In the observed nmr doublet, at least in poly(benzyl glutamate),[20] the random-coil peak does not shift significantly as one goes through the helix-random-coil transition, but merely changes intensity. If the doublet is not a result of molecular weight heterogenity, then the unshifting random-coil peak must mean that at least in short chains the partially helical and completely helical molecules contribute separately to the nmr spectrum. This is the best experimental evidence to date which indicates helix and random-coil nucleation is indeed slow.

It is of interest to note that nmr spectra of polypeptides in aqueous solution generally do not show the double peak in the helix-coil transition region. According to our model the double peak is likely to occur only when a significant amount of all random-coil molecules exist. For a given s value, the fraction of all random-coil molecules is a strong function N and σ, as shown in Figure 10. These values are roughly independent of whether a single-helix or multiple-helix partition function is used. It is obvious from Figure 10 that one would not expect to see the double maximum if the chain length is too large, or the cooperativity too small. Thus poly(glutamic acid), characterized[36] by a σ value of the order of 10^{-3}, should have a less pronounced double maximum at any chain length than poly(benzyl glutamate) in mixed organic solvents. In fact one way to decide if the model and assumptions presented here give a good description of the experimental systems would be to correlate the appearance of the double maximum with the cooperativity parameter in a series of polymers and solvents.

Isotopic Exchange. The isotopic exchange of the amide proton in the polypeptide backbone with solvent has been investigated, with particular interest in the effect of conformation on the exchange rate.[37-39] Previously we have shown by utilizing Ising model statistics and assuming that the rate-limiting step was not the conformational lifetimes, experimental and calculated exchange rates were in reasonable agreement for both homopolymers and copolymers. Inasmuch as the lifetime for isotopic exchange in small model compounds is of the order of seconds, the assumption of conformational lifetimes short in comparison to exchange now seems fully justified.

Recently, however, a much more detailed study of isotopic exchange in poly(glutamic acid) has appeared[40] which yielded information on the exchange rate as a function of chain position and chain length. Even though the largest chain length studied was less than 100 units their interpretation of the exchange data yielded a "fluctuation frequency" of helical structure varying by 10^{13} sec^{-1}. Considering the Ising model parameters for this system there is no way in which the usual Ising model statistics could give rise to this large variation in helical lifetimes.

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Separation of Atactic and Syndiotactic Methyl Methacrylate Polymers by Thin-Layer Chromatography

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ABSTRACT: Separation of atactic and syndiotactic methyl methacrylate polymers (PMMA) has been investigated with the thin-layer chromatographic technique (tlc). Mixtures of ethyl acetate (ETOAc) and isopropyl acetate (*i*-PrOAc) and of acetonitrile (MeCN) and methanol (MeOH) were found to be effective as developer. Values of R_f (normalized rate of flow of the polymeric species) obtained with the mixture (ETOAc + *i*-PrOAc) increased with decrease in both syndiotactic content (T_s) and molecular weight (M), whereas those with the mixture (MeCN + MeOH) increased with increase in T_s but with decrease in M. No solvent pair which allows the separation solely by the difference in T_s has been found. These development characteristics were discussed on the basis of separation mechanisms proposed previously. The R_f values determined with each mixture were expressed as a function of T_s and M. With the aid of the functions thus established, a procedure to estimate T_s of a given sample from values of R_f obtained by the use of both mixtures was described, and proved to be applicable. A PMMA sample, which has been artificially prepared so that it had appreciable heterogeneity in T_s as well as M, was chromatographed with the mixture (MeCN + MeOH), and into two components. Despite such success in the separation it is pointed out that the experimental procedure was too complicated to be applied generally to practical problems, this being indicative of the limitation of applicability of tlc to polymer fractionation.

When the chemical constitution of a substance is to be determined, one should first investigate whether or not it is of a single component. In the field of polymer chemistry, such investigations often encounter various difficulties for lack of knowledge of an adequate separation technique. This situation appears to be quite in strange contrast to the advanced developments being currently accomplished in instrumentation for the determination of chemical structure. At present only gel permeation chromatography (GPC) finds practical, heavy use for the purpose of separating polymeric substances and this is by molecular size.[1]

Recently we have demonstrated that thin-layer chromatography (tlc) allows mixtures of isotactic and syndiotac-

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Table I
Polymerization and Characterization of Sample PMMA

Sample Code	Initiator	Polymerization Condn	$M_w \times 10^{-3}$	Tacticity T_i	Tacticity T_h	Tacticity T_s
sA-2[a]	Uv–benzoin	Bulk at −50°	246	0.04	0.16	0.80
sA-3[a]			186			
MB20		Bulk at −20°	279	0	0.26	0.74
OMB-2[a]		Bulk at 0°	633	0	0.29	0.71
OMB-3[a]			285			
30MT-2[a]		Toluene at 30°	279	0.05	0.29	0.66
74MB		Bulk at 74°	795	0.06	0.33	0.61
42M	$(C_6H_5)_2Na$	H_4furan at −78°	1240[b]	0.07	0.40	0.53
41M			514[b]			
31M			200[b]			
74MB20[c]	Uv–benzoin	Bulk at 74°, −20°	500	0.03	0.31	0.65

[a] Fractionated sample. [b] Determined by light scattering. [c] For the detail, see text.

tic poly(methyl methacrylate) (PMMA) to be separated into components.[2] This result has been further utilized to explore the stereocomplex formation in tactic PMMA and the structure of the stereoblock PMMA.[2,3] In these studies, tlc proved to be an indispensable separation technique, which accomplishes things high-resolution nmr cannot. However these successful applications of tlc have been still restricted to separation of stereoregular polymers by difference in their steric isomerism.

In the present work an attempt is made to extend the applicability of tlc to separation of atactic and syndiotactic PMMA. For the purpose of the study, MMA monomer was photopolymerized under various conditions. It is shown that separation according to the content of syndiotactic triads was effected. However the separation procedure applied was somewhat complicated because values of R_f (normalized rate of flow of the polymeric species) were dependent not only on the syndiotactic content but also on the molecular weight. In view of this result the limitation of applicability of tlc to polymer chemistry is pointed out.

Experimental Section

Sample Polymers. Two PMMA polymers, coded sA series, which have been used for our previous work,[2] were adopted for the study. The polymerization and characterization have been described elsewhere.[2] The other sample polymers with moderate-to-high syndiotactic contents were prepared in bulk and in toluene at different temperatures (−50°, 74°) using ultraviolet light in the presence of benzoin as photosensitizer.[4] Some of the samples thus obtained were fractionated at 40° with acetone and methanol as solvent and precipitant, respectively. Fractions having suitable molecular weights were subjected to tlc experiments as reference samples. A sample coded 74MB20 was prepared artificially on purpose that it has a large heterogeneity in syndiotactic content. The polymerization was carried out first at 74° for 30 min, followed by a further run at −20° for 180 min. The conversion of monomer to polymer was 5.9 wt %. Sample polymers coded M series were prepared in H_4furan at −78° with sodium biphenyl–H_4furan solution as initiator.[5] The samples were characterized by viscometry and high-resolution nmr spectroscopy. Intrinsic viscosity, $[\eta]$, was determined in chloroform at 25° and converted to weight-average molecular weight (M_w) by using the relation, $[\eta] = 4.8 \times 10^{-5} M_w^{0.8}$, established for conventional PMMA.[6] The nmr spectra were taken with a JNM-C-6OHL spectrometer (Japan Electron Optics Lab., Co., Tokyo) from 5 to 10% solutions in deuteriochloroform at 70°. The tacticity was assessed by applying the method proposed by Bovey and Tiers,[7] designating T_s, T_h, and T_i for the content of syndiotactic, heterotactic, and isotactic triads, respectively. The results of characterization are summarized in Table I.

Experimental Procedures. The general procedure of tlc experiment has been reported in our previous papers.[2,3,8-10] Thin layers with a thickness of 0.25 mm were prepared with Kieselgel G (E. Merck AG., Darmstadt, Germany). Immediately before use, the gel layer was activated by heating at 110° for 1 hr. In order to obtain good reproducibility of the experiment all the development runs were made in a S chamber thermostatted at 22°. This precaution was found especially important for the present experiments. Chromatograms were stained with a 1% methanol solution of iodine. More detailed descriptions of the procedure in each case will be given below.

The molecular weight distribution of some samples was determined with a Shimadzu gel permeation chromatograph Model 1-A (Shimadzu Seisakushyo Co., Ltd., Kyoto). H_4furan was used as eluent and the flow rate was adjusted to 1 ml/min.

Results and Discussion

Choice of Solvents as Developer. Preliminary tlc experiments were made to search for single solvents which allow migration of the PMMA samples. The results are summarized in Table II, in which the solvents used are arranged in the order of increasing eluting strength in the sense of "eluotropic series."[11] For later discussion the solvents used are classified into four groups according to their eluting strength and dissolving power toward the sample polymer, as noted in the table. It is found that sample migration occurs only with solvents belonging to group (3), namely, ethyl acetate and acetonitrile, which have fairly high eluting strengths as well as good dissolving powers toward PMMA. However, any single solvent could neither develop the syndiotactic and atactic sample at different migration rates nor give intermediate R_f values. Further tlc experiments were, therefore, attempted with binary mixtures of solvents, which belong respectively to different groups. Mixtures of the types [(1) + (3)], [(2) + (4)], [(2) + (3)], and [(3) + (4)] proved to give intermediate R_f values, where [(i) + (j)] indicates a mix-

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Table II
Choice of Solvents as Developer for Atactic and Syndiotactic PMMA

Solvent	Dielec Const	Dissolving Power	R_f sA-3	R_f 31M	Classification
n-Hexane	1.89	N[a]	0	0	Group (1)
Cyclohexane	2.02	N	0	0	
Benzene	2.27	S[b]	0	0	Group (2)
Chloroform	4.81	S	0	0	
Isopropyl acetate		S	0	0	
Ethyl acetate	6.02	S	1	1	Group (3)
Methyl ethyl ketone	18.51	S	1	1	
Acetonitrile	37.5	S	1	1	
Isopropyl alcohol	18.3	N	0	0	Group (4)
Methyl alcohol	32.6	N	0	0	

[a] Nonsolvent for PMMA. [b] Solvent for PMMA.

ture composed of solvents belonging respectively to group (i) and (j). The development characteristics observed with each mixture were different from one another, depending on its physicochemical action upon the sample polymer.

The development characteristics exhibited by solvent pairs [(1) + (3)] and [(2) + (4)] were quite different from those by other solvent pairs, indicating that different separation mechanisms were operative at different solvent compositions. A typical example has already been reported, which was found with mixtures of chloroform and methanol,[12] *i.e.*, of the type [(2) + (4)]. Although each of these solvents is nondeveloper for PMMA, the mixture could afford different R_f values at different volume fraction of methanol v_2. The R_f value, which was zero at $v_2 = 0$, went up steeply to unity when v_2 was increased to 0.15 and this value was kept constant until v_2 approached 0.6, whereas in the range of $0.6 < v_2 < 0.8$, a steep decrease of R_f from unity to zero was observed.

The drastic change of R_f with v_2 has been interpreted in terms of two different mechanisms:[13] one of which involves an adsorption–desorption process and the other a phase-separation process. The interpretation has been supported experimentally by Otocka *et al.*[14] The chromatographic behavior of PMMA in the range of $0 < v_2 < 0.15$ is dominated by the former process; while that in the range of $0.6 < v_2 < 0.8$ by the latter process. In addition it should be mentioned that any molecular weight dependence of R_f did not appear in the former range of v_2 whereas it appeared distinctly in the latter range.

On the other hand, with mixtures of the type [(2) + (3)], the value of R_f became higher with increasing content of (3), *i.e.*, the more polar component. With mixtures of the type [(3) + (4)], which have the highest eluting strength among those tested, the polymer ceased to migrate when the content of (4), *i.e.*, nonsolvent for PMMA, was increased to a certain extent. Along the line of the argument mentioned above one may conclude that adsorption–desorption and phase-separation processes are predominantly operating in the developments with the solvent pair [(2) + (3)] and [(3) + (4)], respectively.

The experiments made so far proved that neither the type [(1) + (3)] nor [(2) + (4)] was suitable for the purpose, since the developments with these mixtures were insensitive to changes in the syndiotactic content. Finally combinations of isopropyl acetate and ethyl acetate (*i*-PrOAc + EtOAc), and of acetonitrile and methanol (MeCN + MeOH), which belong to the type [(2) + (3)] and [(3) + (4)], respectively, were found to be most effective in the resolving power with respects to the syndiotactic content and other chromatographic characteristics required as developer.

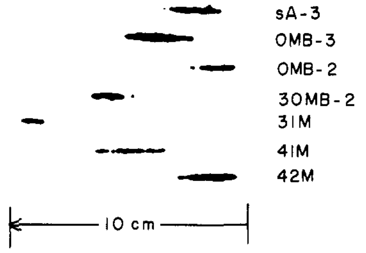

Figure 1. Chromatogram obtained for syndiotactic and atactic PMMA with mixture of ethyl acetate and isopropyl acetate (mixing ratio 25:8 by volume).

Development by Adsorption Mechanism. The chromatographic behavior of PMMA with different content of syndiotactic triads (T_s) and molecular weight has been investigated first with the mixture (*i*-PrOAc + EtOAc), which will develop the polymers according to adsorption mechanism. The samples employed were atactic samples coded 42M, 41M, and 31M, which have different molecular weight but the same value of T_s, and also syndiotactic samples coded 30MT-2, OMB-3, and sA-2, which have different values of T_s but similar molecular weights. In addition, another syndiotactic sample OMB-2, which has nearly the same value of T_s as OMB-3 but a higher molecular weight, was tested being assumed to be "unknown" sample. These seven samples were subjected to tlc experiment by the use of mixture (*i*-PrOAc + EtOAc) having a composition of 8:25 by volume. In regards to the composition of developer it should be mentioned that when the composition was shifted very slightly so as to increase the content of EtOAc, *e.g.*, by 1%, all the samples migrated up to the proximity of solvent front, and *vice versa*. The development run was completed within 30 min.

The chromatogram is shown in Figure 1, from which one sees that the R_f values decrease with increase in T_s but, at the same time, decrease with increase in molecular weight. The lower R_f value found for OMB-2 may be attributed to its high molecular weight. Thus it was confirmed that the mixture (*i*-PrOAc + EtOAc) exerts strong influences upon R_f not only with respect to T_s but also to molecular weight. The change in R_f with molecular weight is irreconcilable with our theory that no distinct molecular weight dependence of R_f appears so far as the developer is composed of good solvents toward sample polymer so that only adsorption–desorption process is operative.[12,13] However, the other solvent pairs of type [(2) + (3)], such as chloroform + ethyl acetate, chloroform + 2-butanone, and benzene + acetonitrile, exhibited little changes in R_f with molecular weight (and also with T_s), and this result does support the above-mentioned theory. In regards to these observations it is noticed that the molecular weight dependence of R_f was found only with the pair whose component solvents have the smallest difference in their dielectric constants among the pairs tested. On this basis one may indicate a hypothesis that the R_f value becomes dependent on molecular weight, as the difference in dielectric constants of component sol-

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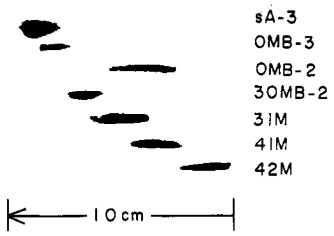

Figure 2. Chromatogram obtained for the same samples as in Figure 1 by concentration gradient development using acetonitrile and methanol. For the detail, see text.

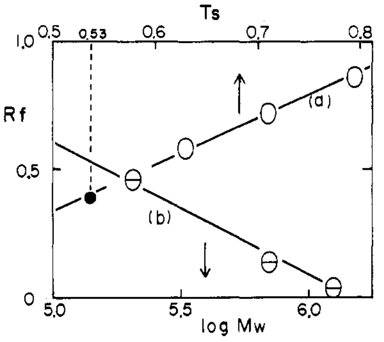

Figure 3. Syndiotactic content (T_s) and molecular weight (M_w) dependence of R_f values evaluated from the chromatogram given in Figure 2: line (a) indicates T_s dependence observed at the same molecular weight level (M_w 27 × 10^4); while line (b) M_w dependence at the same level of T_s (0.53). For the explanation of filled circle, see text.

vents tends to be small. A more quantitative discussion on this problem will be given elsewhere.

A brief discussion on syndiotacticity effects upon R_f explored by the mixture (*i*-PrOAc + EtOAc) is made below. First one should recall a tlc result on PMMA obtained with EtOAc:[2] R_f(iso) ≈ 0, R_f(syn) ≈ 1, and R_f(ata) ≈ 1, where R_f(x)'s denote those for isotactic, syndiotactic, and atactic PMMA, respectively. Referring to this result, we admixed *i*-PrOAc having a little lower eluting strength than EtOAc to EtOAc in order to suppress the migration of syndiotactic and atactic PMMA so that intermediate R_f values are obtained, and established that $0 \approx R_f(\mathrm{iso}) < R_f(\mathrm{syn}) < R_f(\mathrm{ata}) < 1$. At present we have no pertinent elucidation for the separation mechanism that resulted in $R_f(\mathrm{syn}) < R_f(\mathrm{ata})$. It is only pointed out that the result appears to be analogous to our previous observation for equimolar styrene-methyl methacrylate copolymers with different chain architecture:[9,10] $0 = R_f(\mathrm{block}) < R_f(\mathrm{alternating}) < R_f(\mathrm{statistical}) < 1$.

Development by Phase-Separation Mechanism. Another chromatogram for the same polymer samples was obtained with the mixture (MeCN + MeOH) by adopting concentration gradient development. Before the experiment a mixture of MeCN (20 ml) and MeOH (40 ml) was placed in a thermostatted S chamber. To this initial solvent a constant volume (1.1 ml) of MeCN was added dropwise under stirring while the solvent front ascended by a constant height (0.5 cm), so that the speed of addition was synchronized with that of the ascending solvent front. The total volume of MeCN added was 22 ml, and the final composition (MeCN-MeOH) was 46:54 by volume.

The chromatogram is shown in Figure 2, which indicates that the R_f value is again dependent not only on T_s but also on molecular weight. It should be pointed out that the T_s dependence of R_f observed with this solvent pair is just opposite to that with the pair (EtOAc + *i*-PrOAc). In relation to this finding, phase-equilibrium experiments were carried out for a 0.5% solution of syndiotactic sample sA-3 and an atactic sample 31M in an MeCN-MeOH mixture with the same composition as that attained at the final stage of the development. These samples have similar molecular weights (see Table I). Precipitation occurred for 31M below 29°, while no precipitation was observed for sA-3 even at 0°. This result allows us to interpret the increase of R_f with T_s, according to the theory that a phase-separation process is predominantly operating during the development with this solvent pair.[12,13] It is further mentioned that this T_s dependence was observed commonly for the other solvent pairs of the type [(3) + (4)].

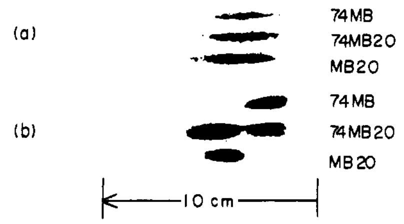

Figure 4. Chromatographic behavior of sample 74MB20, and reference samples, 74MB and MB20: (a) and (b) show chromatograms obtained with mixture of ethyl acetate and isopropyl acetate, and with mixture of acetonitrile and methanol, respectively.

Procedure for Determination of Syndiotactic Content. The subject of determination of the T_s of sample OMB-2, which we have postulated to be unknown, is discussed below. The possibility of the determination depends solely on whether or not the effect of T_s upon R_f can be distinguished from that of molecular weight. Thus the first step is to establish the T_s dependence of R_f at the same molecular weight level. This was done with R_f values for the syndiotactic samples having similar molecular weights ($M_w \approx 27 \times 10^4$), which were obtained by analyzing the chromatogram shown in Figure 2. Line (a) drawn in Figure 3 indicates the T_s dependence. Our next concern was to investigate influences of molecular weight, which will be imposed upon the T_s dependence of R_f. For this purpose we have first established the molecular weight dependence of R_f at the same level of T_s by making use of data obtained for the atactic samples. This is shown by line (b) in Figure 3. Then a R_f value, which should be expected for an atactic sample having a M_w of 27 × 10^4, was estimated by interpolating line (b). This was found to be 0.41, which will, in turn, be identified with that to be expected for PMMA of T_s = 0.53, because the atactic samples tested have this common T_s value. When this data point is plotted on the $R_f - T_s$ scale, one finds that this point falls just on line (a), as a filled circle in Figure 3 shows.

The above finding may permit us to presuppose that the slope of T_s dependence of R_f is little affected by molecular weight difference at least within a molecular weight range from 1 × 10^5 to 7 × 10^5 (see Table I). Under such an assumption, curve fitting was made for lines (a) and (b), and the R_f value was expressed by

$$R_f = 1.73T_s - 0.51 \log M_w + 2.2 \qquad (1)$$

for the data points obtained with the mixture (MeCN + MeOH). The same procedure was applied to the result obtained with the mixture (*i*-PrOAc + EtOAc). This led us to

$$R_f = -1.74T_s - 0.08 \log M_w + 6.0 \qquad (2)$$

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.

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Conformation and Flexibility Parameter of Polymeric Chains

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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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