

MODEL SUBSTANCES AS TOOLS IN POLYMER SCIENCE

O. WICHTERLE

*Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
Prague, Czechoslovakia*

INTRODUCTION

The word model is used for any structurally analogous substance, which can, with advantage, be compared with substantially more complicated structures. The advantage of using model substances as tools in polymer science follows from the fact that the simple substance is more easily prepared in a perfectly defined state. Macromolecular science offers many occasions for the use of this research technique since it permits the preparation of general and typical trait of polymers in the repetition of structural units; these groups can also be incorporated or simulated by a similar group either individually or in a small number in small molecules.

A comparison of polymeric substances with the analogous low-molecular ones may have a number of purposes.

(1) To compare the reactivity of the reactive groups of the analogue bound by low-molecular chains with the reactivity of the same groups bound to a macromolecular skeleton. From this comparison, some qualitative correlation rules may be derived. By means of these rules it is possible to forecast the reactivity of polymers from the known reactivity of simple substances, and apply in this way the entire experience of classical organic chemistry. The concern may be either with the reactivity of groups, whose conversion is not connected with a substantial alteration of the macromolecular structure (polymer analogue reactions, ion-exchangers, redox-exchangers) or with reactions which affect the macromolecular chain (destruction, cross-linking of the polymers, etc.).

(2) To deepen the knowledge of the mechanism of macromolecular syntheses. In the case of synthetic polyreactions, which are not of chain character, this effort is practically identical with the general interest of organic chemistry. Specific modelling is, however, required by chain reactions, for which the individual partial reactions may be elucidated by means of models.

(3) To examine the structure of the polymeric chain by comparing some properties of the polymer (especially spectra of all possible kinds) with the properties of the analogues (synthesized model substances of reliably known structure).

The interest in model substances thus penetrates into many fields of polymer science. The organic chemist is the joint collaborator, and generally his possibilities are the limiting factor. Without mobilizing the preparatory

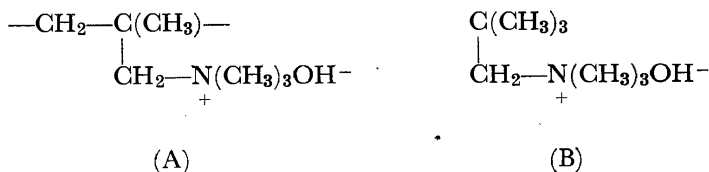
methods of modern organic chemistry, of its art and experiences we could not succeed. Of course I am unable to describe here the participation of organic chemists in the preparation of the generally very complicated substances, frequently with maximum demands with respect to structural and stereochemical individuality and purity. I need only mention, in general, that the participation of organic chemists is the strongest bond with which— notwithstanding the ever rising degree of physicalization—polymer science continues to be bound to general organic chemistry.

MODELS OF THE REACTIVITY OF POLYMERS

Polymer analogue reactions

In comparing the reactivity of isolated groups it is a rule that the character of the reactive group bound to the suitably selected model (i.e. such a model which also simulates the screening effect of the vicinal part of the macromolecular chain) does not differ essentially from the character of the same group in the polymer. This rule has served in countless cases to allow macromolecular variants of low-molecular reagents to be found, and led to an unprecedented evolution of ion-exchange and oxidation–reduction exchange resins.

Considering, however, the quantitative reactivity indices, the relation of the simple model to the polymer is found to be more complicated. Comparing the monofunctional compound with a polymer analogue we shall find a quantitative agreement even in the kinetic data in such reactions, in which there is no interaction of two or more of such groups. Therefore we may *a priori* expect very good agreement in the case of reactions taking place in a monomolecular mechanism. For example, we may state that of all possible structures of anion exchangers, the structure (A) with the basic chain would be optimal, because the model substance (B) compared to



other simple quaternary bases is the most thermally stable one¹.

The course of reactions, in which the mechanism of two or more groups is engaged, is substantially influenced by the spatial possibilities of the mutual influence of reactive groups which occur repeatedly in the polymer. The significance of stereochemistry for these interactions has already been discussed in detail by Smets in his lecture at the Symposium in Prague². In that lecture it was also stressed that it was possible to interpret the mechanism of this mutual influence by means of two- or polyfunctional models with precisely defined conformation of the reactive groups. In the present symposium we are also encountering studies which use an exact model to

solve the influence of tacticity on the course of a reaction involving two or more groups (polyvinyl alcohol and heptane-2,4,6-triol acetalization)³.

Besides stereochemical effects, specific strain of the macromolecular structure could change the reactivity. The saponification rate of polymethacrylic acid diglycol esters, depends strongly on whether the glycol is ester-bound by one or both hydroxyl groups to the polymethacrylic acid⁴. With the large distance of the two hydroxyl groups the direct effect of esterification of the one diglycol end on the hydrolytic capacity of the ester group on the other end may be neglected, a fact which becomes evident from practically equal rates of hydrolysis of the mono- and diester of this glycol with monocarbonic acids⁵. The outstanding stability of the ester cross-links in glycol-methacrylate gels might perhaps best be explained by the fact that due to the general tension in chains the angle of the C—C—O bond in the basic planar structure of the ester rather tends to be opened, which fact hinders the narrowing of this angle in the formation of the tetrahedral transition state which is a condition of hydrolysis.

Polymer degradation

The chemistry of model substances is doubtless the only way to progress in the, as yet very imperfect, understanding of thermal oxidation of photochemical degradation processes of polymers.

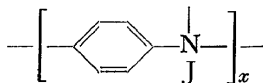
The first step in any discussion of degradation problems is the finding of those locations in the polymer which are most responsible for degradation. It must be decided whether these are locations with a regular structure, which are an absolutely prevalent part of the polymer, or whether these are exceptional sites (terminal groups, structural defects), which are present only in a slight proportion, but may be exceptionally sensitive to the destructive effect of heat, light or oxygen.

The object on which attention has concentrated most in this respect is polyvinyl chloride (PVC). A comparison of the stability against destruction of low-molecular PVC models of absolutely regular structure with the much lower stability of the polymer has led to the justified suspicion that the low stability of the polymer is caused by abnormal structures which may occur in it⁶. Therefore research investigations on the destruction of PVC have been oriented to these defect structures. The problems such as the part played in the destruction, e.g. by double bonds, from which the decomposition might set out, as well as the mechanism of this decomposition can again be solved only on the base destruction experiments with simple unsaturated model chlorides.

The technically significant photodegradation of polyamides has also been elucidated by means of simple model amide. It has been shown that the weak spot is the C—H bond vicinal to the nitrogen atom, and that amides substituted on these bonds are practically not oxidized⁷. In agreement with this fact is the formation of radicals in the α -position with respect to the nitrogen atom, established by means of e.s.r. techniques on model amides as well as on polyamides⁸.

In addition to model substances representing chemical reactivity of polymers there are certain physical reactions or properties which can be elucidated by means of suitable models. The electric conductivity of polyconjugated

polymers in relation to the length of polyconjugated chains was investigated recently with polyphenylenimines



It was shown that the top value of conductivity was reached just in a sequence of three phenyleneimino groups⁹. This result is in agreement with the observed independence of the conductivity of polymeric acetylenes on their molecular weight¹⁰. This indicates that in long polyconjugated chains the sections of undisturbed conductivity are rather short.

MODELS OF POLYMERIZATION MECHANISM

The principle of many macromolecular syntheses is simply the polymeric version of low-molecular synthesis, known for a long time and investigated in detail. In such cases known reactions are model reactions in the first approximation. The specific deviations produced by the increasing chain length were studied with higher-order models. We should mention at this point the classical work of Flory¹¹ and others, who have shown with models of esterification with varying chain lengths, that significant deviations are actually concerned only with the first members of these model series. By means of models the natural assumption has been verified that the asymptotic approach of reactivity to the final reactivity of a very long chain demands models with a higher number of units in the case of short monomeric model units¹², and that on the other hand in the case of polymers having longer units (Nylon-6) the reactivity of the terminal groups is well represented already by the simplest low-molecular models^{13, 14}. Confronting low-molecular model reactions with analogous polymer syntheses we are, beside these quantitative kinetic details, interested especially in the side reactions, including those of catalytic systems to which no attention was paid earlier, if they take place only in a slight fraction of a per cent. For example in anionic caprolactam polymerization the C—C condensation of amide derivatives had to be verified by means of model substances. Being negligible in current organic syntheses this side reaction had not yet been found and examined in transamidation reactions. Nevertheless, in this macromolecular version it has a very substantial significance for the degree of branching and life-time of a catalyst¹⁵.

To elucidate the mechanism of radical polymerizations model reactions were used for every partial reaction. Relatively least typical is the model technique for the chain growth reaction proper, since an enormous amount of kinetic data has been collected for reactions of a monomer with a free radical in the form of copolymerization parameters, from which known approximations may be used to derive the relations of each monomer to a full scale of various free radicals. Nonetheless low-molecular models helped to amplify this experience, e.g. by comparing the reactivity of primary normal alkyl radicals of different lengths with ethylene the variation of the kinetic reaction constants of ethylene addition have been studied to obtain a picture of the practically constant rate of growth reaction starting

from the first step already¹⁶. For anionic polymerization, simple models of living polymers have been prepared by Szwarc, by means of which it was possible to eliminate the difference between the first step, in which the catalyst interferes as a foreign type ion, and the following steps in which the growing anion practically does not change any more¹⁷. Ziegler's work was, in its time, pioneering, leading to an understanding of the polymerization mechanism of dienes by alkaline metals.

In the field of transfer reactions, polymerization of monomers dissolved in the respective model substances gave an answer to the problem of branching caused by a reaction of the polymer radical with the polymer chain^{18, 19}. Data obtained by other methods have strongly overestimated the participation of this reaction. But even the model method could lead to inaccurate results, if an imperfectly terminated model was used, containing active end groups instead of transfer-inert terminal methyl groups. For this reason complications occurred, e.g. when low polymers or telomers were used, in which the high transfer activity of the terminal group interfered^{20, 21}. The true low values of transfer by the polymer (the value of the transfer constant is of the order of 10^{-4}) explain why analytical methods leading to a direct determination of the branching locations have failed. In the special case of polyvinylchloride, which polymerizes under strongly heterogeneous conditions, no simple relation could be found between model transfer and branching²².

It was attempted to determine branching in the polymer analytically under the assumption that a tertiary chlorine atom is located at the branching site. The content of tertiary chlorine atoms, however, remained within the limits of error even when the sensitivity of the spectroscopic determination was increased by selective substitution of the tertiary chlorine atom with the strongly absorbing phenoxy group²³.

Experiments with the bimolecular reaction of model radicals prove the termination mechanism more conclusively than indirect methods based on a comparison of molecular weights. Overberger²⁴ proved this by means of models closely approximating the steric and polar properties of the polystyrene radical. The radical prepared from the respective azohydrocarbon showed that the polystyrene radical terminates exclusively by recombination.

STRUCTURAL MODELS

The structure of the homopolymers of non-symmetrical models may be discussed in succession on several levels: (i) the structure of the chains without respect to stereo-isomerism; (ii) stereochemical structure; (iii) conformation structure schematized by the staggered angles; (iv) absolute conformational structure.

Except for the highly crystalline polymers with practically pure tacticity whose structures in the crystal domains may be studied directly by x-ray analysis, the only method for the study of the steric structure of amorphous polymers is by a comparison of the polymer with suitable models, in which the structural problems over all levels mentioned are more easily determined.

The characteristic trait of this kind of research is the experience that all the steps of a more and more exact view of the structure cannot be carried out in

succession and for each step separately and with the use of a single specific method. Their discovery takes place usually in parallel and with the simultaneous or suitably alternating application of several experimental and computation methods. Even those methods which in the field of the simplest low-molecular substances are sometimes able by themselves to offer an unequivocal conclusion about the structure, e.g. n.m.r. or i.r. spectra, are unable to offer any sufficient information about polymers, unless their results are mutually confronted.

The forms of both i.r. and n.m.r. spectra are sensitive to the configurational and conformational structures of molecules. Parameters obtainable from n.m.r. spectra are the chemical shifts and spin-spin coupling constants. From the value of chemical shifts, configurational and conformational structure cannot be derived directly, but symmetry properties of the molecules can in some cases be used to decide between several structures to be considered. This is the case with the 2,4-disubstituted pentanes, the so called dimer models of stereoregular vinyl polymers. As explicitly shown in Bovey's lecture²⁵ in the preceding polymer symposium in Prague, configuration of these molecules can be determined from the equivalence or non-equivalence of methylene protons. On the other hand, vicinal coupling constants are known to be a function of the dihedral angle, and this angular dependence can be utilized for conformational structure determinations. Also the applications of these techniques to conformational structure determinations in vinyl polymers and their models have been extensively summarized in last year's lectures of Shimanouchi²⁶ and Bovey²⁵.

A specific feature of n.m.r. spectra of compounds existing in the form of several rotational isomers in mobile equilibrium is the fact that both the chemical shifts, and the coupling constant are a weighted average of the values corresponding to the individual conformers. Without additional information, the structure and population of conformers can therefore be determined from n.m.r. spectra only in cases where the number of conformers considered does not exceed two. Already the simplest model of a stereoregular vinyl polymer, the 2,4-disubstituted pentane, has 6 energetically different conformers in each configuration. For this reason, additional information on conformer population must be sought on the basis of other methods.

Besides theoretical energy calculations, infrared spectra represent the most important source of information on this point. Contrary to n.m.r. spectra, the infrared spectrum is composed of superimposed spectra of all conformers present; however, generally valid rules connecting conformational structure and the form of infrared spectra do not exist. A determination of conformational structure from the frequencies and intensities of infrared bands requires therefore a very thorough analysis of the character of all the bands concerned, and such an analysis has to be performed individually for each type of polymer. PVC is an example of a polymer the infrared spectra of which have been analyzed in this manner to a considerable detail.

Although the structure of PVC model compounds has been solved in papers which have been presented at the Prague symposium or earlier²⁶⁻³⁵, I should like to review the principles on which this analysis was based, as

this is a typical example of how a judicious combination of infrared and n.m.r. methods can contribute to the solution of a complex structural problem.

Conformational studies of PVC model compounds were based on the finding that C—Cl stretching vibrations are a function of the spacial arrangement of the conformer³⁶, and frequency ranges of CCl stretching vibrations of various structural types have been determined in a great number of simple compounds³⁷. These established frequency ranges have been applied by Shimanouchi³⁷ to the analysis of the vibrational spectra of DL-2,4-dichloropentane as a model of syndiotactic diads in PVC, and of *meso*-2,4-dichloropentane as a model of isotactic diads in PVC. Spectra of the isotactic model were found to exhibit only bands corresponding to the TG conformation (which is a part of a three-fold helical form); spectra of the syndiotactic form contained only bands corresponding to the straight chain zig-zag TT conformation. This result was surprising because the existence of the folded GG form could not be excluded on steric grounds.

A more recent analysis of n.m.r. spectra²⁸ of the same models confirmed the presence of the TG⁺, G-T helical forms in the isotactic isomer; in addition to the information already known from infrared spectra, it revealed the existence of a mobile equilibrium between the right- and left-handed helical forms. In the DL-isomer, analysis of n.m.r. spectra seemed to contradict results obtained from infrared; values of vicinal coupling constants and their temperature dependence indicated the presence of both the TT and GG forms. An explanation of the absence of the CCl-stretching band of the GG form in the infrared spectrum had therefore to be sought. Results obtained on stereoisomers of 2,4,6-trichloroheptane³⁴, the trimer model of PVC, together with some theoretical considerations^{38, 39} seem to indicate that in the case of two or more interacting chlorine atoms separated by one methylene group the frequency ranges established in monochloro derivatives need no longer be valid. Combining in an analogous manner the information on i.r. and n.m.r. data, the conformational structure of all the three stereoisomers of 2,4,6-trichloroheptane was established^{33, 34}.

PVC is also an example of a polymer where the relation between model compound and polymer structure could be demonstrated. Assuming in the polymer the existence of only those conformation forms found in the model compounds an infrared method of tacticity determination in amorphous samples of PVC was worked out, based only on the intensity of the isotactic CCl-stretching band^{40, 41}. The tacticity value obtained by this method is in good agreement with the value found independently by Bovey⁴², using an n.m.r. method with α -deuterated PVC.

Using this tacticity value, together with band shapes derived from model compound spectra, a theoretical spectrum of the CCl-stretching region of amorphous PVC can be constructed⁴⁰. Excellent agreement with the shape of the experimental spectrum indicates that the assumption of comparable conformational structure of models and polymer was sound. By measuring specifically deuterated samples of PVC, Yoshino⁴³ has shown the methylene proton band of PVC to be sensitive to tetrad configuration. The chemical shifts of methylene protons in various types of tetrads are in good agreement with the trends observed in n.m.r. spectra of dimer and trimer models.

It follows of course from Yoshino's finding that the stereoisomers of the tetramer are the smallest units modelling rigorously the n.m.r. spectra of PVC.

From this short review it is evident that a combined infrared and n.m.r. study of model compounds can yield important information on the structure of polymers. Of other vinyl polymers, model compounds have recently been studied in poly(vinyl alcohol)⁴⁴⁻⁴⁷, poly(vinyl acetate)^{48, 28, 45}, poly(methyl acrylate)⁴⁹⁻⁵², polystyrene^{51, 53-55} and polyacrylonitrile^{29, 56, 57}, based mainly on n.m.r. Due to the lack of parallel detailed infrared studies, some simplifying assumptions on conformer populations had to be made. In all these cases it will be necessary to supplement the n.m.r. data with detailed analysis of i.r. spectra of both models and polymers. Such an analysis could, in the future, probably be performed in the case of polystyrene and poly(acrylonitrile) in which conformation sensitive bands are known to exist.

Of all the above mentioned procedures, conformational structure may be determined with an accuracy which is limited by the simplifying assumption of the existence of pure staggered conformational forms.

Studies of this type are expected to be further refined by investigations of deviations from this schematic assumption. Deviations from exact staggered angles can be expected *a priori*, and have in some cases been proved experimentally⁵⁸, e.g. by diffraction studies. Their order of magnitude is in line with some of the inconsistencies observed in the analysis of n.m.r. spectra⁵⁹. Deviations from staggered bond angles will evidently prove important in correlations of polymer properties with calculated conformational structures⁶⁰; such correlations are the main aim of conformational studies, and one of the highest aims of polymer science in general.

References

- 1 J. Štamberg and I. Petrariu. *Coll. Czech. Chem. Commun.* **32**, 798 (1967).
- 2 G. Smets. *Pure Appl. Chem.* **12**, 211 (1966).
- 3 K. Shibatani, K. Fujii, J. Ukida, and M. Matsumoto. Paper presented at the International Symposium on Macromol. Chem. (IUPAC), Tokyo-Kyoto, 1966.
- 4 J. Štamberg and S. Ševčík. *Coll. Czech. Chem. Commun.* **31**, 1009 (1966).
- 5 J. Meyer. *Z. Physik Chem. (Leipzig)* **67**, 257 (1909).
- 6 M. Asahina and M. Onozuka. *J. Polymer Sci.* **A2**, 3505, 3515 (1964).
- 7 W. H. Sharkey and W. E. Mochel. *J. Am. Chem. Soc.* **81**, 3000 (1959).
- 8 K. Ulbert. *Coll. Czech. Chem. Commun.* **30**, 3285 (1965).
- 9 J. Honzl, K. Ulbert, V. Hádek, and M. Tlustáková. *Chem. Commun.* 440 (1965).
- 10 B. E. Davydov, private communication.
- 11 P. J. Flory. *J. Am. Chem. Soc.* **61**, 3334 (1939).
- 12 W. Kuhn. *Ber. dtsh. chem. Ges.* **65**, 1179 (1932).
- 13 D. Heikens. *J. Polymer Sci.* **22**, 65 (1965); **35**, 277 (1959).
- 14 K. G. Wyness. *Makromol. Chem.* **38**, 189 (1960).
- 15 J. Sebenda. *Coll. Czech. Chem. Commun.* **31**, 1501 (1966).
- 16 M. Szwarc and J. H. Binks. *Theoretical Organic Chemistry*, Kékulé Meeting, London, 1958, Butterworths, London, 1959.
- 17 M. Szwarc. *Makromol. Chem.* **35**, 141 (1960).
- 18 D. Lím and O. Wichterle. *J. Polymer Sci.* **29**, 579 (1958).
- 19 E. Votavová and D. Lím. *Coll. Czech. Chem. Commun.*, in press.
- 20 G. V. Schulz, G. Henrici, and S. Olivé. *J. Polymer Sci.* **17**, 45 (1955).
- 21 G. Henrici-Olivé, S. Olivé, and G. V. Schulz. *Makromol. Chem.* **23**, 207 (1957).
- 22 M. Kolínský, M. Ryska, M. Bohdanecký, P. Kratochvíl, K. Šolc, and D. Lím. *J. Polymer Sci., C* **16**, 485 (1967).

MODEL SUBSTANCES AS TOOLS IN POLYMER SCIENCE

- 23 A. Caraculacu, O. Wichterle, and B. Schneider. *J. Polymer Sci.* **16**, 495 (1967).
 24 C. G. Overberger and A. B. Finestone. *J. Am. Chem. Soc.* **78**, 1638 (1956).
 25 F. A. Bovey. *Pure Appl. Chem.* **12**, 525 (1966).
 26 T. Shimanouchi. *Pure Appl. Chem.* **12**, 287 (1966).
 27 T. Shimanouchi and M. Tasumi. *Spectrochim. Acta* **17**, 755 (1961).
 28 D. Doskočilová and B. Schneider. *Coll. Czech. Chem. Commun.* **29**, 2290 (1964).
 29 P. E. McMahon and W. C. Tincher. *J. Mol. Spec.* **15**, 180 (1965).
 30 T. Shimanouchi, M. Tasumi, and Y. Abe. *Makromol. Chem.* **86**, 43 (1965).
 31 S. Satoh. *J. Polymer Sci.* **A2**, 5221 (1964).
 32 D. Lím, M. Kolínský, J. Štokr, and J. Petránek. *J. Polymer Sci.* **B4**, 577 (1966).
 33 T. Shimanouchi, M. Tasumi, and Y. Abe. *Makromol. Chem.* **86**, 43 (1965).
 34 D. Doskočilová, J. Štokr, B. Schneider, H. Pivdová, M. Kolínský, J. Petránek, and D. Lím. *J. Polymer Sci. C*, **16**, 215 (1967).
 35 H. Pivcová and B. Schneider. *Coll. Czech. Chem. Commun.* **31**, 3154 (1966).
 36 J. K. Brown and N. Sheppard. *Trans. Faraday Soc.* **50**, 1164 (1954); **48**, 128 (1952); **50**, 535 (1954).
 37 J. J. Shipman, V. L. Folt, and S. Krimm. *Spectrochim. Acta* **18**, 1603 (1962).
 38 N. B. Colthup. *Spectrochim. Acta* **20**, 1843 (1964).
 39 S. Enomoto, C. G. Opaskar, and S. Krimm. *J. Polymer Sci.* **16** (4), 2263 (1967).
 40 B. Schneider, J. Štokr, D. Doskočilová, M. Kolínský, S. Sýkora, and D. Lím. Paper presented at the International Symposium on Macromol. Chem. (IUPAC), Prague, 1965.
 41 J. Štokr, B. Schneider, M. Kolínský, M. Ryska, and D. Lím. *J. Polymer Sci.* **A5**, 2013 (1967).
 42 F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, in the press.
 43 T. Yoshino and J. Komiyama. *J. Polymer Sci.* **B3**, 311 (1965).
 44 D. Lím, E. Votavová, J. Štokr, and J. Petránek. *J. Polymer Sci.* **B4**, 581 (1966).
 45 D. Doskočilová, J. Štokr, E. Votavová, B. Schneider, and D. Lím. *J. Polymer Sci. C4*, **16**, 2225 (1967).
 46 Y. Fujiwara, S. Fujiwara, and K. Fujii. *J. Polymer Sci.* **A1**, 257 (1966).
 47 S. Fujiwara, Y. Fujiwara, K. Fujii, and T. Fukuroi. *J. Mol. Spec.*, in the press.
 48 J. Štokr, B. Schneider, and J. Vodňanský. *J. Polymer Sci.* **B2**, 783 (1964).
 49 D. Lím, B. Obereigner, and D. Doskočilová. *J. Polymer Sci.* **B3**, 893 (1965).
 50 K. Matsuzaki, T. Uryu, A. Ishida, and M. Takeuchi. *J. Polymer Sci. C4*, **16**, 2099 (1967).
 51 D. Doskočilová and B. Schneider. *J. Polymer Sci.* **B3**, 213 (1965).
 52 D. Doskočilová, S. Sýkora, H. Pivcová, B. Obereigner, and D. Lím. Paper presented at the International Symposium on Macromol. Chem. (IUPAC), Tokyo-Kyoto, 1966.
 53 F. A. Bovey, F. P. Hood, E. Pier, and H. E. Weaver. *J. Am. Chem. Soc.* **87**, 2060 (1965).
 54 F. A. Bovey, F. P. Hood, E. W. Anderson, and L. C. Snyder. *J. Chem. Phys.* **42**, 3900 (1965).
 55 D. Lím, M. Kolínský, J. Petránek, D. Doskočilová, and B. Schneider. *J. Polymer Sci. B*, in the press.
 56 K. Matsuzaki, T. Uryu, M. Ohada, K. Ishigura, T. Ohhi, and M. Takeuchi. *J. Polymer Sci.* **B4**, 487 (1966).
 57 R. Yamadera and M. Murano. Paper presented at the International Symposium on Macromol. Chem. (IUPAC), Tokyo, 1966.
 58 R. A. Bonham, L. S. Bartell, and D. A. Kohl. *J. Am. Chem. Soc.* **81**, 4765 (1959).
 59 T. Yoshino, Y. Kihuchi, and J. Komiyama. *J. Phys. Chem.* **70**, 1059 (1966).
 60 P. H. Flory, J. E. Mark, and A. Abe. *J. Polymer Sci.* **B3**, 973 (1965).