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THERMODYNAMICS AND STRUCTURE OF THE ORDERED AMORPHOUS PHASE IN POLYMERS

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Experimental data are analysed to show that the activation enthalpy and the structural entropy appear to follow empirical relations for structural relaxation of polymeric systems. The relations indicate that melting temperature, glass transition temperature, relaxation time, coefficient of thermal expansion of free volume are interrelated in polymers. The parameters of structural relaxations, measured by mechanical and dielectric spectroscopies, are reviewed for polyethylene, poly(4-methyl-1-pentene) and a liquid-crystalline polynorbornene derivative. The thermodynamic parameters obtained from calorimetric measurements, are reported for zero heating rate extrapolation and they are used in the empirical relation, which combines the Arrhenius and the Vogel–Fulcher formulae.

Keywords: *polymer, relaxation time formula, structural relaxation, thermodynamics*

Introduction

When a liquid is cooled below the freezing temperature, it usually undergoes a first order phase transition into a crystal. However, there are many materials which can be easily supercooled. If crystallisation can be avoided by large cooling rates, most supercooled liquids will enter a metastable glassy state [1, 2]. The supercooled state and the glass transition have been a subject of intensive research. There are some outstanding questions which still remain to be answered. Is there a true glass transition in the thermodynamic sense? Is there a single relaxation mechanism governing different structural relaxations observed in various materials, e.g. low mass molecular substances or polymers? The most apparent dynamic feature of the glass transition, from one hand, is the rapid increase of the characteristic relaxation time on cooling. The most obvious thermodynamic signature of the transition, from the other hand, is the drop in the measured specific heat or other thermodynamic quantities, which occurs over a narrow range of temperature. Despite the observation of these two signature features in numerous materials and much theoretical work, there is still no fundamental theory of the glass transition, which would be commonly accepted. A wide variety of measurement techniques, including dielectric and mechanical spectroscopies, calorimetry and others have been used to study the approach to the glass transition. Although some general features are similar for all materials, the details of their behaviour during the transition vary. The relaxation behaviours do not obey a simple dependence on frequency (time), and the shape of the relaxation varies with temperature, even in measurements of the same compound using experimental probes prepared under different thermodynamic conditions. Different expressions have been used to fit these behaviours including that of Vogel–Fulcher (V–F), $\tau=\tau_0\exp[B/(T-T_0)]$, Arrhenius, $\tau_0\exp(E/k_BT)$, scaling, $\tau=\tau_0[(T-T_0)/T_0]^\gamma$, and variations of these forms [3, 4]. While to able to fit the data over limited ranges of temperature, no single form has yet been found that fits the range covered by experiment.

One of the common experimental methods used to probe dynamics of a supermolecular structure of the polymeric systems is to measure dielectric or mechanical relaxation [5]. However, particularly problematic is the fact that different samples of the same polymer have generally been investigated by different techniques, which required special samples treatment. Owing to the conditions of preparation, different supermolecular structures have been created. That might be a reason, why in spite of long interest paid to structural relaxation, the correlation between different physical properties has not been properly addressed [6–9]. For example, the specific heat has a special importance because it is the thermodynamic measure of temperature-induced structural changes in the polymer. Therefore, the piece of the sample for DSC investigation must be cut down directly from the same specimen which is prepared for mechanical, dielectric or X-ray measurements. The results presented by different authors using various experimental techniques could very often describe various supermolecular structures of the same polymer [10–12]. In such a case, there was no sense to compare results

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presented in different papers, especially, when the thermal history of the samples was not described precisely and one could not be sure that the same structure of the investigated sample was formed.

In this paper, we give a through discussion of our experiments and their interpretation, and we present calorimetric results evaluated for zero heating rate. Certainly, one can never be sure that the results of such an extrapolation are accurate. However, we feel that it makes more sense to extrapolate a series of non-equilibrium measurements to zero heating rate than it does to extrapolate a dynamical quantity to zero frequency like for modulated DSC. New formula for the relaxation time evaluation, τ, is proposed. In order to find out one mathematical formula describing the structural relaxations, α, some assumptions must be taken that is discussed in the next section. The results of a comprehensive study on a large group of samples of various supermolecular structures, including 3 different polymers, are analysed with respect to the effect of the crystalline (liquid-crystalline) phase on the relaxation of the amorphous-crystal interphase, i.e. α_c relaxation. To examine the mobility of the chains building the interphase, the mechanical (DMTA) or dielectric (DETA) spectroscopy was used. DETA and DMTA data are discussed with respect to the results of some additional experiments, dealing with a free volume (positron annihilation lifetime spectroscopy, PALS) and a crystals structure (wide angle X-ray scattering, WAXS, small angle X-ray scattering, SAXS).

Background

Amorphous fractions

It is commonly accepted that the α relaxation reflects correlated segmental motion of polymer chains building an amorphous phase. However, many polymers, especially those having simple chemical structure, are semicrystalline. It means that some part of the chain is located in the amorphous region while the other part builds the crystalline domains [13]. It was shown, the domains of long-range order distinctly influence the arrangement of the chains within the amorphous regions [14–16]. It resulted in the appearance of two amorphous fractions in one polymeric specimen. The fractions were named: 'real' and 'ordered' amorphous phases. An immediate consequence of the different structure was various change of the specific heat at T_g, resulting from an entropy changing with temperature. The 'real' amorphous fraction exhibited typical step-wise transition with a relatively small change of the specific heat at T_g (DSC). The 'ordered' fraction was usually observed in DSC traces as an endothermal peak following the abrupt change of a base line. However, in some cases, when both supermolecular structures did not differ distinctly, T_g-distribution took place due to overlapping of the glass transitions of the both amorphous structures in a narrow temperature range.

All cases of the amorphous supermolecular structures mentioned above were found and described for polyethylene (PE) [17], poly(4-methyl-1-pentene) (PMP) [15, 18] and a polynorbornene derivative (CK) [16, 19]. Those studies covered a group of semicrystalline and liquid-crystalline polymers. Some general conclusions concerning the glass transition were drawn. The co-existence of the amorphous and crystalline (liquid-crystalline) phases resulted in different properties of the 'real' and 'ordered' amorphous phases. It was shown that the 'ordered' amorphous phase could be treated as a 'fingerprint' of the possible crystallisation [20]. The experimental evidences showed that two fractions of the amorphous phase were created in one polymeric material [15–20]. The experimental findings could be summarised in the following:

(S1) The amorphous structure, A_g, which never forms crystalline domains due to spherical restrictions.

(S2) The amorphous structure, A_c, which is completely influenced by the crystallites. That would be a case of highly crystallised polymer, i.e. PE.

(S3) The amorphous structure, A_p, a medial case between A_g and A_c, which is observed in semicrystalline polymers, when the crystallisation process is not completed due to fast cooling regime and some kind of recrystallization (cold crystallisation) is possible.

Structural relaxations, α

The molecular dynamics in polymeric systems takes place on an extraordinary wide time scale. The α relaxation is a link between microscopic and macroscopic times. It is well know that its temperature dependence follows the Vogel–Fulcher equation [4–5]. Although the physical meaning of the parameters used in this equation is not clear, the applicability of the V–F equation over several decades in time would suggest that the formula is a significant for the dynamics of the glass transition. Besides the α relaxation, β relaxation is also observed in a polymeric system. While the high temperature α relaxation is named the structural relaxation, the β relaxation is treated as a local motion of small fragments of side chains or side groups. When the chemical constitution of polymer is more complicated, the other low temperature relaxations can be observed. Usually they are well separated in a frequency (temperature) scale and exhibit an Arrhenius type temperature dependence. The activation parameter of this relation, which is interpreted as an activation enthalpy of the relaxation process, determines the mobility of chains building the supermolecular structure.

Semicrystalline polymers exhibit a morphology of lamellar crystals located in an amorphous matrix. The matrix is not homogenous in a morphological sense. Although some fraction of the chains attains the mobility level of the liquid-like state as temperature is increased above T_g, it has been shown, that a portion of the amorphous phase (the interphase) remains still rigid above T_g [13, 15–16]. The crystalline phase reduces the segmental mobility of the chains located in the interphase. The main consequence of this is that the glass transition of the interphase is extended towards the high temperature and the second α relaxation appears. The glass transitions for both fractions of the amorphous phase are observed in DSC curves, that was mentioned above. The α relaxations, related to these glass transitions, exhibit different features [21, 22]. The relaxation behaviour of the 'real' amorphous fraction, α_g, unperturbed by the crystals, obeys the V–F relation. The relaxation of the 'ordered' amorphous fraction, α_c, exhibits the activation dependence and the Arrhenius relation can be applied for the relaxation time calculation.

Empirical relationship

Assumptions

The mechanism of the structural relaxation must involve main-chain motion avoided by co-operative motion of neighbouring segments along the backbone. This intramolecular co-operativity should require intermolecular action, too. The interaction might be represented by the free volume parameter, δ^* [22]. The correlation between this parameter and the structural parameter, β, was defined in a previous paper [22], where some discussion for the various amorphous fractions of chosen polymer was presented. The β parameter can be evaluated either from the parameter definition or as a parameter of a curve fitting [21]. The curve describes the temperature dependence of the relaxation time for the supermolecular structure, being under consideration. Generally speaking, both structural relaxations, i.e. α_g and α_c, reflect a possible motion of the main chain forming the various amorphous fractions. Therefore, the next fundamental question emerges: is it possible to describe the α relaxations only with one mathematical formula? In order to find the formula the following assumptions are taken based on the experimental evidences:

(A1) Structural relaxation is a thermally activated process, $\tau \rightarrow f(1/T)$.

(A2) Number of mers taking part in the relaxation increases with temperature due to the free volume increase, $n_\alpha \rightarrow f(T)$.

(A3) Enthalpy of the process activation is a function of the mers number and of the average enthalpy of the macromolecules interaction, $\Delta H_\alpha \rightarrow f(n_\alpha, H_i)$.

(A4) H_i decreases with temperature due to the free volume increase, i.e. the spherical restriction is gradually reduced on heating from the polymer glass temperature to the melting temperature of the polymer crystals.

Besides the pure mathematical assumptions concerning the formula construction, another assumption must be taken. All of the parameters must possess physical sense (interpretation). Although the formula is the pure empirical one, the parameters should be obtained from other than mechanical or dielectric measurements, it means, the glass transition temperature is defined in a thermodynamic sense. It is not a dynamic parameter evaluated from the dielectric spectroscopy [9]. All used temperatures (T_g, T_m) are evaluated for the zero heating rate extrapolation based on DSC measurements.

Formula

The empirical relationship referred to above mentioned assumptions combines the Arrhenius and Vogel–Fulcher eqations for the temperature dependence of the relaxation time.

$$\tau = \tau_1 \exp\left(\frac{\Delta H_\alpha}{\Delta C_p(T_g)}\frac{1}{T}\right) \tag{1}$$

where τ_1 the relaxation time at high temperature ($T \rightarrow \infty$, a mathematical approximation, in practice, it must be the τ value in a liquid-state at temperature below the temperature of polymer decomposition), ΔH_α – the enthalpy of activation of the α relaxation, $\Delta C_p(T_g)$ – the change of the specific heat taken at the glass transition temperature. It must be emphasised that the formula describes the dynamics of one system, it means, the thermodynamic parameters, taken from the calorimetric study, must be exactly pointed out for the system which is the subject of the mechanical or dielectric spectroscopy. The same must be true of the free volume and the X-ray measurements.

Very often, the change of specific heat is very small and the base line before and after the transition is not a smooth straight line. It complicates the evaluation of $\Delta C_p(T_g)$, especially, that T_g is pointed out for the ΔC_p calculation as a midpoint of the specific heat change. Such a procedure might produce a relatively big error. Therefore, it was postulated in our previous papers to point out the T_g value from the first derivative of the C_p curve [17, 18, 23]. Then, T_g is defined as an inflection point of the C_p curve and the ΔC_p value is a peak area.

Rather large values of the activation enthalpy, which could be obtained in the case of the Arrhenius relationship application for the α relaxation, suggest that the enthalpy must varied with temperature. As it is postulated in this paper, this thermodynamic parameter should be a function of the number of mers taking part in the process (n_α) and the enthalpy of intermolecular interaction (H_i).

$$\Delta H_\alpha = n_\alpha H_i \tag{2}$$

It is assumed that both n_α and H_i are the functions of temperature given by the following formulae:

$$n_\alpha = n_l \left(1 - \frac{1}{1 + (T/T_c)^\beta}\right) \tag{3}$$

$$H_i = H_l \exp\left(\frac{\Delta T^*}{T - T_0}\right)^2 \tag{4}$$

where $\Delta T^* = T_m - T_t$, T_m – the melting temperature of the crystalline (liquid-crystalline) phase, T_t – temperature of the transition involving the α relaxation, T_0 – temperature at which the relaxation starts, T_c – temperature at which 50% of the mers is activated for the co-operative motion. The β parameter is calculated using the experimental thermodynamic parameters taken from DSC measurements after their zero heating rate extrapolation. The following definition of the β parameter was postulated [21, 22]:

$$\beta_d = 2\left(\frac{T_g}{T_m - T_t}\right)^2 \tag{5}$$

To adopt Eq. (1) for all cases described in literature some further assumptions must be done. This lets to obtain two relations of relaxation time, which are realised by the modified functions similar to either the Arrhenius or the Vogel–Fulcher functions. The assumptions arisen from the experimental evidences are the following for the different fractions of the amorphous phase:

(A5) the 'real' amorphous phase (A_g); $T_m=0$, $T_t=T_g$ that implies $\beta=2$ and the adequate functions of the n_α and H_i variables

(A6) the 'ordered' amorphous phase (A_c); $T_t=T_m$ that implies $\beta=\infty$, $n_\alpha=n_l$ and $H_i=H_l$

(A7) the 'semi-ordered' amorphous phase (A_p); $T_g<T_t<T_m$ that implies $2<\beta<\infty$ and the adequate n_α and H_i functions.

The available literature data did not provide the best possible test of Eq. (1). The results of DSC, DMTA or DETA, obtained by different authors, should have been used with caution. Possible errors of the fitting procedures for the relaxations (α_g, α_c) were large because of the varied nature of both data and samples. A better test could be made if the experimental errors were reduced by making all measurements of mechanical and thermal properties on the same polymer sample, i.e. with the same thermal history. Nevertheless, the data did tend to support the validity of Eq. (1) that was shown previously for PE and CK [22]. The study of the α_g relaxation requires further measurements, therefore in this paper, the α_c relaxation is only discussed for our previous experimental data in details. Because in the case of A_c the linear relationship in the log scale is fitted, the obtained results are not calculated with large error. The following formula for the 'ordered' amorphous fraction ($T_t=T_m$, $\beta=\infty \Rightarrow n_\alpha=n_l$, $H_i=H_l$) is obtained:

$$\tau = \tau_1 \exp\left(\frac{n_l H_l}{\Delta C_p(T_g)} \frac{1}{T}\right) \tag{6}$$

It must be emphasised that the fitting procedure gives $n_l H_l$ as a one parameter, ΔH_α. It means, that to know the enthalpy, the number of mers must be established from other experiments and vice verse, to know the number of mers, the enthalpy of interaction should be calculated based on some model. Unfortunately, there is no simple model giving such an opportunity. However, the n_l value could be taken from experiments which have established the number of mers required for the T_g value stability [24–26] or the experiments which directly study the relaxation phenomenon in an external field (electric [27], mechanical [28, 29]).

Also, some preliminary results of fitting for the 'semi-ordered' amorphous fraction are presented. In this case, accordingly to assumptions A1–A4 and A7 ($T_g<T_t<T_m$, $2<\beta<\infty$), Eq. (1) is written as

$$\tau = \tau_1 \exp\left(\frac{n_l H_l}{\Delta C_p(T_g)}\left(1 - \frac{1}{1 + (T/T_c)^\beta}\right)\exp\left(\left(\frac{T_m - T_t}{T - T_0}\right)^2\right)\frac{1}{T}\right) \tag{7}$$

where β is the fitting parameters and the other terms have the same meaning as in Eqs (1)–(4). Because there are five fitting factors in Eq. (7) (sometimes their number can be reduced to three factors), the fitting errors are larger than for Eq. (6). Therefore, they have to be used with caution for further analysis of the supermolecular structure.

Results and discussion

Thermal history of the samples

Three groups of polymers were studied using DSC, DMTA, DETA, WAXS, SAXS and PALS. The samples of each polymer were prepared with different thermal history. In that way various supermolecular structures of the polymer of the same chemical constitution were formed. The structural parameters were determined and the morphologies of the crystalline or the liquid-crystalline phases were described [15–23, 30, 31].

Polyethylene was prepared from melt, PE, and was mixed with two different fillers: natural chalk (10 mass%-PE(Ca/1), 20 mass%-PE(Ca/2), 40 mass% -PE(Ca/3)) and carbon black (PE(S), PE(S/d)– a sample additionally drawn). Poly(4-methyl-1-pentene) was prepared from melt, PMP, and as membranes cast from carbon tetrachloride solutions (2 mass%–PMP(C/2), 3 mass%–PMP(C/3), 5 mass%– PMP(C/5)). All of the membranes were transparent except the membrane cast from the solution obtained at boiling temperature of the solvent, PMP*(C/2). All samples were not additionally annealed and were investigated just after preparation. Samples of the liquid-crystalline polynorbornene derivative were prepared from melt. Various liquid-crystalline phases were obtained under different thermal regimes. It was possible to form smectic A, nematic or completely amorphous structures (CK(s1), CK(n1), CK(a)). The CK(s1), CK(n1) samples held at 294 K several days exhibited structural changes, however, the liquid-crystalline structures were preserved in both cases (CK(s2), CK(n2)). The amorphous sample and the smectic one were additionally annealed at 343 K over 48 h. The annealing process changed the amorphous arrangement of the mesogens and then smectic A structure was obtained, CK(a/s). The annealing of the smectic sample shortened the distance between the layers built by the mesogens [CK(s$^+$)].

Data analysis

Thermodynamic parameters of the second glass transition, the melting process (isotropisation in the case of liquid crystals) and the α_c relaxation are collected in Tables 1a and b. In order to show some correlations between the glass transition and the structural relaxation process of the adequate supermolecular structure, data are presented in three groups. The activation enthalpy of the α_c relaxation was calculated using Eq. (6) for semicrystalline polymers (PE, PMP). In the case of the CK samples some curvature was observed [19] therefore Eq. (7) was applied. It will be shown below that this studied relaxation occurred rather in the A_p fraction of the amorphous phase, it means that $2<<\beta<<\infty$. The results are presented in the last column of Tables 1a and b. In all cases, some value of the activation enthalpy is obtained. It was impossible using only V–F relationship. Contrary to the CK samples, the dependencies (concerning the structural relaxation) for PE and PMP presented the straight lines [15, 17], hence, the activation enthalpies could be calculated from Arrhenius relationship. However, it must be emphasised that the properties of the PMP membranes and the mechanism of the diffusion process through the membranes were be much better understood when the new formula had been used for the calculation of the activation enthalpy. Moreover, the unexpected values of the diffusion coefficients were also explained [21].

The calculation, performed using Arrhenius relationship, gave very large values of the activation enthalpy for both α relaxations. The values were larger than the energy required for the macromolecules decompositions. It is worth noticing that the value presented in Tables 1a and b is a product of two variables: n_l – the number of mers taking part in the process in a liquid-state; H_l – the enthalpy of intermolecular interaction in a liquid-state calculated per one mol of mers. Hence, ΔH_α should be divided by the n_l value, which usually is between 20–30 units for LC polymers [26] and higher for semicrystalline polymers [24, 25]. The ΔH_α values for studied three polymers are approximately equal in the case when the crystal morphology is the same, even if the amounts of crystalline phase differ. For example, it was found for PE that the natural chalk did not modify the crystalline phase [30]. The amounts of that phase for PE(Ca/1), PE(Ca/2) and PE(Ca/3), calculated from DSC traces, were comparable. Additionally, the same melting temperatures and similar shapes of the endotherms suggested that the crystalline phase of those samples should exhibit the same morphology. However, the values of the thermodynamic parameters and DMTA measurements confirmed that the contribution of the ‘ordered’ amorphous phase increased with the chalk contents in the composites. Owing to the facts mentioned above, one might conclude that the supermolecular structure of that amorphous fraction was not changed. Therefore the same activation enthalpies, however calculated using Eq. (6), were obtained for the PE(Ca) composites. We can find a similar situation for the PMP membranes [15, 18, 21]. It was proved that the crystalline phase was built by the crystallites of the same crystal units although the amounts of the crystalline phase in the PMP systems were slightly different. A detailed description of the membranes formation, with special attention to the parameters influenced the supermolecular structure, was done in our previous papers [21, 23].

The ΔH_α values for PE and PMP were calculated from Eq. (6) while for CK from Eq. (7). It means that β was taken as an infinite parameter for polyolefines

Table 1a Data of the second glass transition and the melting process for the polyethylene (PE) and poly(4-methyl-1-pentene) (PMP). The activation enthalpy of the α_c relaxation related to the adequate glass transition (the 'ordered' amorphous fraction) is given in the last column. The values were calculated using Eq. (6) based on the data published previously in our paper

Sample	$T_g(2)$/K	$\Delta C_p(T_g(2))$/J mol^{-1} K^{-1}	T_m/K	ΔH_m/kJ mol^{-1}	ΔH_α/kJ mol^{-1}
PE_g	353.3	2.5	386.0	1.70	–
PE	321.6	10.1	388.2	2.90	362±4
PE(Ca/1)	322.7	11.5	383.8	2.67	465±5
PE(Ca/2)	321.7	12.3	384.1	2.67	461±5
PE(Ca/3)	320.6	13.5	385.5	2.71	466±5
PE(S)	347.3	16.1	379.6	2.90	197±2
PE(S/d)	328.8	5.6	381.2	2.23	81±1
PMP_g	377.1	8.1	501.7	1.22	–
PMP	383.2	24.4	499.0	2.26	893±5
PMP(C/2)	376.9	15.1	499.2	2.65	96±4
PMP^*(C/2)	382.1	7.6	501.7	3.43	99±3
PMP(C/3)	380.4	5.6	500.0	2.44	92±3
PMP(C/5)	377.1	5.0	501.0	1.47	94±4

Table 1b Data of the second glass transition and the isotropisation process of the polynorbornene derivatives. The activation enthalpy of the α_g relaxation related to the adequate glass transition (the 'semi-ordered' amorphous fraction) is given in the last column. The values were calculated using Eqs (7) based on the data published previously in our paper

Sample	$T_g(2)$/K	$\Delta C_p(T_g(2))$/J mol^{-1} K^{-1}	T_m/K	ΔH_m/kJ mol^{-1}	ΔH_α/kJ mol^{-1}
CK(s1)	312.30	37.0	415.2	6.94	77±8
CK(s2)	319.30	31.0	414.8	7.02	76±6
CK(a/s)	304.10	48.0	414.1	8.58	74±6
CK(s^+)	319.50	3.0(?)	415.9	7.27	5.7 (?)
CK(n1)	306.00	158.0	414.4	7.08	307±28
CK(n2)	307.60	138.0	414.2	6.49	274±28
CK(a)	298.60	87.0	413.9	7.03	2232±112

(PE, PMP), and $n_\alpha=n_l$ and $H_i=H_l$. Application of Eq. (7) for the CK or PE/PMP systems means that β should possess some finite value and the 'semi-ordered' or 'real' amorphous fractions are taken into account. The values, calculated from the parameter definition (β_d) or the equation fitting (β_f), are presented in Table 2. The β_f values are given with some fitting errors. The errors are rather big. It is connect with the number of experimental points, which in many cases did not reach 30 points obtained in 5 decades of measurement frequencies. One can easily find that the percentage of the mers taking part in the α_g relaxation at T_g is not the same in all CK cases. (Let us remember that CK is a complex system including mesogens, norbornene segments and alkyl side-chains. All of the moieties exhibited their own characteristic behaviours. The mesogens forced creation of a liquid-crystalline structure while the alkyl side chains exhibited tendency to side-chain crystallisation. Moreover, the norbornene main-chain under specific conditions adopted a helical structure. Although, the concept of two glass transitions in the CK systems was proposed in our previous paper, most likely, three transitions should be taken into account for proper explanation of the mers activations. In this paper only fluidity of the main-chains is analysed. From one hand, the fluidity is restricted by the alkyl chains mobility, from the other hand, is blockaded by liquid-crystalline structure. The possible dynamics and thermodynamic situation together with the model of supermolecular structure were discussed earlier [16, 19, 31]).

The chains mobility might be reflected by the n_α/n_l ratio, which represents the amount of the mers taking part in the relaxation process at some temperature. The ratio calculated from Eq. (3) for the CK and the PMP 'semi-ordered' structures is presented in Table 2. For comparison of the mers activity, the calculation were done at two temperatures, it means, at the glass temperature of each structures and at 293 K. Also, the temperature of activation of all mers taking part in the structural

Table 2 The fitting parameters calculated for the α_g relaxation occurred in the 'semi-ordered amorphous phase. β_d was calculated from the definition of this parameter (Eq. (5), [21, 22]). The ratio n/n_l (calculated from Eq. (3)) gives the relative number of mers taking part in the process at T_g and room temperature. n_l is a number of mers taking part in the relaxation in a liquid-state

Sample	β_d	β_f	$n_\alpha/n_l(T_g)$	n_α/n_l(293 K)	T_{99}/K
PE	64.9	59.1±1.8	?	?	?
PMP(C/2)	5.2	5.6±0.3	0.45	0.39	723.3
CK(s2)	19.1	20.0±1.3	0.53	0.17	399.0
CK(s^+)	18.7	18.3±0.9	0.53	0.19	407.6
CK(s1)	18.1	18.9±1.0	0.43	0.18	403.8
CK(n2)	17.9	17.0±1.3	0.37	0.21	415.5
CK(n1)	17.7	15.9±1.8	0.36	0.22	422.6
CK(a/s)	17.6	16.8±1.1	0.33	0.21	416.8
CK(a)	17.0	18.9±2.1	0.24	0.18	404.7

relaxation was calculated, T_{99}. The temperatures found for all CK structures belong to the temperature range of the isotropisation of the polynorbornene derivative (Table 1b). It would mean that the number of mers, n_α, is activated successively with increasing temperature up to the isotropisation process of the liquid-crystalline phase, which disturb the fluidity of the norbornene backbone. The T_{99} temperature found for the 'real' amorphous structure of PMP(C/2) is much higher than the melting temperature. It would mean that the number of activated mers increases even in the liquid-state of PMP, hence, the degree of intramolecular cooperativity increases. The structural study of the membranes showed that this tendency is characteristic for semicrystalline PMP. The β value for the structural relaxation (the temperature range of the first glass transition: PMP(C/2)–$T_g(1)$=308.2 K, $C_p(T_g(1))$=10.1 J mol^{-1} K^{-1}) suggests that the α_g relaxation rather occurs in the 'real' amorphous fraction. Because β=5.6 (in the case of the 'ordered' amorphous structure β=∞), one may conclude that this fraction of the PMP amorphous phase is not influenced by the crystalline phase at all. The question whether the tendency observed for the studied examples is a feature of the α_c or α_g relaxations for the broader group of polymers is still open and this idea require further investigation.

Unfortunately, it was impossible to calculate the n_α/n_l ratio and the T_{99} temperature for PE. In this case also two fractions of the amorphous phase and two structural relaxations were found. One of them was completely influenced by the presence of the crystals in the matrix, and the results are presented in Table 1a (β=∞). The second one, exhibited low temperature relaxation with T_g=183, was not studied extensively. The β values were calculated based on the literature data and the procedure was described in our previous paper (results of the temperature dependency of the specific volume were analysed [32] and free volume approximation was done [22]).

Conclusions

Application of new formula for the calculation of temperature dependence of the relaxation time exhibited the existence of some correlation between thermodynamic and structural parameters. Moreover, we distinguished two fractions of the amorphous phase that gave better description of polymer properties and the phenomenon were also better understood. The proposed definition of the relaxation time combines the experimental data of different techniques. The value of the β parameter gives some knowledge of the supermolecular structure of the amorphous phase. According to the β value, it will be possible to describe the strength of the influence of the crystal (liquid-crystal) phase on the polymeric amorphous structures, from weak to strong ($2\leq\beta\leq\infty$). This is quite similar to the classification of the glasses, which recognise the fragile and strong glasses. However, the relation proposed in the approach, presented here, includes only the fitting parameters, which can be compared with the parameters measured in experiments. Moreover, the mathematical formula gives the answer on a question concerning the origin of the α relaxations, described by the new relations, that is in agreement with the experimental observation. The value of β parameter would give also information about a degree of order existed in the amorphous phase, that could be useful for the description of material properties. It is tempting to believe that the new formula and the model presented in this paper will advance the theoretical understanding of the molecular mechanism of the α relaxation. In order to predict the polymer behaviour for engineering application, it is very important to know which fraction is created by macromolecules. It will allow the better modelling of the polymeric materials for utility purpose.

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