Segment size in synthetic polymers by the spin-probe method

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Following the approach of Kusumoto an equation is derived which relates the correlation time for the tumbling of a nitroxide spin probe in a polymer matrix with the parameter f, the ratio of the volumes of the probe and the polymer segment undergoing motion at $T > T_g$. For poly(vinyl acetate) probed with a series of nitroxides the correlation between f and the molecular volumes of the probes is poor, possibly because of wide variations in probe flexibility and polarity. An approximate version of the equation also permits evaluation of f from the parameter T_{50G}. Values of f calculated in this manner for the probe 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl-benzoate in nine different polymers suggest that polymers with high glass transition temperatures have relatively bulky segments.

Keywords Spin probe; electron spin resonance; free volume; glass transition; poly(vinyl acetate); segment size

INTRODUCTION

The electron spin resonance (e.s.r.) spectrum of a paramagnetic molecule, such as a nitroxide radical, can be analysed to yield information on its motion[1-3]. When dispersed in a polymer matrix the motions of such radicals are sensitive to the motions of the surrounding polymer molecules, and their e.s.r. spectra can therefore yield information on the dynamics of the macromolecules in the matrix. This is the basis of the now familiar spin-probe experiment[4,5].

The rotational diffusion of a nitroxide probe is characterized by a correlation time τ and to date most spin-probe studies have been concerned with correlation times in the range 10^{-7} to 10^{-11} s. At low temperatures when $10^{-9}\ \mathrm{s} < \tau < 10^{-7}$ s the probe is said to be in the slow motion regime and shows a strongly assymmetric spectrum which closely resembles the powder average. It has high- and low-field extrema which have a field separation of 60–65G, the separation varying gradually and monotonically with the rotational correlation time provided that this lies within the above range. As the temperature is raised the mobility of the probe increases and eventually the e.s.r. spectrum acquires the motionally narrowed form consisting of three equally spaced (to first order) lines of equal intensities but unequal widths, the outer lines being separated by 30–40G ($2a^N$). This dramatic change in the spectrum occurs as the correlation time τ decreases through the value *ca.* 3×10^{-9} s into the fast regime where $\tau < 10^{-9}$ s. With spin-probed polymers this transition from the slow to the fast regime generally occurs over a narrow temperature range and it has become accepted practice to characterize the transition region by the empirical parameter T_{50G}[4,5]. This is the temperature at which the extrema separation is 50 gauss.

A correlation has been established between T_g and T_{50G}[6], and indeed it has been argued that T_{50G} is no more than a high frequency glass transition temperature[6,7]. The effective rotational frequency at T_{50G} is about 5×10^7 Hz which explains why T_{50G} is generally greater than T_g (classically measured at *ca.* 1 Hz). Kusumoto has suggested that at temperatures $> T_{50G}$ the probe responds to the free volume in a manner similar to that of a polymer segment at or above T_g. From this assumption he extended Bueche's theory[9] for polymer segmental motion to spin-probe motion and hence derived the relationship:

$$T_{50G} - T_g = 52[2.9f(\ln 1/f + 1) - 1] \qquad (1)$$

where f is the ratio of the molecular volumes of the probe to the polymer segment undergoing local motion at T_g. Kusumoto has employed equation (1) to estimate the effective volume of segments of various polymers and we have done likewise in a previous study of spin-probed poly(vinyl acetate)[10].

Equation (1), however, suffers from the limitation that it is restricted to systems for which $f < 1$ because it goes through a maximum at $f = 1$, where $(T_{50G} - T_g)$ has the value 98.8°C. In fact, there are cases on record[11] in which $(T_{50G} - T_g)$ substantially exceeds 98.8°C. This discrepancy between theory and experiment together with the improbable prediction from equation (1) that beyond a certain critical size T_{50G} should decrease with increasing probe size, led us to re-examine the derivation of equation (1). In this paper we derive an alternative to equation (1) which is based on fewer assumptions and in which there is no enforced upper limit to f.

THEORETICAL

By applying Bueche's theory to the motion of a spin-probe in a polymer matrix Kusumoto[8] showed that the rotational jumping frequency φ of the probe is given by

$$\varphi = \varphi_0 \exp\left[-\left(\beta_p^* + \ln\frac{v_m}{v_p}\right)\frac{v_p^*}{v_f} - \frac{v_p}{v_m}\right] \qquad (2)$$

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where v_p and v_m denote molar volumes of the probe and of the polymer segment respectively, v_p^* is the minimum free volume required by the probe to rotate, v_f is the average free volume per segment, and $\beta_p^* = \ln(v_p^*/v_f) - 1$. Above T_g the free volume v_f changes with temperature according to[9]

$$v_f = v_{fg} + v_{mg}\Delta\alpha(T - T_g) \tag{3}$$

where v_{fg} and v_{mg} are the average free volume and the occupied volume of a segment at T_g respectively. $\Delta\alpha$ is the difference between the thermal volume expansion coefficients above and below T_g.

Substituting equation (3) into equation (2) and rearranging yields the equation

$$T - T_g = \left[\frac{\left[\beta_p^* + \ln\frac{v_m}{v_p}\right] v_p^* v_{fg} v_m^*}{\ln(\varphi_0/\varphi) v_{fg} v_m^* - v_p v_m^* v_{fg}/v_m} - v_{fg}\right] \Bigg/ v_{mg}\Delta\alpha \tag{4}$$

where v_m^* is the minimum free volume required by a segment to jump. Equation (1) is derived from equation (4) by:

(i) assuming that $\beta_p^* \simeq 1$ according to Bueche's treatment for pure polymer,

(ii) substitution of the Doolittle relations, $v_{fg}/v_{mg}\,\Delta\alpha = 52$ and $v_m^*/v_{fg} = 40$, which incorporate average values of the WLF parameters C_{2g} and C_{1g} respectively,[12]

(iii) assuming that $\ln \phi_0/\phi \gg f$,

(iv) assuming that $v_p^*/v_m^* = v_p/v_m = f$, and

(v) assuming that $\varphi_0 = 10^{14}$ according to Bueche, and by setting $T = T_{50G}$ where it is assumed that $\phi \simeq 10^8$.

The above assumptions and the use of the Doolittle relations to achieve generality are not unreasonable but it is possible to simplify equation (4) using fewer approximations as follows.

First, there is no need to equate β_p^* to unity. According to Bueche[9], it is β_m^*, which refers to motion of a polymer segment, that is close to unity. However, $\beta_m^* = \ln(v_m^*/v_f) - 1$ and hence

$$\beta_p^* = \beta_m^* + \ln(v_p^*/v_m^*) \tag{5}$$

Now[9]

$$\beta_m^* = 2.303\, C_{1g} v_{fg}/v_m^* \tag{6}$$

and hence

$$\beta_p^* = 2.303\, C_{1g} v_{fg}/v_m^* + \ln(v_p^*/v_m^*) \tag{7}$$

At $T \to \infty$, $v_f \to \infty$ and from equation (2) the upper limit for the frequency of probe motion ϕ_∞ is given by

$$\phi_\infty = \phi_0 \exp[-v_p/v_m] \tag{8}$$

Also[9]

$$v_{fg}/(v_{mg}\Delta\alpha) = C_{2g} \tag{9}$$

and

$$\tau/\tau_\infty = \phi_\infty/\phi \tag{10}$$

where τ is the correlation time for probe tumbling at temperature T and τ_∞ is the correlation time at the limit of $T \to \infty$.

Substituting equations (7), (8), (9) and (10) in equation (4) gives

$$T - T_g = C_{2g}\left[\frac{2.303\, C_{1g} f}{\ln(\tau/\tau_\infty)} - 1\right] \tag{11}$$

in which $f = v_p/v_m = v_p^*/v_m^*$ as in Kusumoto's treatment.

To obtain f from equation (10) at $T = T_{50G}$ it is necessary to estimate a value of $\ln(\tau_{50G}/\tau_\infty)$. Following Kusumoto[8] and setting $\ln(\tau_{50G}/\tau_\infty)$ to 13.8 gives

$$T_{50G} - T_g = C_{2g}\left[\frac{2.303\, C_{1g} f}{13.8} - 1\right] \tag{12}$$

or $f = (T_{50G} - T_g + C_{2g})13.8/2.303\, C_{1g} C_{2g}$.

Equation (12) is our alternative to equation (1). If particular values of the parameters C_{1g} and C_{2g} are not available average values may be substituted in equation (12) as in equation (1).

DISCUSSION

Unlike equation (1), equation (12) does not predict an upper limit to $(T_{50G} - T_g)$. It can therefore be applied to those cases where $(T_{50G} - T_g) > 98.8°C$ or where $f > 1$. Both equations predict a lower limit to the value of $(T_{50G} - T_g)$. When f is zero, equation (1) gives $(T_{50G} - T_g) = -52°C$, which is simply minus the average value for polymers of the parameter C_{2g}. Equation (12) also yields $-C_{2g}$ as the lower limit of $(T_{50G} - T_g)$. It follows that the lower limit of T_{50G} is $(T_g - C_{2g})$. This value is physically reasonable because, according to equations (3) and (9), $(T_g - C_{2g})$ is the temperature at which the free volume in the system is zero. Equation (12) thus encompasses the rarely observed situation where $T_{50} - T_g < 0$. The contrasting relationships between $(T_{50G} - T_g)$ and f from equations (1) and (12) are depicted graphically in *Figure 1*. Both curves were computed using average values 17.4 and 51.6 of the parameters C_{1g} and C_{2g} respectively.

By measuring T_{50G} for the same spin probe in a series of polymers it should be possible to compare the relative volumes of the relaxing segments within the series because $1/f$ is (volume of the polymer segment) ÷ (volume of the

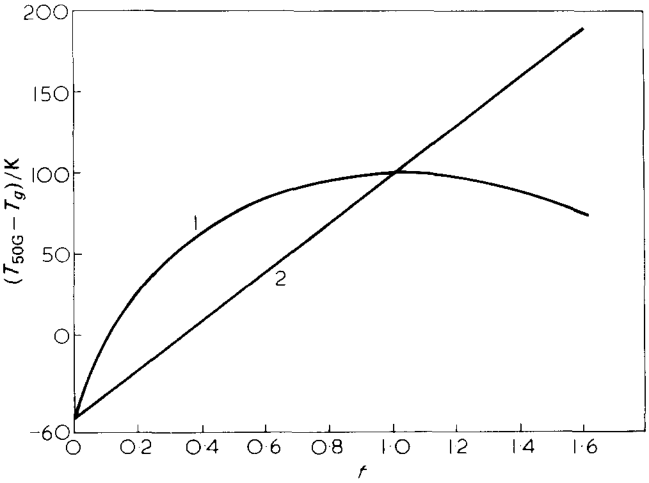


Figure 1 Relationship between $(T_{50G} - T_g)$ and the parameter f: 1, according to equation (1); 2, according to equation (12)

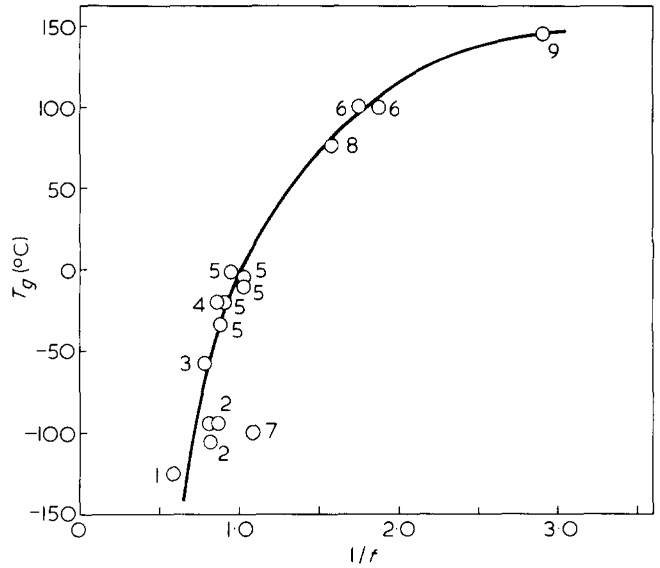


Figure 2 Relationship between T_g and $1/f$. The parameter f for the probe 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl-benzoate calculated from equation (12) using T_{50G} and T_g data from ref. 6. Values of C_{1g} and C_{2g} from ref. 13 except for points 7, 8 and 9 where the average values 17.4 and 51.6 were used. 1, Polydimethylsiloxane; 2, polybutadienes; 3, 50/50 ethylene/propylene copolymer; 4, polypropylene; 5, styrene/butadiene copolymers; 6, polystyrenes; 7, polypentenamer; 8, poly(vinyl chloride); 9, polycarbonate

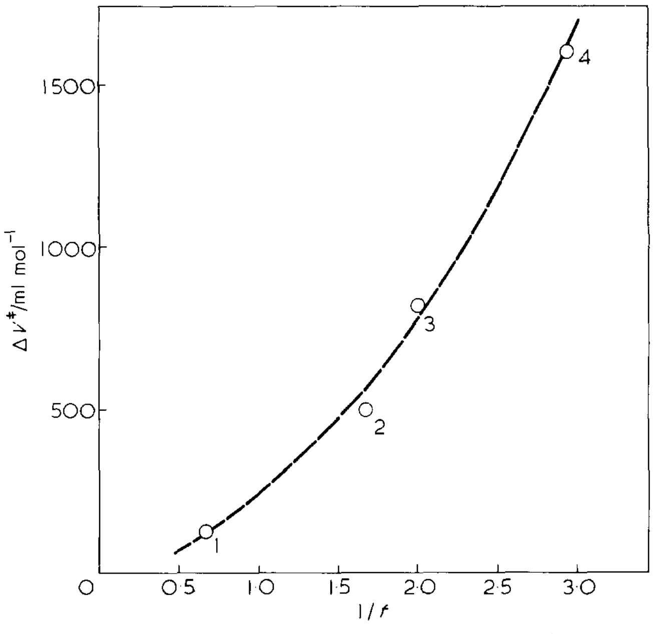


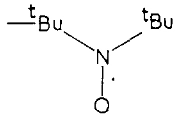
Figure 3 Relationship between volume of activation $\Delta V^{\ddagger}$ at the glass transition and $1/f$. Values of $\Delta V^{\ddagger}$ from ref. 14. 1, Polydimethylsiloxane; 2, poly(vinyl chloride); 3, polystyrene; 4, polycarbonate

probe) and the probe volume is constant. Boyer and Kumler[6] have measured T_{50G} for a range of polymers with the probe 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl benzoate. These data, together with literature values of C_{1g} and C_{2g}[13], were taken to calculate values of f from equation (12) with $\ln(\tau_{50G}/\tau_{\infty}) = 13.8$. Where no estimates of the parameters C_{1g} and C_{2g} were available the average values 17.4 and 51.6 respectively were used. The results of these calculations are plotted in *Figure 2* which indicates that a high glass transition temperature is associated with a bulky segment. It should be noted that the trend in *Figure 2* is *not* an artefact that arises because C_{1g} and C_{2g} in equation (12) tend to increase and decrease respectively, as T_g increases. If all values of f for the polymers in *Figure 2* are computed with average values of C_{1g} and C_{2g} the same trend is produced, though the scatter of points is greater. The relationship between the size of the relaxing segment and T_g value suggested by *Figure 2* is physically quite reasonable and accords with the established relationship[14] between T_g and the activation volume at T_g, $\Delta V\ddagger$. Indeed, in *Figure 3* are plotted activation volumes at T_g *versus* $1/f$ for four of the polymers in *Figure 2*. The relative segment sizes as measured by the spin-probe method lie in the same order as the activation volumes $\Delta V\ddagger$. These observations give at least semi-quantitative support to the assumptions involved in the derivation of equations (11) and (12).

Evaluation of the parameter f using equation (12) suffers from the disadvantage that estimated values of τ_{50G} and τ_{∞} have to be employed. It is further assumed that these estimated values are applicable to all probes in all polymers. This rather drastic approximation can be avoided by determining values of τ for probe tumbling in the polymer at a number of temperatures at which the probe responds to the polymer segmental motion and using the linearised form of equation (11)

$$\ln \tau = \ln \tau_{\infty} + f\left[\frac{2.303\, C_{1g} C_{2g}}{T - T_g + C_{2g}}\right] \tag{13}$$

Provided f does not vary significantly with temperature a plot of $\ln \tau$ *versus* $2.303\, C_{1g}\, C_{2g}/(T - T_g + C_{2g})$ should be a straight line with slope f. Methods for calculating τ from a linewidth analysis of the e.s.r. spectrum of a nitroxide probe or label are well documented[2]. This procedure should yield a more reliable value of f since it is no longer necessary to estimate τ_{∞}. Unfortunately, there are few reports on spin-probe studies which include correlation time measurements. A recent article by Kusumoto is an exception and by way of illustration we have taken his correlation times[15] for the following probes in poly(vinyl acetate)



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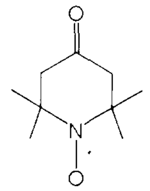

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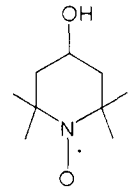

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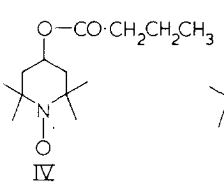

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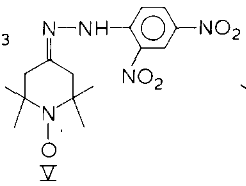

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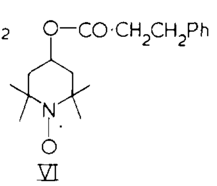

VI

and have plotted them in *Figure 4* according to equation (13). For this purpose the values of C_{1g}, C_{2g} and T_g were 15.6, 46.8 and 305K respectively[13].

The points in *Figure 4* can be fitted well to smooth curves which approximate to straight lines. A deviation from linearity would arise if f varied with temperature, which is quite possible, or if there were inaccuracies in the

Table 1 Values of the parameter f for probes I to VI from the lines in *Figure 4*

Probe	I	II	III	IV	V	VI
Molecular volumes of probes ($Å^3$)	165	169	177	239	305	310
f (from equation (13))	0.77	0.86	0.71	0.85	0.71	0.82
f (from equation (14))	0.40	0.52	0.34	0.51	0.34	0.46

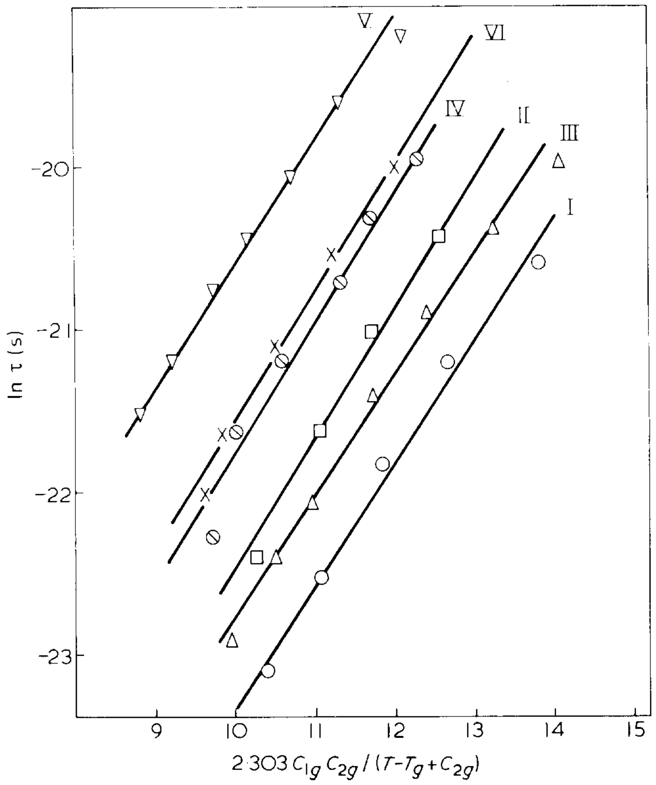

Figure 4 Plots of ln τ *versus* $2.303\ C_{1g}C_{2g}/(T - T_g + C_{2g})$ for spin probes I to VI in poly(vinyl acetate). Values of ln τ taken from *Figure 9(b)* of ref. 15

values of T_g or C_{2g} in equation (13). Another more likely cause of deviation from linearity is an enthalpic interaction between the probe and the polymer. This point is discussed in more detail later.

From the slopes of the best straight lines through the points in *Figure 4* (by the method of least squares) values of f were calculated. These are shown in *Table 1* alongside molecular volumes[16] of the probes I to VI. The slopes of these lines are all closely similar and there is no clear correlation between probe size and f. Using his less refined treatment Kusumoto succeeded in fitting T_{50G} data for these six probes to a common curve of T_{50G} *versus* f and presented this apparent correlation between probe volume and f as experimental verification of his theory[15]. We believe that the evidence in *Table 1* proves that no such relationship exists for these six probes, certainly not in poly(vinyl acetate). This conclusions is not occasioned by some error in equation (13) which does not exist in Kusumoto's derivation. His counterpart to equation (13) is

$$\ln \tau = \ln \tau_0 + \frac{2.303\ C_{1g}\ C_{2g} f(\ln 1/f + 1)}{T - T_g + C_{2g}} \qquad (14)$$

Equation (14) retains all the approximations involved in deriving equation (1) except that average values of C_{1g} and C_{2g} have not been used and no particular value of τ_0 has been assumed. If equation (14) is valid then the slopes of the curves in *Figure 4* are equal to $f(\ln 1/f + 1)$. Values of f computed from equation (14) (*Table 1*) are also unrelated to probe molecular volumes. Thus, when applied without assuming a universal value of τ_0, Kusumoto's treatment leads to the same conclusion as ours. The apparent correlation between probe volumes and f adduced earlier must now be regarded as fortuitous.

The derivation of equation (14) takes no account of polymer-probe interactions which must certainly occur and which will depend on the chemical structure of both probe and polymer. Among the six probes used in this study there is a considerable variation in structure, flexibility and polarity, and it is quite conceivable that these factors over-ride the effects of probe volume in this case. If the theory is to be adequately tested with probes of varying molecular volume it is important that other variations in probe character are minimised as far as possible. It is also preferable that the probes cover a wider range of sizes than probes I to VI above. Differences in polymer-probe interactions may also account for some of the scatter points in *Figure 2*.

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Before this manuscript was submitted it was sent to Dr. N. Kusumoto for comment. We then learned with deep regret of his untimely death in 1981. We wish the paper to represent our tribute to him.

REFERENCES

1 Kivelson, D. *J. Chem. Phys.* 1960, **33**, 1094
2 Goldman, S. A., Bruno, G. V., Polnazek, C. F. and Freed, J. H. *J. Chem. Phys.* 1971, **56**, 716
3 Freed, J. H. in 'Spin Labelling', (Ed. L. J. Berliner), Academic Press, New York, 1976, p. 53
4 Rabold, G. P. *J. Polym. Sci. A-1* 1969, **7**, 1203
5 Boyer, R. F. *Macromolecules* 1973, **6**, 288
6 Kumler, P. L. and Boyer, R. F. *Macromolecules* 1976, **9**, 903
7 Boyer, R. F. *Polymer* 1976, **17**, 996
8 Kusumoto, N., Sano, S., Zaitsu, N. and Motozato, Y. *Polymer* 1976, **17**, 448
9 Bueche, F. 'Physical Properties of Polymers', Wiley, New York, 1962
10 Bullock, A. T., Cameron, G. G., Howard, C. B. and Reddy, N. K. *Polymer* 1978, **19**, 352
11 Törmälä, P. J. *Macromol. Sci.-Rev. Macromol. Chem.* 1979, **C17**, 297
12 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
13 Ferry, J. D. 'Viscoelastic Properties of Polymers', Wiley, New York, 1970
14 Boyer, R. F. and Kumler, P. L. *Macromolecules* 1977, **10**, 461
15 Kusumoto, N. in 'Molecular Motion in Polymers by ESR', MMI Press Symposium Series Vol. 1 (Eds. R. F. Boyer and S. E. Keinath), Horwood Academic Publishers, New York, 1980, p. 223
16 Molecular volumes were calculated by Kusumoto according to the method in A. I. Kitaigorodskii 'Organicheskaya Kristallokhimiay', Izd. Acad. Nauk., U.S.S.R., 1955