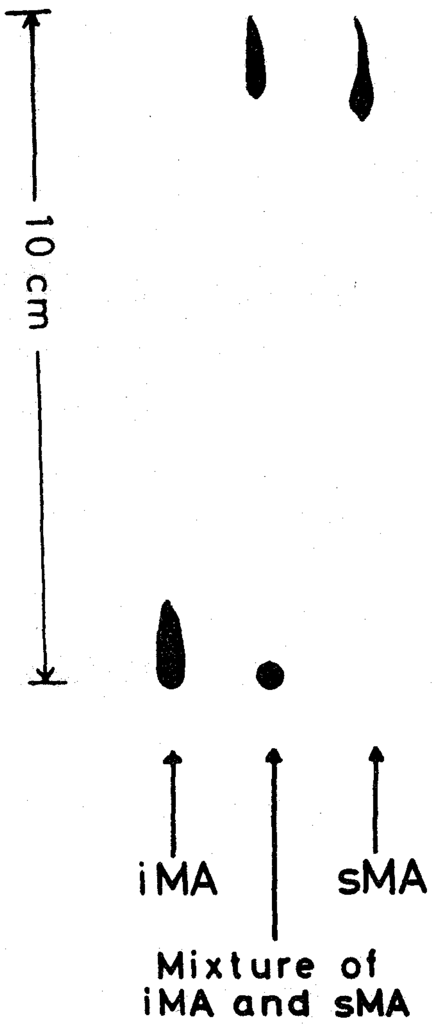


Fig. 6-3 Tlc chromatogram obtained for isotactic and syndiotactic PMMA, and their 1:2 mixture, which were developed by using ethyl acetate as developing agent.

of components yielded 0.69 and 0.31 for the upper and lower spot, respectively, which may approximately correspond to the initial ratio of syndiotactic and isotactic component in the mixture.

It is necessary to know whether the R_f values depend upon the molecular weight of the polymer. It has been reported that the adsorption equilibrium of polymers on a surface can be affected by molecular weight,[16] and oligomers have been fractionated in this manner with respect to molecular weight.[17] On the other hand, Inagaki, et al. have reported recently that the R_f values are almost independent of molecular weight within the molecular weight span studied in the concentration gradient development of styrene-methacrylate copolymers.[1]

Several fractions obtained from iMA and sMA were subjected to the development with ethyl acetate. The results are summarized in Table 6-3. The molecular weight dependence of R_f was not found in this case. The R_f values depend upon the steric isomerism of the polymer under the above developing conditions.

6.5 Stereocomplex Formation in Dilute Solution

This section deals with the formation of stereocomplex between stereoisomeric chains of PMMA.[3-6] Stereocomplex formation was achieved by admixing the stock solutions of the two stereoregular polymers, iMA-3 and sMA-2, in three different ratios (iso/synd), namely 2:1, 1:1, and 1:2. Upon admixture of the two solutions no visible changes in transparency of the resultant solution was observed, differing from the case where the two species in acetone were mixed.

It has been well established in the previous section that when ethyl acetate is used as developing agent, the isotactic PMMA remains

Table 6-3 Molecular Weight Dependence of R_f for Samples

Sample Code	$M_v \times 10^{-5}$	R_f
iMA-3	3.64	0.09
iMA-4	1.65	0.1
sMA-2	2.46	0.90
sMA-3	1.82	0.90
AMA	3.43[a)]	>0.9
PMA	3.25	>0.9

a) Number-average molecular weight determined by osmometry.

on the starting line, while the syndiotactic PMMA (and atactic PMMA) reach the neighborhood of the solvent front. For the present purpose, acetone was, however, used which could develop the both species to the proximity of the solvent front, as shown in Figure 6-4. This chromatogram indicates also that the 1:1 mixture could not be separated into components at all. In this connection it is of interest to note that to obtain such a chromatogram, the spot formed on the thin layer from the mixture in chloroform had to be moistened with a drop of acetone in advance of the development; nevertheless a slight ascendance of the spot lying on the starting line was unavoidable in every case. This feature may be related to the conclusion that the stereocomplex formation is promoted much more in polar solvent,[6a] and also to our observation made upon admixture of the two species in chloroform.

The next experiment was made for the mixture with the different compositions. The chromatogram was shown in Figure 6-5. From the figure it is seen that the mixture, except for that of the 1:1 ratio, yield a lower and an upper spot, which appear at the starting line and in the vicinity of the solvent front, respectively. To collect the polymer species involved in each spot for assigning the steric structure, the same development was carried out for the mixtures of 1:2 and 2:1 (iso/synd) ratios with the thin layer of i mm thickness. The adsorbed species were recovered by extraction with hot acetone.

The stereoregularity of these extracts was assessed on the basis of nmr specta. Figures 6-6a and 6-6b illustrate the 60 Mc/sec. nmr spectra of the upper and the lower portion originating from the 1:2 mixture, respectively. The nmr data permit us to confirm that the

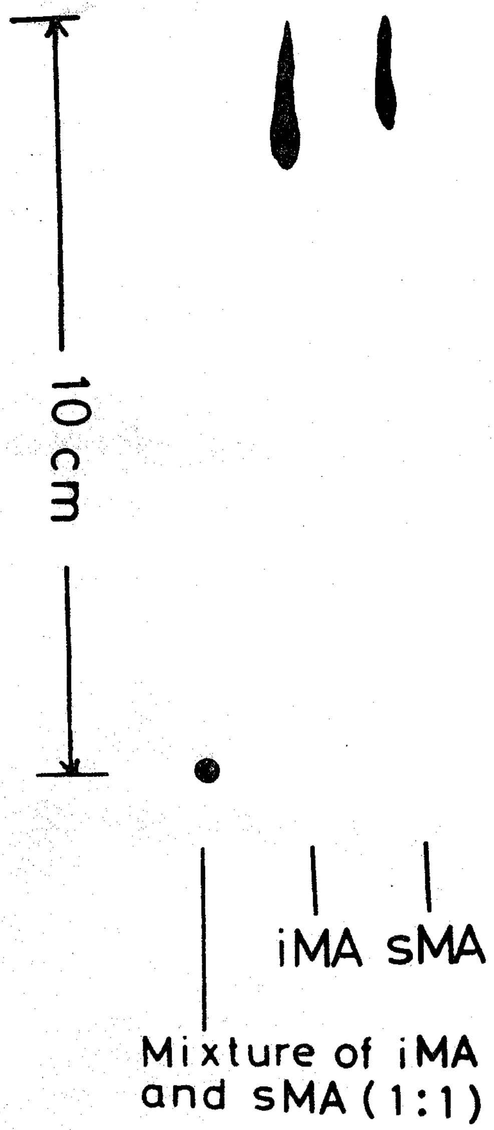


Fig. 6-4 Tlc chromatogram obtained for isotactic and syndiotactic PMMA, and their 1:1 mixture by using acetone as developer.

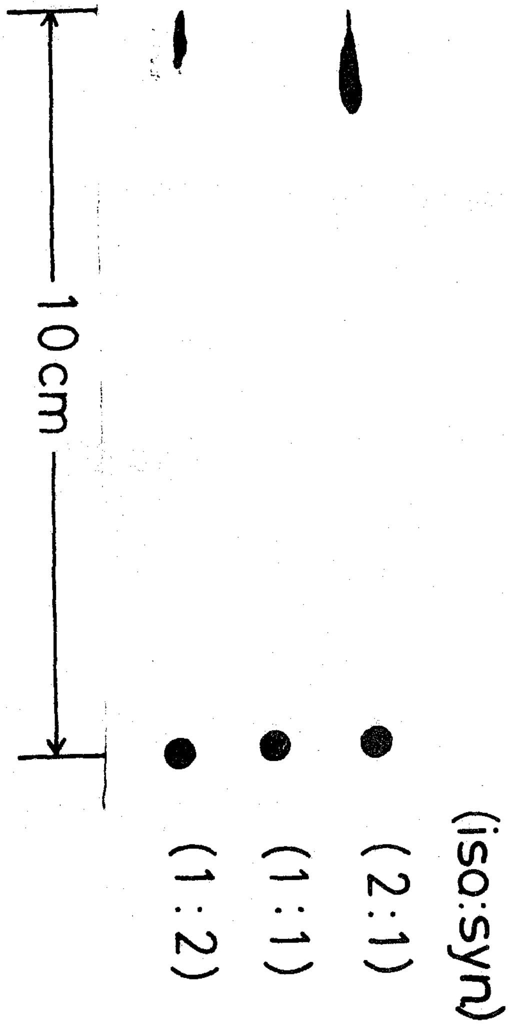


Fig. 6-5 Tlc chromatogram obtained for the mixtures of isotactic and syndiotactic PMMA in different mixing ratios by using acetone as developer.

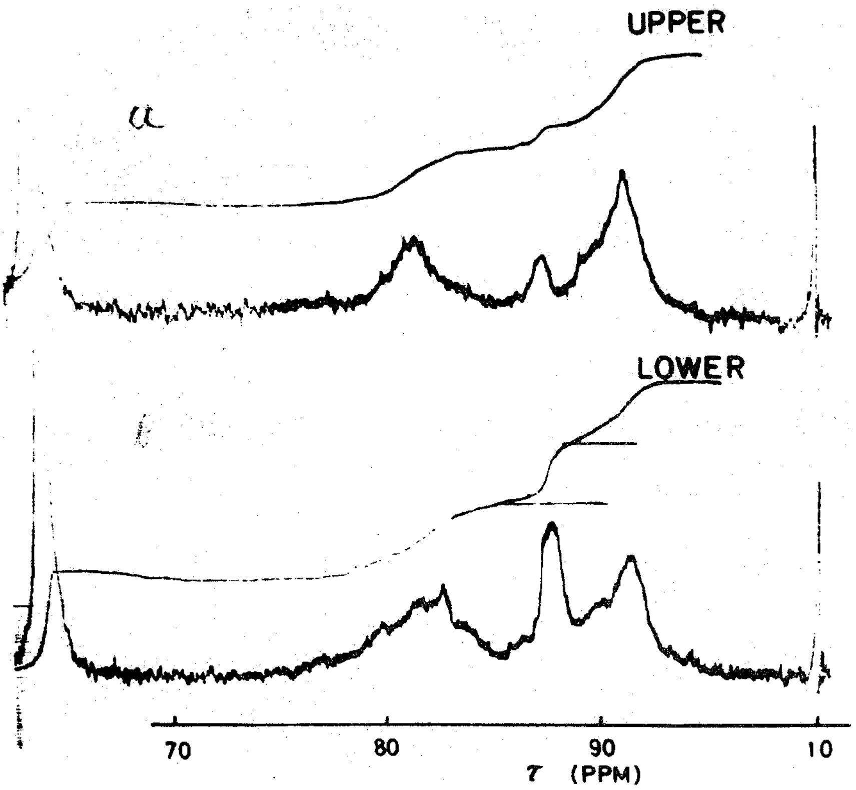


Fig. 6-6 Nmr spectra, obtained in 10% $CDCl_3$ solutions at 60 Mc./sec. and at $30^{\circ}C$, of polymers involved in the upper(6a) and the lower spot(6b) in the chromatogram obtained by development of the 1:2 (iso/synd) mixture with acetone.

upper spot contained highly syndiotactic species, while the species in the lower spot could be identified with that of the 1:1 mixture. For the 2:1 mixture the species involved in the lower spot was assigned by nmr to the same stereoisomeric composition as the 1:1 mixture. This means, in turn, that the upper spot should contain the isotactic species, though its analysis was not made. These observations thus suggest that this type of aggregation phenomena may occur stoichiometrically at a unique composition between equivalent portions of isotactic and syndiotactic PMMA. Our preliminary result obtained by ultracentrifugation of the mixtures appears, however, to reveal that the 1:2 (iso/synd) complex also might be formed as the result of further aggregation between the 1:1 complex and the syndiotactic polymer. We may conclude that two different structure for the stereocomplexes are possible depending on the relative amount of syndiotactic to isotactic PMMA.[3-6] These findings are well explained by the fact that in the chromatographic separation, the adsorbate-adsorbent interaction is more dominent than the adsorbate-solvent interaction or the interaction between unlike steric isomers (unlike adsorbates).

6.6 Steric Structure of the So-called Stereoblock PMMA

In an attempt to investigate the steric structure of the so-called stere-block PMMA, we have applied tlc technique to sample BMC and DPM using ethyl acetate as developing agent. Figure 6-7 shows the chromatogram thus obtained, in which the two species, the 1:2 mixture, and an atactic PMMA (AMA) prepared with an anionic polymerization technique[11] were developed simultaneously for comparison. This result indicates

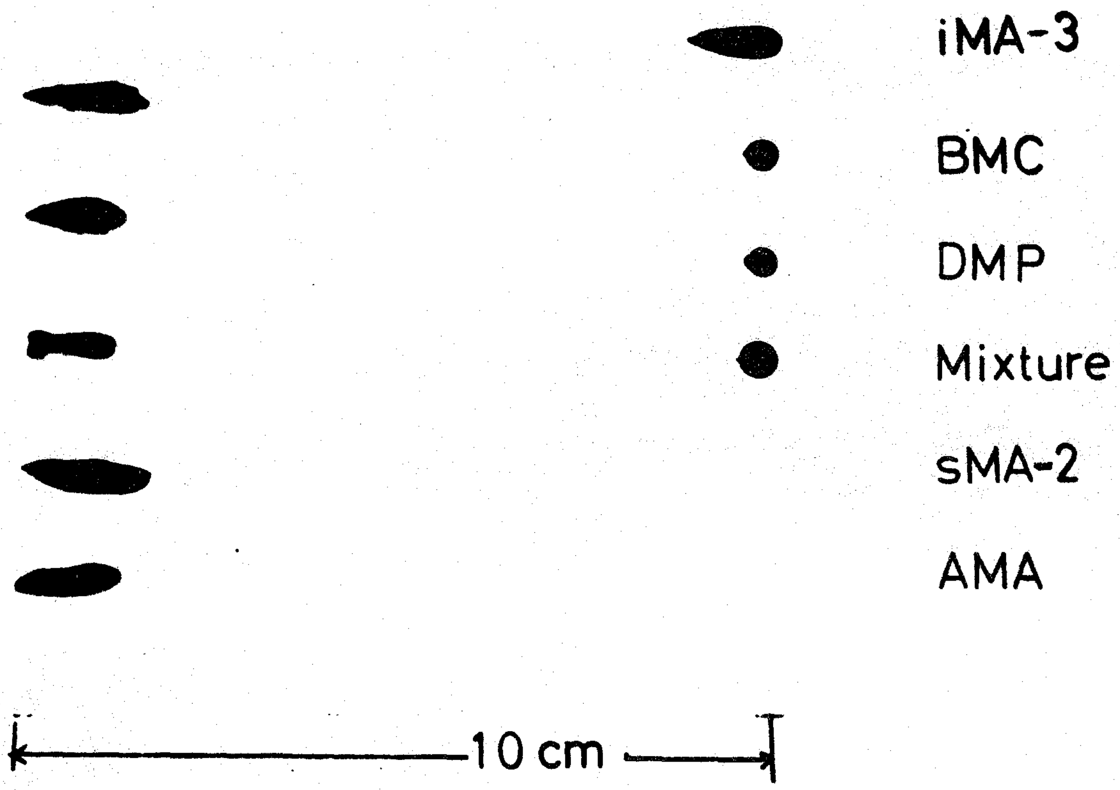


Fig. 6-7 Tlc chromatogram obtained by development of different stereoisomeric types of PMMA with ethyl acetate, viz. isotactic(iMA-3), stereoblock(BMC and DMP), the 1:2 mixture, syndiotactic(sMA-2), and atactic(AMA) PMMA, in order from top to bottom.

that the sample BMC and DPM are distinctly separated into an upper and a lower spot.

By using the same procedure employed for the stereoisomeric mixtures the polymer species involved in each spot recovered and subjected to the nmr analysis. In connection with the extraction of polymer from the thin layer it should be denoted that the species thus separated were no more insoluble in acetone in contrast to the fact that the original samples were insoluble in this solvent. Figure 6-8a shows the nmr spectrum for sample BMC; Figures 6-8b and 6-8c those for the species contained in the upper and the lower spot, respectively. The spectrum for the upper spot indicates the dominant α-methyl peak at 9.13τ and the single β-hydrogen contribution;[15] for the lower spot the dominant α-methyl peak at 8.80τ accompanied by four peaks for the β-hydrogens. Besides the peak appears for the both species at 8.98τ, which may be assigned to the heterotactic sequences. On the basis of the nmr data we may conclude that the main components involved in the upper and the lower spot are assigned to the syndiotactic and the isotactic PMMA, respectively, though these polymers contain considerable amounts of the heteretactic sequences.

The relative amount of the two components separated from original sample BMC was determined by a photometric procedure established previously. Using the photofilm of chromatogram stained with methanol solution of iodine the area and the blackness of the spot were measured. Figure 6-9 shows the intensity of blackness of film for sample BMC as a function of distance r from the starting point. The total blackness corrected against the area was then converted to the amount of

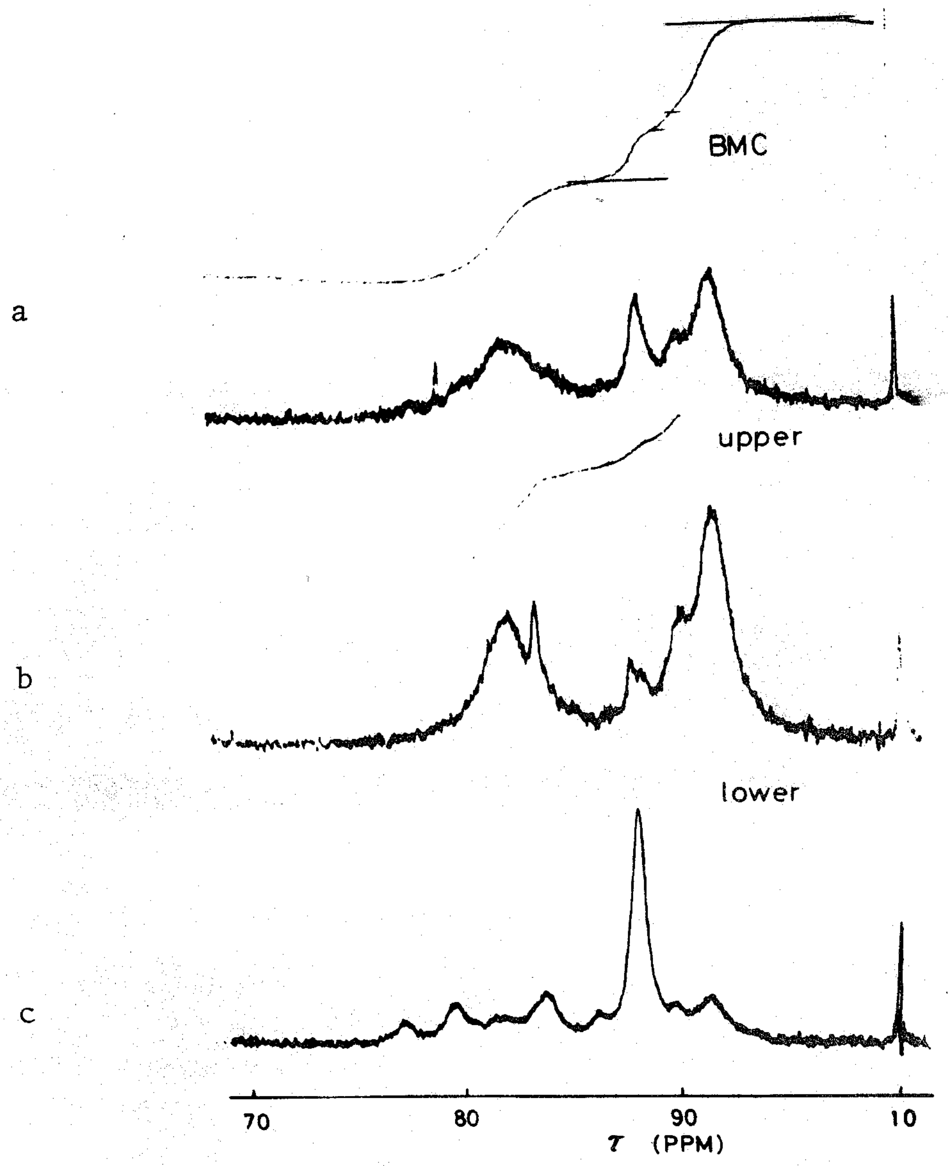


Fig. 6-8 Nmr spectra, obtained in 10% $CDCl_3$ solutions at 60 Mc./sec. and at $30^{\circ}C$, of original stereoblock polymer BMC, the species contained in the upper and the lower portion separated from BMC with ethyl acetate as developer.

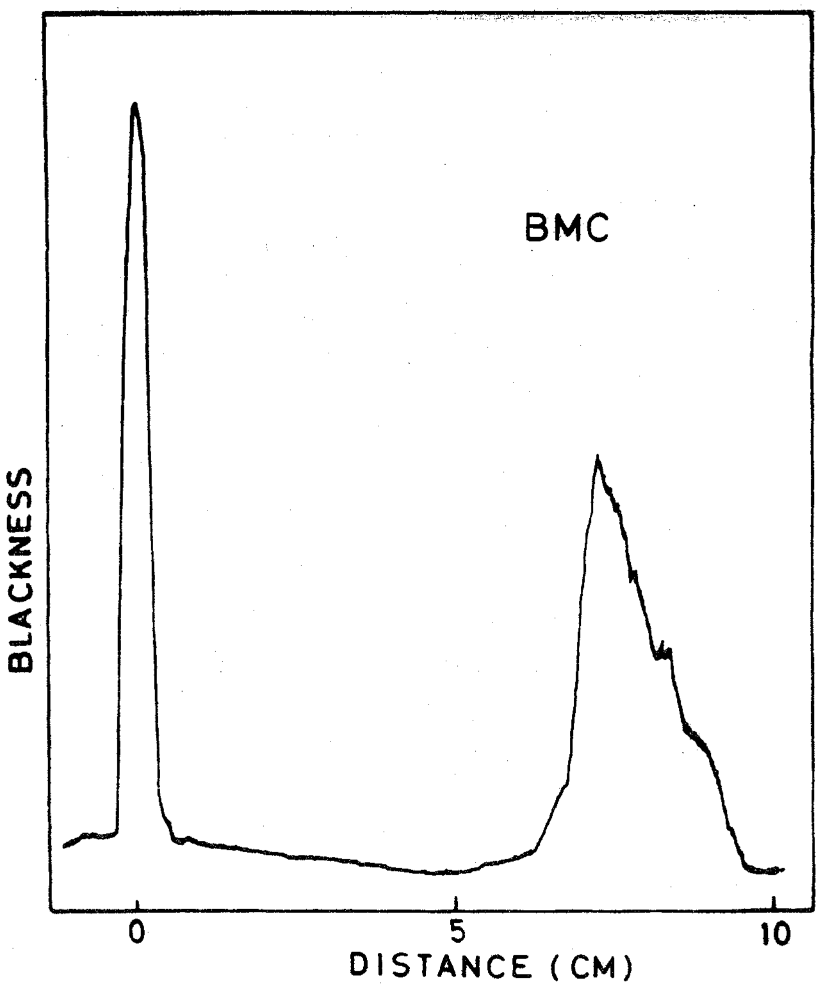


Fig. 6-9 Intensity of blackness of film as a function of distance r from starting point.

polymer by taking into consideration a factor 1.3_2 that is caused by the difference in the blackness of the isotactic and syndiotactic PMMA; iodine molecules have an affinity for the isotactic polymer which is higher by a factor of 1.3_2 than that for the syndiotactic polymer. The final estimation of the relative amount yielded 0.71 and 0.29 for the syndiotactic and the isotactic portion, respectively, and this is good agreement with that reported by Liquori, et al.[8]

References

(1) H. Inagaki, H. Matsuda, and F. Kamiyama, Macromolecules, 1, 520 (1968).

(2) F. Kamiyama, H. Matsuda, and H. Inagaki, Makromol. Chem., ~~in press.~~ 125, 286 (1969).

(3) (a) W. H. Watanabe, C. F. Ryan, P. C. Fleisher, Jr., and B. S. Garrett, J. Phys. Chem., 65, 896 (1961); (b) C. F. Ryan and P. C. Fleisher, Jr., ibid., 69, 3384 (1965).

(4) (a) A. M. Liquori, G. Anzuino, M. D'Alagni, P. De Santis, and M. Savino, Nature, 206, 358 (1965); (b) A. M. Liquori, M. De Santis, M. Savino, and M. D'Alagni, J. Polymer Sci., B-4, 943 (1966).

(5) R. Chiang, J. J. Burke, J. O. Threlkeld, and T. A. Orofino, J. Phys. Chem., 70, 3591 (1966); (b) J. Dayantis, C. Reiss, and H. Benoit, Makromol. Chem., 120, 113 (1968).

(6) H. Z. Liu and Kang-Jen Liu, Macromolecules, 1, 157 (1968).

(7) (a) T. G Fox, B. S. Garret, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell, and J. D. Stroupe, J. Amer. Chem. Soc., 80, 1768 (1958); (b) J. D. Stroupe and R. E. Hughes, J. Amer. Chem. Soc., 80, 2341 (1958).

(8) A. M. Liquori, G. Anzuino, M. D'Alagni, V. Vitagliano, and L. Constantino, J. Polymer Sci., A-2, 6, 509 (1968).

(9) V. Crescenzi, M. D'Alagni, A. M. Liquori, L. Picozzi, and M. Savino, Ric. Sic., 33, 123 (1963).

(10) T. G Fox, W. E. Goode, S. Gratch, C. M. Huggett, J. F. Kincaid, A. Spell, and J. D. Stroupe, J. Polymer Sci., 31, 173 (1958).

(11) A. Roig, J. E. Fiqueruelo, and E. Llano, J. Polymer Sci., B-3, 171 (1965).

(12) W. E. Goode, F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, J. Polymer Sci., 46, 317 (1960).

(13) J. Bischoff and V. Desreux, Bull. Soc. Chim. Belges., 61, 10 (1952).

(14) U. Baumann, H. Schreiber, and K. Tessmar, Makromol. Chem., 36, 81 (1960).

(15) F. A. Bovey and G. V. D. Tiers, J. Polymer Sci., 44, 173 (1960).

(16) (a) F. Patat, E. Killmann, and C. Schleibener, Fortschr. Hochpolym. Forsch., 3, 332 (1964); (b) R. R. Strombery, J. Phys. Chem., 69, 3955 (1965).

(17) (a) K. Burger, Z. Anal. Chem., 169,(4), 259 (1963); (b) K. Konishi and S. Yamaguchi, Anal. Chem., 38, 1755 (1966).

ACKNOWLEDGMENTS

I should like to express my sincere thanks to Prof. H. Inagaki, my major advisor here at Institute for Chemical Research, Kyoto University, for his guidance, assistance, constant encouragement, and detailed criticism of the entire manuscript; my study under him during these eight years has been a most rewarding experience.

It is a great pleasure to express my graditude to Prof. M. Horio for his generosity and constant encouragement.

I am greatly indebted to

Prof. M. Kurata and Dr. T. Kotaka of this Institute, for their invaluable advices and helpful discussions.

Mr. S. Ohta of Ubbe-Nitto Chemical Co. Ltd. for his helpful discussion and much direct aid.

Drs. Y. Murakami of Teijin Co. Ltd., H. Ohnuma, H. Suzuki, and N. Donkai of this Institute, for comradeship and much direct aid.

members of this Institute, in particular, members of Prof. K. Kobayashi's Laboratory for their valuable discussions and kind assistances.

the many persons whom it has been my privilege to know here at Prof. H. Inagaki's Laboratory who have contributed their advices and assistances to me during the course of this study.

Finally I express my cordial thanks to Nitto Spinning Co. Ltd. and Ubbe-Nitto Chemical Co. Ltd., for their generous support.

List of Papers

Each Chapter of the present thesis was described on the basis of following papers published by the author: Chapter 3 concerns (1) and (2); Chapter 4 (3), (4), and (5); Chapter 5 (6), (7), and (8); Chapter 6 (9) and (10).

(1) H. Inagaki, T. Miyamoto, and S. Ohta, "Unperturbed Dimensions of Polypropylene and Polyethylene", J. Phys. Chem., 70, 3420 (1966).

(2) T. Miyamoto, S. Ohta, and H. Inagaki, "Dilute Solution Properties of Syndiotactic Polypropylene", Report at the 14th Polymer Symp. Japan, 1965; Reports on Progress in Polymer Physics in Japan, 9, 33 (1966).

(3) H. Inagaki and T. Miyamoto, "Einkristalle von syndiotaktischem Polypropylen aus verdünter Lösung", Makromol. Chem., 97, 267 (1966).

(4) H. Inagaki and T. Miyamoto, "Unperturbed Dimensions and Conformations of Polymer Chains in Dilute Solution, -A Discussion on the Single Crystal Growth from Dilute Solution", Inter. Symp. on Macromol. Chem. Tokyo, 1966, Reprint No. 2.3.09.

(5) T. Yagi, T. Miyamoto, and H. Inagaki, "Dilute Solution Properties of Poly-ε-caprolacton", Report at the 17th Polymer Symp. Japan, 1968.

(6) T. Miyamoto and H. Inagaki, "Microstructures of Polypropylene Chains with Low-Molecular-Weights and Tacticities", Reports on Progress in Polymer Physic in Japan, 11, 457 (1968); Report at the 16th Polymer Symp. Japan, Fukuoka, 1967.

(7) T. Kotaka and T. Miyamoto, "Structure and Dilute Solution Properties of Macromolecules", High Polymers, Japan, 17, 629 (1968).

(8) T. Miyamoto and H. Inagaki, "The Structural and Steric Isomerism of Polypropylenes", J. Polymer Sci., A-2, in press.

(9) H. Inagaki, T. Miyamoto, and F. Kamiyama, "Separation of Stereospecific Polymers with Respect to Their Steric Isomerism by Thin Layer Chromatography", J. Polymer Sci., B, ~~in press~~. 2, 329 (1969).

(10) T. Miyamoto and H. Inagaki, "Thin Layer Chromatographic Studies on Specific Interactions between Stereoisomeric Chains of Polymethyl Methacrylate", ~~submitted to~~ "Macromolecules", in press.

The following is the list of papers reported by the author and his collaborator except for above papers included in the present thesis.

(1) H. Inagaki and T. Miyamoto, "Preparation of Block Copolymers of A-B-A Type and its Behavior in Dilute Solution", Makromol. Chem., 87, 166 (1965).

(2) H. Inagaki and T. Miyamoto, "Intrachain Interactions and Molecular Shape of A-B-A Type Block Copolymers in Dilute Solution", Report at the 14th Polymer Symp. Japan, 1965.

(3) T. Miyamoto and H. Inagaki, "Grignard-Initiated Polymerization Methyl Methacrylate in the Presence of Methyl Methacrylate Polymers with Different Steric Isomerisms", submitted to "~~J. Polymer Sci., B~~".
"Polymer Journal"