The R_f values found for sample OMB-2 with the mixture (MeCN + MeOH) and (*i*-PrOAc + EtOAc) were 0.41 and 0.25, respectively. By making use of these values, eq 1 and 2 were solved simultaneously to estimate T_s and M_w for OMB-2. The calculation yielded 0.76 and 59×10^4 for T_s and M_w, respectively, which were in fairly good agreement with those determined by nmr and viscometry, *i.e.*, $T_s = 0.71$ and $M_w = 63.3 \times 10^4$.

Chromatograohic Behavior of Sample 74MB20. With the knowledge of tlc results described above, we have investigated the chromatographic behavior of sample 74MB20. The development was first made with a mixture (*i*-PrOAc + EtOAc), whose composition was 8:25 by volume, by the usual ascending method. Reference samples 74MB and MB20 were developed simultaneously on the same chromatoplate. The chromatogram is shown in Figure 4a, from which one finds that no chromatographic distinguishment among the samples can be made. On the other hand, these samples were chromatographed with a mixture (MeCN + MeOH) by the concentration gradient technique. The development was started first with 20 ml of MeOH (initial solvent). When the solvent front reached a level at which the sample had been spotted, 20 ml of MeCN was admixed dropwise to the initial solvent at a constant rate. The chromatogram is given in Figure 4b. Appreciable separation of 74MB20 into two components takes place in contrast to Figure 4a. It is also noticed that from the chromatographic viewpoint, the component showing the higher R_f may be identified with MB20; while the other with 74MB. The identification was ensured by GPC experiments on these samples. The elution curves indicated that 74MB20 consisted roughly of two species with different molecular weights, and the peaks at the lower and higher elution volume found for 74MB20 appeared closely to those for 74MB and MB20, respectively.

In connection with this tlc result we will point out that appreciable separation accomplished for 74MB20 with the mixture (MeCN + MeOH) was certainly a piece of luck. In other words: if the sample were composed of one component having a higher M_w and T_s, and the other having a lower M_w and T_s, no separation would have occurred so far as this developer was employed (refer to Figure 3). Thus the tlc experiment made for 74MB20 should be regarded as only a special example that demonstrates a limitation upon the applicability of tlc. Hence this result will not be useful to the practical problem. Despite such recognition, we will emphasize that this tlc experiment suggests the urgent necessity of new development in separation science for polymeric substances. The reason will be clearly understood by taking a nmr spectrum for 74MB20. The spectrum presents nothing but a conclusion that the sample has a tacticity of 0.66, 0.31, and 0.03 for the fractions of syndiotactic, heterotactic, and isotactic triads, respectively.

Conclusion

The tlc experiments performed so far suggest no developer system for which the R_f value is dependent solely on T_s without interference of molecular weight. Even in the separation that must be predominated by adsorption–desorption process,[12,13] the R_f value did depend strongly on molecular weight. This means that the separation of syndiotactic and atactic PMMA is a much more hazardous task than that of syndiotactic and isotactic PMMA.[2] The reason may consist in too small differences between adsorptive forces onto adsorbent exerted by the syndiotactic and atactic macromolecules. Therefore the separation of syndiotactic and atactic PMMA may be one example which is indicative of the limitation of applicability of tlc as a separation tool for polymeric substances.

Acknowledgment. The authors thank Dr. T. Kotaka of this Institute, Dr. J. L. White, Department of Chemical and Metallurgical Engineering, the University of Tennessee, and Dr. E. P. Otocka, Bell Laboratories, for their valuable comments made during the preparation of this manuscript. F. K. thanks Dr. N. Sagane, Director of the Research Laboratory, Sekisui Chemical Industrial Co., Ltd., for kindly delegating him to this Institute. A part of this study was supported by Grant C-755 255 from the Ministry of Education for the academic year 1971.

Conformation and Flexibility Parameter of Polymeric Chains

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Received May 2, 1972

ABSTRACT: Inspection of the relationship between steric factor, σ, and the crystalline unit cell volume per main-chain bond, V_c, revealed the difference in behavior for polymers with an extended conformation of monomeric units in the crystalline state (EC polymers) and for polymers with a helical one (HC polymers), the resulting equations between respectively $V_c = 14\sigma$ and $V_c = 4.4\sigma^{3.5}$ (in Å^3). The origin of the observed difference is tentatively attributed to intrinsic differences in angles of internal rotation around single bonds.

It is well known[1,2] that the most important property of macromolecules responsible for properties of bulk polymers[3,4] is chain flexibility. The value of the so-called steric factor, σ, is often used as a quantitative measure of an equilibrium (thermodynamic) flexibility of polymeric chains. This value is defined as [5-7] $\sigma^2 = \langle r_0^2 \rangle / \langle r_f^2 \rangle$, where

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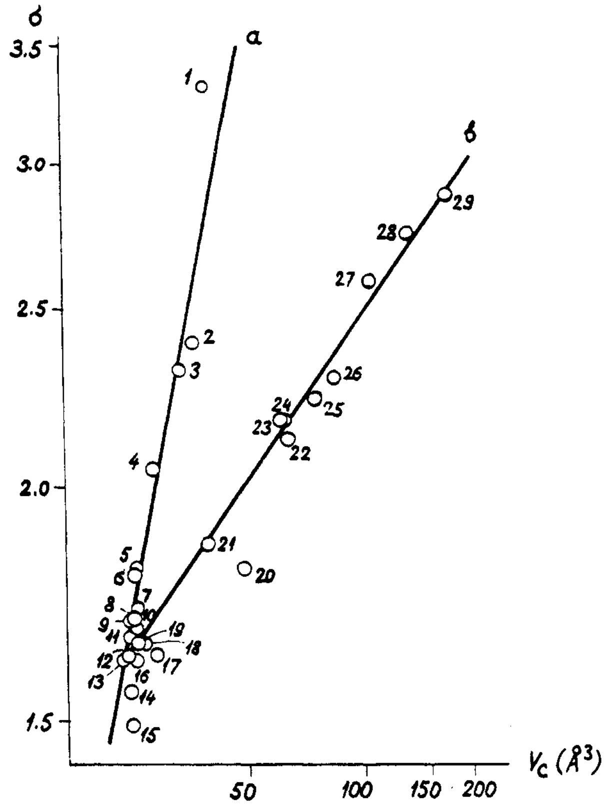

Figure 1. Double-logarithmic plot of σ *vs.* V_c for some polymers. Numbers on the points refer to the following polymers: (1) poly(tetrafluoroethylene), (2) poly(acrylonitrile), (3) poly(vinyl chloride), (4) poly(vinyl alcohol), (5) poly(hexamethylene dibutylsebactate), (6) poly(hexadecamethylene sebacate), (7) poly(hexamethylene sebacate), (8) poly(ethylene adipate), (9) poly(decamethylene oxide), (10) poly(tetramethylene oxide), (11) nylons 6 and 66, (12) poly(decamethylene sebacate), (13) poly(hexamethylene·oxide), (14) poly(hexamethylene maleate), (15) poly(hexamethylene fumarate), (16) poly(hexamethylene succinate), (17) poly(propylene oxide), (18) poly(ethylene oxide), (19) poly(epichlorohydrin), (20) poly(isobutylene), (21) poly(propylene), (22) polypentene-1, (23) polybutene-1, (24) poly(methyl methacrylate), (25) polystyrene, (26) poly(*o*-methylstyrene), (27) poly(1-vinylnaphthalene), (28) polyacrylamide, and (29) poly(*N*-vinylcarbazole).

$\langle r_0^2 \rangle$ and $\langle r_f^2 \rangle$ are, respectively, the mean-square end-to-end distances of an "unperturbed" macromolecule and of a model freely rotating chain. It has been suggested[7] that the stiffness of macromolecules, as reflected through the parameter σ, should increase with the increased size of pendant side groups. In fact, the existence of an approximate proportionality between σ and the volume of side groups, V, was experimentally confirmed[7-10] for some polymer series. However, it was noticed[7,10] that the experimental points for some polymers widely deviate from the general behavior. For example, very large deviations of experimental values of σ for poly(vinyl alcohol) and poly(acrylonitrile) from the correlation line $\sigma = f(V)$ for many vinyl polymers was interpreted as a result of a specific interaction between these polar polymers and solvents.[10] It is the purpose of the present note to demonstrate that this is not the only explanation of the observed effect.

According to modern concepts,[5-7] the magnitude of σ is determined mainly by short-range intramolecular interactions involving about 2 to 4 main-chain bonds. On this basis, one may suggest that the stiffness of a macromolecule as a whole may be empirically approximated as a sum of "stiffness increments" per main-chain bond in the repeating unit.[11] It can be deduced from the results in[7-10] that the magnitude of such a "stiffness increment" should vary proportionally to the volume of the side groups, V. Following this line of thought and recalling that the stablest conformations of monomeric units in the chain in solution are identical with those in a crystalline state,[5] it is reasonable to expect the existence of a correlation between σ and the value of the volume of a crystalline unit cell per main-chain bond of polymer, V_c.

In Figure 1 we show a double-logarithmic plot of σ *vs.* V_c for a number of polymers. Values of V_c were calculated using the unit cell parameters tabulated in ref 12 and 13. For the majority of polymers the values of σ were taken from ref 7, 13, and 14. For polybutene-1 we used the value $\sigma = 2.2$ calculated from the data[15a] of viscosity measurements. (To assure the internal consistency of the correlation, we used the values of σ calculated according to Kurata-Stockmayer[7] or Stockmayer-Fixman[15b] methods using the data of intrinsic viscosity measurements and the value[7] of the Flory constant, $\Phi = 2.87 \times 10^{21}$ dl/g.) Values of σ for poly(epichlorohydrin), poly(hexamethylene oxide), and poly(decamethylene oxide) were taken from the ref 16–18. Unit cell parameters for these polymers are given in ref 19 and 20. Values of σ and V_c for poly(*N*-vinylcarbazole) are given in ref 21 to 23.

Inspection of the data presented in Figure 1 clearly shows that the behavior of the plot $\sigma = f(V_c)$ is different for polymers with extended (planar) conformation of a monomeric unit (these will be referred to below as EC polymers) and for polymers with helical conformation in the crystalline state (HC polymers). It is convenient to express the dependence of σ on V_c for EC and HC polymers in the form of the empirical eq 1a and 1b, respectively.

$$V_c = 14\sigma \text{ (Å}^3\text{)} \tag{1a}$$

$$V_c = 4.4\sigma^{3.5} \tag{1b}$$

Straight lines (a) and (b) in Figure 1 (log scale) were drawn according to eq 1. The results obtained clearly

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show that for EC polymers the increase of the chain stiffness with the increase of the bulkiness of side groups is much more pronounced than for HC polymers. In light of this finding the apparently "anomalous" behavior of poly(vinyl alcohol) and poly(acyrylonitrile) becomes quite normal. In fact, the experimental values of σ for these polymers which enter the group of EC polymers, were compared by Dondos and Benoit[10] with those for HC polymers, and on this basis were judged as anomalously high. However, evidence presented above suggests that in spite of an unquestionable influence of a solvent polarity on unperturbed dimensions of many polar polymers,[7,10,24] in the case considered here the influence of a crystalline conformation of a monomeric unit seems much more significant. It is worth noting that the points A, a, and b in Figure 1 of ref 10 corresponding to the EC polymers, poly(ethylene), poly(vinyl alcohol), and poly(acrylonitrile), perfectly fall on the straight line as they should. Moreover, the point of intersection of the straight lines (a) and (b) in Figure 1 has the coordinates V_c = 22.4 Å^3 and σ = 1.6 which nearly coincide with the experimental figures,[7,12] V_c = 22.9 Å^3 and σ = 1.63, for a linear polyethylene. This phenomenon, also found in the analysis of dependence of some other properties of bulk linear polymers on the chain flexibility,[4] suggests that linear poly(ethylene) can be thought of as an "initial" member of "homologous" series of EC and HC polymers.

The relationships found in this work might be of value in qualitative discussion of some experimental results. For example, the point 1 for poly(tetrafluoroethylene) in Figure 1, which has the coordinates, V_c = 39.5 Å^3 and[25] σ = 3.3, lies close to the line (a) for EC polymers, although the crystalline conformation of this polymer is not perfectly planar but rather is slightly helical.[5,12,13] Evidently, this is a reflection of a slight opening of backbone valence angles due to the repulsions between neighboring fluorine atoms. This leads to the increase in identity period per bond which approaches the value characteristic of EC polymers. Moreover, one might expect that the values of σ for a great number of polyethers, polyesters, and polyamides should be in the vicinity of the value, σ = 1.63, for poly(ethylene), because all these polymers have approximately the same V_c values. Therefore, the scatter of experimental values of σ for these polymers seen in Figure 1 should be attributed to specific solvent effects.

Inspection of the Figure 1 reveals, further, that eq 1b rather adequately accounts for the observed dependence of σ on V_c for HC polymers with different types of helices, for example, 3/1 helix (isotactic polypropylene, polystyrene, etc.) as well as 4/1 helix (poly(1-vinylnaphthalene)). In our opinion, this means that the most stable conformations of monomeric units in isolated chains are identical with the most stable crystalline conformations for these polymers.[5] This conclusion makes one to believe that the wide deviation of σ value for poly(isobutylene) (point 20 in Figure 1) from the line (b) for HC polymers might be caused by differences in chain conformations of this polymer in the crystalline state and in solution. This hypothesis seems to be qualitatively confirmed by the fact that for poly(isobutylene) there exist at least six almost equienergetic conformations of a monomeric unit which correspond to a minimum of intramolecular interaction energy.[5] Thus, in this case the choice of the preferred type of conformation for a crystalline state will be controlled by requirements of an optimum intermolecular packing.[26] The values of σ, calculated with the aid of parameters of some possible crystalline forms, of poly(isobutylene),[5] are in the range from 1.4–2.5, whereas according to our scheme (Figure 1) the existence in an unperturbed state of poly(isobutylene) molecules of a 8/5 helix[12] with V_c = 48.5 Å^3 should give σ about 2.0. This figure is well within the predicted range.[5] Identical calculation carried out for poly(4-methylpentene-1) ($V_c \doteq$ 84.5 Å^3) and for poly(vinylcyclohexane) (V_c = 93.5 Å^3), according to the eq 1b, gives σ = 2.3 and 2.4 for these polymers, respectively. Earlier[14] we have estimated the value of σ for poly(4-methylpentene-1) to be about 2.1.

In summary, the results described in this paper illustrate the very definite correlation between the crystalline conformation of chain repeating unit and the flexibility parameter of isolated polymeric molecules. It is reasonable to suggest that a theoretical justification can be attached to this phenomenon, especially taking into consideration the fact that conformational properties of macromolecules both in an isolated state as well as in crystal are mainly governed by the values of angles of internal rotation.[5]

Acknowledgment. The author expresses his appreciation to Professor Yu. S. Lipatov for helpful interest in the work.

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