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STABILITY OF SUPERMOLECULAR STRUCTURE BELOW T_g
A role of free and specific volumes in local relaxations

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A comprehensive description of the changes occurring in the amorphous phase (‘real’ and ‘semi-ordered’) by means of mechanical spectroscopy, differential scanning calorimetry, dilatometry and positron annihilation lifetime spectroscopy are presented. The knowledge of the dynamics of poly(methyl-4-pentene-1) in a vicinity of the glass transition temperature is extended. The relationship between the free and the specific volumes is defined in the glass transition zone and below the zone. The results for the aging effect of the polymer system are also presented. The role of free and specific volumes in the structural and local relaxation are discussed.

Keywords: *free volume, polymer, specific volume, supermolecular stucture*

Introduction

The model relationship between free (V_F), occupied (V_0) and specific (V_S) volumes has been presented/discussed in handbooks [1, 2] and papers [3, 4]. It is commonly accepted that all of the volumes should increase with rising temperature. The model assumes the linear temperature relations for all of them, Fig. 1. One can easy find that if we measure specific (dilatometry, DIL) or free (positron annihilation lifetime spectroscopy, PALS) volume, we are able to estimate the glass transition temperature, T_g. This parameter is the most characteristic and important for polymers. It decides, very often, whether or not polymeric material may be used for some application because it decides about stability of a polymer structure and possible molecular dynamics, which can influence a supermolecular structure of the material. It is very difficult, due to strong anisotropy of polymeric systems, to obtain volumetric results. It is well known that every technique must apply some simplicities for the evaluation of the parameters. PALS assumes the spherical shape of the cavities, unoccupied places by the matter, and that the intensity of the measured relative intensity of the longest lived component of positron lifetimes is proportional to the number of the cavities. Generally speaking, we receive information about a free volume of the system. The volume increases with temperature rising, changing a slope of the line representing the temperature function, $V_F \rightarrow f(T)$ [5–7]. We can find a similar situation for the evaluation of the specific volume from dilatometric measurements. Basing on an expansion test, performed in one dimension, we calculate the coefficient of thermal expansion and we conclude about the thermal properties of the studied system. The problem is that it is very difficult to secure the same sample orientation for the both techniques. Lack of the same orientation may lead to the false conclusions.

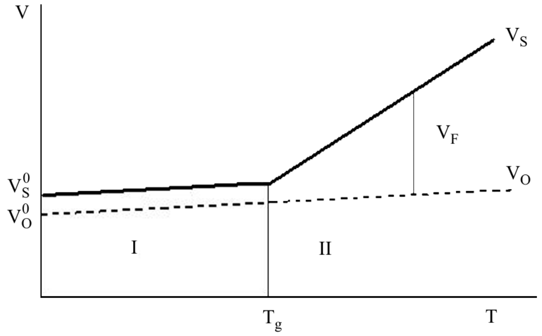

Fig. 1 A general scheme of relation between V_S, V_0 and V_F in two temperature regions, below (I) and above (II) T_g

In this paper we give a report on the PALS, DIL, DSC and DMTA studies performed for a polymeric system in a glass transition zone and below the zone. We discuss the role of the free and specific volumes in the relaxation processes observed by DMTA (or DETA) and their significance for thermodynamic calculations of the state functions.

Experimental

The polymeric samples are the same as used in the previous works poly(methyl-4-pentene-1), PMP) [7–9]. The experimental methods, i.e. differential

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scanning calorimetry (DSC), dynamic thermal analysis (DMTA), positron annihilation lifetime spectroscopy (PALS), and dilatometry (DIL) were applied for the description of the systems morphology and the segmental mobility of the polymer chains. The standard procedures (calibration, calculation) during all measurements were adapted [5, 10–12].

In spite of the well known basic thermal methods (DSC, DMTA, DIL), the PALS technique, in our opinion, requires more detailed description for better interpretation of the presented results. The PALS spectra were analysed using the package programs written by Kirkegaard *et al.* [12]. The total number of counts accumulated in our spectra was relatively small ($0.26\cdot 10^6$) and this was why we decided to analyse them in two-step process. As the first step of approximation, two exponential components were fitted to the measured spectra with no constraints on lifetimes and intensities during numerical analysis. As statistics of obtained spectra was relatively low, we decided to fit three components, but a lifetime of one of them was fixed. We fixed the lifetime of the second component, τ_2. According to our former measurements we chose 380 ps for the fixed τ_2 value. The results of the three-component fits were very similar, as far as the values of the longest lifetimes and the relative intensities of the longest lifetimes were concerned, to the results of the two-component fit. In this situation we present the results of the three components analyses. The shortest (the mean lifetime equal to 125 ps) lived component, τ_1, is usually attributed to para-positronium (p-Ps) annihilation. In our case, because of the relatively poor time resolution, it might contain not only p-Ps annihilation contribution but also contributions from positronium compounds. This lengthens our τ_1 values from about 150 ps to about 340 ps. The intermediate component, τ_2, describes the annihilation of the free positrons. Its value was fixed at 380 ps in the presented results. Finally, the longest lived component, τ_3, is attributed to the pick-off annihilation of o-Ps in the amorphous regions of the polymer. According to a model proposed by Tao [13] and Eldrup *et al.* [14], the longest lived component of the positron lifetime spectrum may be correlated with the mean radius of the free volume cavity in the polymer matter. They proposed an equation:

$$\begin{aligned}\tau_3 = {} & 0.5[1 - R/(R+0.1656) + \\ & 1/2\pi \sin[2\pi R/(R+0.1656)]]^{-1}\end{aligned} \tag{1}$$

where τ_3 is the o-Ps lifetime expressed in nanoseconds, R is the mean radius of the spherical well expressed in nm and 0.1656 nm is an empirical constant.

Calorimetric measurements were performed using a Perkin Elmer DSC7 type and the first heating run was recorded. The glass transition temperature (T_g) was defined from the inflection point of the change in a heat flow *vs.* temperature curve therefore the first derivative of the DSC trace was analysed. The melting temperature (T_m) was defined as the extremum of the melting endotherm. The analyses were performed under following conditions: environment: nitrogen atmosphere; flow rate: 20 mL $\min^{-1}$; sample pan: aluminium, reference: empty aluminium pan; sample size about 5 mg; heating rate: 20 K $\min^{-1}$; calibration procedure: done with indium standard.

Positron annihilation lifetime spectroscopy (PALS) was used to evaluate free volume in polymers. A conventional slow-fast coincidence spectrometer with plastic scintillators (two cylindrical Pilot U scintillators, their dimensions are: ϕ=1.5" and h=1.0") was used. The time resolution of the spectrometer was determined by analysing the positron lifetimes in Kapton foils. 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, $10^{-4}/10^{-5}$ mbar, within a temperature range from 8 K to room temperature.

Mechanical thermal analysis was carried out in a shear mode with a TA DMA Q 800 system. Real and imaginary part of Young's modulus were obtained within a temperature range from 125 to 475 K. The measurements were performed for 1 Hz at a heating rate of 1 K $\min^{-1}$.

Dilatometric measurements were carried out with using of a Beahr DIL 801 type in an atmosphere of helium. The temperature measurement range was 93–475 K. The dynamic temperature mode was applied: a heating rate 1 K $\min^{-1}$.

In order to minimize the effect of the influence of the sample preparation on the results, one bigger piece of the studied material went the same thermal treatment and then it was cut down into small pieces of size, which was necessary for each applied technique. The influence of the sample preparation and the applied technique on the signal acquisition by different measurement instruments (DSC, DMTA, PALS) was discussed previously [15].

Results and discussion

The selected results obtained from PALS and DIL are presented in Fig. 2. The curves represent obtained data for the unprocessed in our laboratory samples of PMP. The relative units, in both cases, are applied in order to better show the parameter changes for PALS (R – a diameter of the average cavity) and DIL (l – a sample elongation). The obtained data were scaled at 100 K for the better results comparison. It means that the relative values are zero for both data at 100 K. The

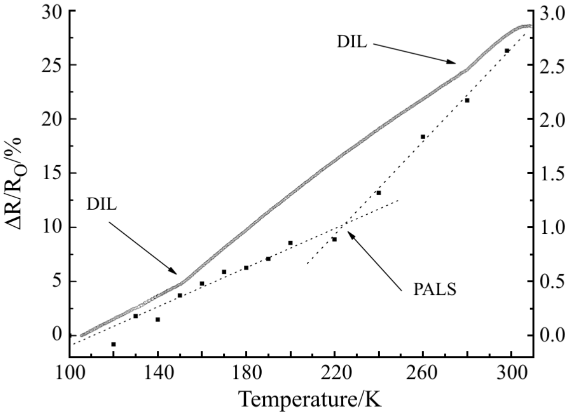

Fig. 2 Relative changes of the parameters obtained from PALS (left scale) and DIL (right scale). The temperatures of the transitions are pointed out by arrows

DIL curve exhibits two characteristic points (150.5, 280.0 K) at which the slop of the curve changes distinctly. These points could reflect the change of the structure. It must be emphasised that the both temperatures are far below the glass transition temperatures of the studied system, which is 307.9 K for the first glass transition (the value estimated from a DSC curve), and the second glass transition temperature is 383.2 K. Both temperatures have been evaluated from the runs performed at 20 K min^{-1}. The melting temperature is 499.1 K and the enthalpy of the melting is 26.9 J g^{-1}, that gives 38.6% of crystallinity. (The subject of the crystallinity estimation from DSC curves and a validity of such an estimation were discussed, and moreover, the comparison of this method with other one was done earlier [9, 11, 15].) Two points found in the DIL curve below the glass transitions mean that not only it is possible to observe the changes concerned the structural relaxation but also the local relaxations influence the thermal expansion of the polymeric system. The PALS data are presented as points. One can easy find that two lines can be fitted giving their intersection at 222.7 K. This temperature does not agree with the transitions found by DIL. Another surprising fact concerns the value of the relative change of *R* in the studied temperature range. We should take into account that the *R* value reflects only the average radius of the cavity. There is no precise knowledge on the number of the cavities and their distribution. The model, commonly accepted, applied for the *R* evaluation does not give univocal information about the total free volume of the system. However, the relative intensity of the ortho-Ps lifetime component (I_3) is assumed to be proportional to the number of the free volume cavities, as it gives information on the ortho-Ps formation probability. Therefore, there are two possible scenario: a – the free volume increases much more than the specific volume as *R* rising and the number of the cavities is constant with increasing temperature but this would implicate some decrease of V_0; b – the number of the cavities adequately decreases with rising temperature, that compensates such a drastic increase of the *R* value, giving a slight increase of the total free volume of the system. The second one seems to be more likely. It would mean that the small cavities join into the bigger one as the cooperative motions start to play a significance role for the structural relaxation.

It is well known that every structural changes are reflected in measurements of the adequate physical parameters. Owing to this fact, the comprehensive study of one system should be done. In our studies we applied PALS, DIL, DMTA, DSC and WAXS. It must be emphasised that samples for each methods are always prepared under the same condition in order to avoid the influence of the used technique on the obtained results. The comparison of the results concerning the structural studies of PMP are presented in Figs 3a and b. The experimental points (with statistical error bars) exhibit the change of the lifetime of the third component (τ_3) of the PALS curves. This component is proportional to the *R* value, that was described in experimental. The measurements were performed for a commercial sample (solid symbols) of PMP and 12 months later (open symbols) for the same PMP material stored at ambient temperature. This temperature was below the glass transition temperature of PMP found by DSC (T_g=307.9 K). It is well known that some structural changes of the polymer system with elapsing time occur due to the relaxation processes. Therefore, we should have expected the decrease of the τ_3 values, as it was reported for other polymeric systems [16]. The results exhibit that the values for both samples are almost the same except for the temperature ranges of the relaxation processes (γ, β and α) found by DMTA. We can see that the temperatures of the transitions pointed out from the

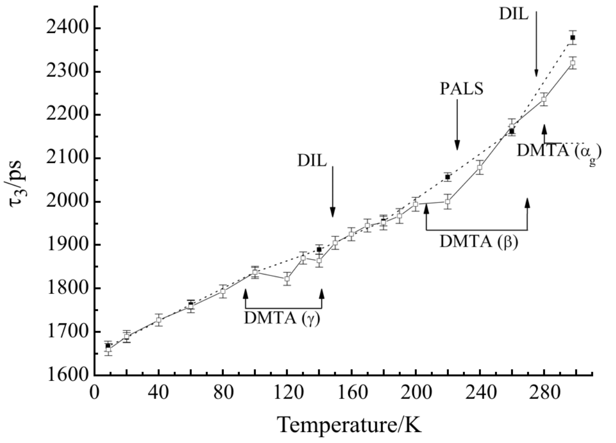

Fig. 3a The comparison of the results obtained by PALS, DIL and DMTA. Open symbols represent data obtained for the same system measured after 12 months

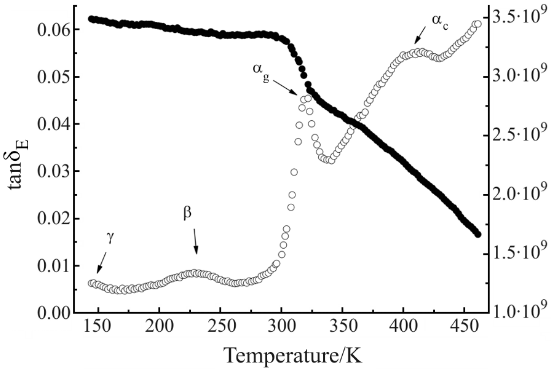

Fig. 3b Relaxation processes found by DMTA: open symbols – tan δ_E; solid symbols – E'

DIL curves are on the temperature scale just above of the higher limits of the γ and β, respectively. The transition temperature estimated from the PALS results is located in the temperature range of the β relaxation. The intensity and position of the relaxation processes can be found in Fig. 3b. The influence of different factors on all relaxations and their origin was discussed in our previous papers ([8, 9] and references therein). The enthalpy of the activation of the α_g relaxation is 185 J mol^{-1} and the relaxation time at room temperature is $1.6\cdot10^4$ s (the value calculated according to the model presented in Refs [4] and [17] is 446 J mol^{-1} and the relaxation time is infinite).

We know that thermal history strongly influence the structure. Here, it should be mentioned that the thermal treatment influences the DIL data and the temperatures of the transitions differ for PMP studied as a thin layer or in bulk. Three curves, presented unprocessed thin sample (PMP_{pl}), thin sample annealed at 353 K over 1 hour ($PMP_{pl\text{–}a}$) and PMP in bulk (PMP_{gr}), are presented in Fig. 4. The unprocessed and bulky samples exhibit two transitions, which temperatures differ. It was mentioned above that the temperatures of the transitions for PMP_{pl} are in agreement with the temperature zones for the local relaxations. There was no opportunity to apply DMTA at low temperature for PMP_{gr} therefore we have no knowledge whether or not the temperatures found by DIL are convergent with DMTA results. $PMP_{pl\text{–}a}$ exhibits only one transition at 150.9 K, that is in good agreement with the result for PMP_{pl}. However, there is no sign in the curve which would confirm the second transition below T_g as was observed for PMP_{pl}.

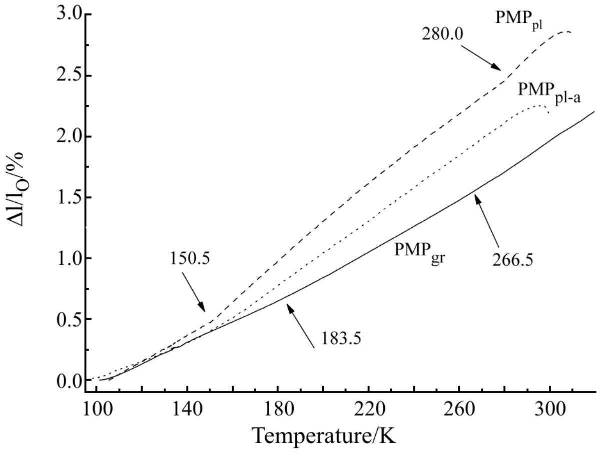

Fig. 4 Relative changes of sample length found for the unprocessed (PMP_{pl} – dashed line), annealed ($PMP_{pl\text{–}a}$ – dotted line) and bulky (PMP_{gr} – solid line) samples. The temperatures of the transitions are pointed out by arrows

The subject of the influence of the free and specific volumes on the macromolecule dynamics in the condensed matter, hence, the state functions of the system require further investigation. It seems to be important from the thermodynamic point of view which volume should be included in the state function and in the function describing the relaxation time. The other problem is to perform comprehensive investigation using the samples with the same thermal treatments in order to compare the results of different techniques.

Conclusions

The DIL and PALS data reveal 2 and 1 transitions, respectively. Moreover, the relative changes of the parameters measured by both techniques are surprisingly different. Larger increase of the *R* value would be indicative of the effect of the cavities joining not only in the glass transition zone, when the cooperative motions occur, but also below T_g. Free volume seems to play a significant role for local relaxation, too. The deviations of the *R* values in the temperature ranges of these relaxation processes could confirm this conclusion. Different slopes of the DIL curve after the γ and β relaxations would mean that this technique is not only sensitive to structural relaxation but also the local relaxations influence the thermal expansion coefficient. For the adequate comparison of the absolute values of the free and specific volumes, the PALS technique should applied new model giving the number of cavities. The comprehensive investigation ought to be performed with using the samples prepared under the same condition in order to minimise the influence of preparation required by different techniques. Especially, one must be careful when the comparison between DSC and other techniques is done.

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