Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 641–650

STRUCTURAL RELAXATION OF THE CONSTRAINED AMORPHOUS PHASE IN THE GLASS TRANSITION ZONE

A. Danch[*] *and W. Osoba*

Instytut Fizyki, Uniwersytet Śląski, Uniwersytecka 4, 40 007 Catowice, Poland

Abstract

The idea of two amorphous fractions in polymer is discussed. In order to clarify the influence of specific arrangement of chains on a glass transition, semi-crystalline polymer with various supermolecular structures was studied. It was possible to find two glass transitions well separated. The orientation of the amorphous regions induced by semi-crystallinity results in the appearing of the constrained and unconstrained amorphous structures. Both types of amorphous fractions are distinguished in this paper that give better descriptions of α-relaxations. In a serious of experimental studies of chains mobility and free volume, our attention has been given to elucidation of the correlation between the glass transition, the α-relaxation and the free volume of polymeric system. Non-Arrhenius and Arrhenius types of temperature dependence of the relaxation times were found for the 'real' and the 'semi-ordered' amorphous fraction, respectively. Differential scanning calorimetry, dynamic mechanical thermal analysis and positron annihilation lifetime spectroscopy were applied.

Keywords: glass transition, α-relaxation, supermolecular structure

Introduction

Poly(4-methyl-1-pentene) (PMP) is a semi-crystalline polyolefine, which thermomechanical and morphological characteristics were widely discussed [1–5]. Its five crystal modifications (designed I, II, III, IV, V) of the isotactic chain were reported [4, 5]. The I modification is usually obtained when a PMP sample is prepared by a melt process. The other four modifications (II–V) are prepared from diluted solutions. The samples morphology can be described as consisting of lamellar crystals and amorphous material. However, a crystal-amorphous interphase is well known to exist for this type of semi-crystalline polymer including semi-flexible chains [6, 7]. The main consequence of interphase existence is that the polymeric material exhibits extended glass transition, very often, with two well separated T_g values [8]. Moreover, two α-relaxations consisted with two adequate T_g values proved additionally that the amorphous phase might be a two-component system [9–11]. The first relaxation, α_g, (lower T_g) concerns the undisturbed amorphous regions, which properties

---

[*] Author for correspondence: E-mail: danch@us.edu.pl

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

and thermodynamic parameters were identically to those of the bulky amorphous polymer. The second one, α_c, concerns the regions disturbed by the presence of a crystal phase and was related to the higher T_g value. The idea of the extended glass transition applied to the PMP material obtained as membranes well explained various behaviour of those membranes in a diffusion process [12]. The membranes were cast from cyclohexane and carbon tetrachloride solutions. It was found that other polymeric systems, which included liquid-crystalline domains as a one of the components, showed similar thermodynamic behaviour, too [11].

Dynamic mechanical (DMTA) and dielectric thermal analysis (DETA) exhibit a small number of broad loss peaks in the glass transition zone, which presumable arises from different modes of molecular motion. One of them might reveal micro-Brownian motions of the chains (relaxation). The shape of viscoelastic or dielectric dispersion is expected to reflect in some manner supermolecular structures of polymers. Therefore, it seems to be acceptable that we should distinguish both types of the amorphous fractions of the supermolecular structure to give a better description of the process. It is very difficult to recognise and to identify relaxations which arise from similar mechanisms in different polymers. However, some experimental data, reviewed and collected [13–17], show a common feature: the temperature dependence of the relaxation time (τ) can be described by either the Arrhenius relation or the Vogel–Fulcher (in general non-Arrhenius) relation. Moreover, the position and the shape of the loss peak of the α-relaxation strictly depend on conditions of the sample preparation. Altering thermal history of a sample changes physical properties of polymer [17]. It is known that thermal treatment might drastically influence the supermolecular structure, and hence, the loss peaks measured using dielectric or mechanical spectroscopy should be sensitive to a free volume of the polymer. The free volume (V_f) is defined as a space which is not occupied by the macromolecules and its value is equal a difference between the specific and the occupied volumes of the polymeric system. The linear type functions are suggested for all of the volumes dependencies [16–17]. The specific volume is measured in dilatometric experiments whereas the free volume is estimated from the positron lifetime data.

In this paper, the effect of the free volume on the segmental relaxation behaviour is determined for the PMP samples. In serious of experimental studies of chains mobility and free volume, the correlation between the glass transition, the free volume and the α-relaxation of different polymeric systems was investigated. It must be emphasised that the PMP sample of one type, which was studied using different experimental techniques, had been cut down from one sheet in order to obtain the sample of the same supermolecular structure. It will be shown that one must be careful when the parameters pointed out by different authors are compared (applied) because there is no one universal set of these parameters for the polymer if the thermal histories of the polymeric materials are different. It means that despites of the same measurement conditions the various experimental values can be obtained when different supermolecular structures were created during the sample preparation process. Particularly problematic is the fact that different techniques give information about different physical properties of the sample, so that the basic question of the glass transition temperature (glass transition in general) has not been properly addressed in spite of the long interest. The glass transition temperature was defined from specific volume (dilatometry), heat capacity (DTA, DSC), dielectric permeability (DETA) or Young's modulus (DMTA) measurements [13–17]. The problem is that relatively few experimental studies have been devoted to determine the time dependence of physical properties in the glass transition range.

Experimental

Sample preparation

Two different regimes were applied for the samples preparation: cast from melt or solution. The samples used in positron annihilation lifetime spectroscopy (PALS) were cast from melt as a sheet of 0.5 mm thickness and no further thermal treatment was applied before the measurements. The following polymers were studied: poly(ethylene) of low density (PE LD); poly(propylene) (PP); poly(4-methyl-1-pentene) (PMP); poly(vinyl chloride) (PVC); poly(styrene) (PS).

In the case of mechanical investigations the transparent films were prepared from carbon tetrachloride solutions. The PMP concentration in solution was 2 mass% (PMP_2), 3 mass% (PMP_3) and 5 mass% (PMP_5). Dissolution was only achieved at room temperature. One sample prepared from melt (PMP_m) was studied, too.

The samples were cut down from the films or the sheets mentioned above. The sample shape was adequate for the measurement technique used.

Methods

Dynamic mechanical thermal analysis was carried out in tensile mode with a PL MTA Mk III system. E'' and E' curves were recorded within a frequency range of 0.01–240 Hz and within a temperature range from 283 to 483 K. The same heating rate of 0.5 K min^{-1} was applied for all samples. The samples were cut down as bars nearly the same size.

Calorimetric measurements were performed using a Perkin Elmer DSC7 type and the first heating run (5, 10 and 20 K min^{-1}) was recorded. The glass transition temperature (T_g) was defined from the midpoint of the change in a heat flow *vs*. temperature curve. Also, the first derivative of the DSC trace was analysed when the glass transition was very broad in a temperature scale (PMP_m). The melting temperature (T_m) was defined as the maximum of the melting endotherm. A small piece of the 5 mg sample was used. The calibration procedure and measurements conditions were as before [9, 10, 18].

A conventional slow-fast coincidence spectrometer with plastic scintillators (two cylindrical Pilot U scintillators, their dimensions are: ϕ=1.5" and h=1.0") were used [19, 20]. The time resolution of the spectrometer was determined by analysing the positron lifetimes in Kapton foils. Positron lifetime spectra were accumulated to approximately $(0.5)\cdot 10^6$ counts. A positron source (^{22}Na, about 0.2 MBq) was sealed between two Kapton foils. The source correction was taken into account during numerical evaluations. All of the measurements were performed in vacuum (10^{-8}–10^{-9} mbar, at low temperatures, and 10^{-4}–10^{-5} mbar, at room temperature). Dimensions of the cold head and its high vacuum jacket allowed to install two scintillation detectors at the distance of about 25 mm. It reduced drastically the count rate. One spectrum, so as to reach the proper statistics, was acquired about 24 h. The temperature range of the measurements was from 8.3 to 299 K (±0.03 K). The measurements were started at 299 K and the sample was cooled down to 8.3 K and then it was heated up to 280 K. The measurements were carried out at 40 K spaced intervals for cooling and heating cycles. That resulted, eventually, in the measurements done in 20 K steps intervals in the whole range of the temperature. The sample had been kept 40 to 50 min before we started the lifetime measurement in the newly chosen temperature.

The X-ray scattering diffraction pattern was recorded using a Philips diffractometer with a diffracted-beam graphite monochromator and copper radiation ($CuK_{\alpha}\cong 0.154$ nm).

Results and discussion

Despite differences in chemical composition, polymers share the common feature that the heat capacity (C_p) of polymer increases suddenly in a very small temperature interval as temperature arise. Usually, T_g is defined at the inflection point in the C_p *vs.* temperature curve. The change in the second order thermodynamic properties at the glass transition is associated with the structural changes. This contribution is termed configurational [21, 22]. Below the glass transition, variations of C_p are only associated with vibrational degrees of freedom because in the glassy state the micro-Brownian motions are frozen. It results from the fact that fluidity diminishes when temperature decreases. It seems to be very important whether or not the frozen structure of the glassy polymer includes free spaces which seem to be necessary for the activation of long-range molecular mobility. The free spaces can be determined from the positron lifetimes measurements. It is assumed that the free volume value (V_f) estimates the average size of the cavities distributed in the amorphous regions of the investigated polymer [16, 17, 23–26]. In order to find some correlation between chemical constitution of macromolecules and the V_f values the investigations of the chosen polymers were performed and the results are collected in Table 1. When the data had been ordered according to the monomer size, none correlation was found. Therefore, it was concluded that other parameter must be important, too. It must be emphasised that V_f was estimated from PALS performed at one temperature (298 K) on all polymers. This temperature is higher or lower than T_g of the investigated polymers. Now, the data in the table are divided into two groups. One group includes the polymers for which the measurements were performed below their T_g values (PS, PVC). The second one includes the polymers with lower T_g than the measurement temperature (PMP, PP, PE LD).

Table 1 Glass transition temperatures and free volumes (*) of the chosen polymeric systems: PS-poly(styrene); PVC-poly(vinyl chloride); PMP-poly(4-methyl-1-pentene); PP-poly(propylene); PE LD- poly(ethylene) of low density

System	T_g/K	V_f/Å^3
PS	375	99
PVC	370	82
PMP	308 (383)	134
PP	263	151
PE LD	183 (377)	155

(*) the radius of the free volume was pointed out with accuracy about 0.02 Å

Although, the T_g value found for the PMP sample is higher than the measurement temperature, PMP was numbered among the second subgroup. The reason of such treatment will be discussed in the second part of this section. It is worth noticing that in the case of PMP and PE LD two glass transitions were pointed out. In a recent study [10–12, 27, 28], it was found that the polymeric semi-crystalline sample, in some cases, could create the structure included two amorphous fractions: the ‘real’ and the ‘semi-ordered’ amorphous one. The amount and the properties of those fractions strongly depended on the sample thermal history. The glass transition temperature of the ‘semi-ordered’ amorphous fraction (T_g(2)) is presented in parenthesis. It is easy to find that the measurement temperature was lower than the T_g(2) values both PMP and PE LD. However, some correlation between T_g and V_f can be observed when the first T_g(1) value is taken into account: the lower T_g the bigger V_f is. It seems to be in a good agreement with earlier theoretical prediction concerning the free volume temperature dependence of two amorphous fractions [29]. It was postulated that V_f of the ‘real’ amorphous fraction increase with temperature faster than V_f of the ‘semi-ordered’ amorphous fraction. Most likely, the free volume of the later fraction few increases with temperature even above its T_g(2). Such behaviour would be reflected in the relaxations which, in some cases, exhibit the Arrhenius or non-Arrhenius temperature dependences. This preliminary studies on the free volume of the chosen polymeric systems could not resolve the problem at all. However, low temperature measurements of PMP did not exhibit the linear temperature dependence but the exponential one and rather big V_f increase in the studied temperature range. It is unexpected that the value increase is about 80%, it means from 74 Å^3 at 8.3 K to 134 Å^3 at 298 K (Fig. 1).

The measurements at temperatures above T_g are in progress. It is tempting to believe that high temperature data will advance our knowledge about possible chain fluidity (micro-Brownian motion) that is strictly related to free spaces into the amorphous regions. Moreover, it will give answer on a question concerning the existence of two amorphous fractions in a semi-crystalline system and their different relaxation behaviours. Unfortunately, it is impossible to distinguish the both amorphous fractions in PALS now. Furthermore, the proportion between the both fractions cannot be pointed out. The disadvantages of the applied measurement techniques should be removed in further studies on the

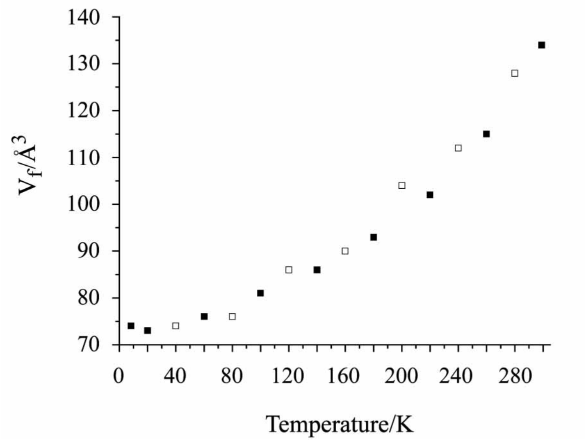

Fig. 1 The temperature dependence of free volume for the PMP sample cast from melt. The values obtained during cooling or heating are represented by solid and open symbols, respectively

supermolecular structure of polymer. This requires some improvements of the model used for the calculation of the V_f value and application of other experimental techniques.

It was shown earlier [9, 10, 27], that it had been possible to prepare the PMP samples in such a manner which created in the semi-crystalline system two amorphous fractions with various supermolecular structures. That was reflected in two relaxations with different temperature dependence observed. Those relaxations were related to the adequate glass transitions observed in DSC traces. As was shown [10], $T_g(1)$ (lower) is related to the transition occurring in the 'real ' amorphous fraction of the amorphous phase whereas $T_g(2)$ (higher) reflects the transition in the 'semi-ordered' amorphous fraction. The DSC curves of the studied PMP samples showed typical behaviour as other curves obtained during previous study [9, 10, 18]. Therefore, only the important thermodynamic parameters are presented in Table 2.

Table 2 Transition temperatures (T_g, T_m), enthalpies of melting (ΔH_m), the change of the specific heats ($\Delta C_p(T_g)$) and enthalpies of the activation of the α_c relaxation $\Delta H(\alpha_c)$. For the comparison, the data of PMP_{CH}, taken from [9] are presented, too

	$T_g(1)$/ K	$\Delta C_p(T_g(1))$/ J mol^{-1} K^{-1}	$T_g(2)$/ K	$\Delta C_p(T_g(2))$/ J mol^{-1} K^{-1}	T_m/ K	ΔH_m/ J g^{-1}	$\Delta H(\alpha_c)$/ J mol^{-1}
PMP_2	308.2	10.2	374.0	15.1	498.2	31.8	53±1
PMP_3	310.3	7.2	380.5	6.1	500.1	29.0	129±2
PMP_5	318.1	6.0	377.1	5.1	501.0	17.5	152±1
PMP_{CH}	300.1	10.2	389.5	–	499.7	38.8	231±2
PMP_m	307.8	3.4	383.2	24.4	499.0*	26.9	304±9

(*) the broad peak with the following local maxima: 474.4; 499.0; 503.6 K was found

For the comparison, the data of the films cast from cyclohexane solution are presented, too [9]. In this study, the PMP films cast from the solutions of various PMP concentration were used in order to produce different supermolecular structures created by the same macromolecule. Also, one sample was cast from melt. All samples exhibit various T_g and ΔC_p at T_g. It means that other factor than a chemical structure of monomer is important. The results collected in Table 2 support the thesis mentioned above that the thermodynamic parameters must be rather related to the supermolecular structure of the polymer, it means a physical structure, and not only to the chemical composition of the macromolecule. Although, the later is very important, too. It is easy to find that $T_g(1)$ and $T_g(2)$ differ for each of the sample but their values are included in rather narrow temperature ranges. The range of temperatures of the $T_g(1)$ values is broader than the range of the $T_g(2)$ values. It is more clear when we take into account the fact that the crystal structure of the samples PMP_2, PMP_3 and PMP_5 is different as compared with the crystal structure of PMP_{CH} or PMP_m. X-ray patterns of the studied PMP samples exhibited the mixture of the II and III modifications for the PMP_2, PMP_3 and PMP_5 and PMP_{CH} [28]. The tetragonal unit cell (the I modification) with the following lattice constants: 1.87±0.02 nm ($a=b$) and 1.36±0.02 nm (c) were found for the sample cast from melt (PMP_m). The patterns were typical for semi-crystalline polymer material with a predominant amorphous phase. Different unit cells of the crystalline structures make that it is difficult to calculate the degree of crystallinity comparison the ΔH_m values of all samples with the value estimated for 100% crystalline polymer because the melting endotherm (DSC) might include the enthalpy concerning the other physical process. Also, the method developed by Wunderlich's group [30], which let us calculate the amount of the amorphous phase in semi-crystalline polymer from the ΔC_p estimated at T_g, may not be applied. One can easy find that this amount calculated from ΔH_m or $\Delta C_p(T_g)$ is drastically different. It would mean that not only the amount of amorphous phases is important for ΔC_p determination but also the arrangement of chains in both fractions. Some deeper insight into the nature of such structures gives free volume studies. Unfortunately, it was impossible to apply PALS to the rather thin films cast from solution. Therefore, mechanical spectroscopy was used to study the effect of specimen treatment on the supermolecular structure. In series of measurements of the PMP samples, which exhibited different T_g and ΔC_p, the chain mobilities were investigated. For better visualisation of the temperature dependence of the structural relaxation in PMP of different supermolecular structures the data are presented in Fig. 2. DMTA spectra exhibited the same relaxation processes ($\alpha_{g,}$, α_c) found for the PMP samples described recently [9, 10]. It was recognised that both of them revealed the mobility of the main chain located into the different fractions of the amorphous phase of the PMP material. As previously, a curve and a straight line could represent $\alpha_{g,}$ and α_c relaxation in the Arrhenius plot, respectively. The highest enthalpy of activation of the α_c relaxation, calculated from the Arrhenius relation ($\Delta H(\alpha_c)$ – the last column in Table 2), was found for the sample cast from melt (PMP_m). Also, the PMP_m data, which represent both relaxations, are shifted towards to higher temperature. It would mean that the molecular motion is more restricted for the structure created in PMP_m.

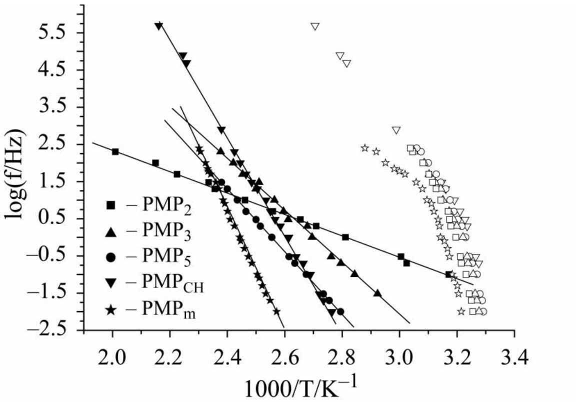

Fig. 2 Arrhenius plot of the studied PMP samples. The open and solid adequate symbols represent the data obtained for the α_g and the α_c relaxations, respectively. The straight lines show the fitting of the data by the Arrhenius relation, which was used for the activation enthalpy calculation. For the comparison, the data obtained for the PMP$_{CH}$ sample are shown additionally [9]

The strong curvature of lines for the PMP$_m$ data of the α_g relaxation in the Arrhenius plot suggests the strong effect of the free volume on this process.

Conclusions

Some preliminary results of the positron lifetime measurements in PMP show that the free volume increase of the amorphous phase is relatively high in the temperature range below T_g. However, this value is still low, even, as compare with the volume of the unit cell of the crystal. The temperature dependence exhibits rather an exponential type of function. The V_f values obtained for the polymers of different chemical constitution of a monomer unit, measured at one temperature, seem to be more correlated with the polymers T_g values than their monomer structure. It would mean that this value must be also correlated with the supermolecular structure, hence, the possible mobility of the macromolecules. Arrhenius and non-Arrhenius types of the relaxation time dependencies were not reflected in the positron lifetime measurements, most likely, due to the calculation model used. It must be emphasised that the most popular, common accepted, model does not assume, for the simplicity of the calculation, the existence of the two amorphous fractions in the system. However, it does not mean that such two fractions do not exist.

In the case of the α_g relaxation, stronger curvature of the relaxation time dependence for the sample cast from melt suggests the stronger influence of the free volume on the relaxation process. For the same sample, the highest enthalpy of activation of α_c relaxation would mean the strongest restriction for the chains mobility taken place in the 'semi-ordered' amorphous fraction. Most likely, the way of casting is important, too. However, this problem was not a subject of the paper. The α-relaxation is deeply related to the glass transition although these two phenomena are distinct but both of them are sensitive to the free volume of the amorphous phase.

* * *

The fruitful discussions with Prof. Franz Stelzer (ICTOS TU Graz, Austria), performed during DMTA measurements in his Lab, and his remarks, which let the authors improve the manuscript, are greatly acknowledged. The authors wish to thank Dr. M. Karolus for the X-ray measurements.

One of us (A.D.) would like to acknowledge the financial support of KBN project no.: 2PO3B 010 22.

References

1 J. H. Griffith and B. G. Ranby, J. Polymer Sci., 44 (1960) 369.
2 D. R. Morrow, G. C. Richardson, L. Kleinman and A. E. Woodward, J. Polymer Sci., A2 (1967) 493.
3 A. Nakijama, S. Hayashi and T. Tanaka, Kolloid -Z.u.Z. Polymere, 233 (1969) 869.
4 G. Charlet, G. Delmas, J. F. Revol and R. St. J. Manley, Polymer, 25 (1984) 1613.
5 G. Charlet and G. Delmas, Polymer, 25 (1984) 1619.
6 J. P. Flory, J. Am. Chem. Soc., 84 (1962) 2857.
7 J. P. Flory, D. Y. Yoon and K. A. Dill, Macromolecules, 17 (1984) 862.
8 L. C. Struik, Polymer, 29 (1987) 1521, 1534; 30 (1989) 799, 815.
9 A. Danch, J. Therm. Anal. Cal., 54 (1998) 151.
10 A. Danch, J. Therm. Anal. Cal., 65 (2001) 525.
11 A. Danch, A. Kocot, J. Zioło and F. Stelzer, Macromol. Phys. Chem., 202 (2001) 105.
12 A. Danch and W. Osoba, 'Influence of the free volume and chain flexibility on transport properties of membranes' in 'Membrane and membrane processes in environmental protection', (Eds M. Bodzek and K. Konieczny), WPŒ, Gliwice 2002.
13 R. F. Boyer, Rubber. Chem. Technol., 36 (1963) 1303.
14 N. G. McCrumm, B. E. Read and G. Williams, 'Anelastic and dielectric effects in polymer solids', Wiley, London 1967.
15 R. Richter and A. Blumen (Eds), 'Disorder effects on relaxational process', Springer Verlag, Berlin 1994.
16 I. M. Ward, 'Mechanical properties of solid polymers', Wiley, London 1971.
17 D. W. van Krevelen, 'Properties of Polymers', Elsevier, Amsterdam 1990.
18 A. Danch and A. Gadomski, J. Thermal Anal., 45 (1995) 1175.
19 J. Borek and W. Osoba, J. Polym. Sci. Part B, 36 (1998) 1839.
20 J. Borek and W. Osoba, Polymer, 42 (2001) 2901.
21 G. P. Johari, J. Chem. Phys., 112 (2000) 7518.
22 P. Richet and M. Toplis, C. R. Acad. Paris, t.2, Serie IV (2001) 191 (and references therein).
23 S. J. Tao, J. Chem. Phys., 56 (1972) 5499.
24 M. Eldrup, D. Lightbody and J. N. Sherwood, Chem. Phys., 63 (1981) 51.
25 Y. Kobayashi, W. Zheng, E. F. Meyer, J. D. McGervey, A. M. Jamieson and R. Simha, Macromolecules, 22 (1989) 2302.
26 Y. Y. Wang, H. Nakanishi, Y. C. Jean and T. Sandreczki, J. Polym. Sci. Part B, 28 (1990) 1431.

27 A. Danch and A. Gadomski, J. Mol. Liq., 86 (2000) 249.
28 A. Danch, M. Karolus and A. Burian, ‘Structural studies of poly(4-methyl-1-pentene) dendrites’ in ‘X-ray investigation of polymer structures II’, (Ed. A. Włochowicz), Proc. SPIE, 4240 (2000) 33.
29 A. Danch, ‘On the influence of the supermolecular structure on structural relaxation in the glass transition zone: free volume approach’ in ‘X-ray investigation of polymer structures V’, (Ed. A. Włochowicz), Proc. SPIE, - in print.
30 H. Suzuki, J. Grebowicz and B. Wunderlich, British Polym. J., 17 (1986) 1.