

EFFECT OF SUPERMOLECULAR STRUCTURE CHANGES ON THE GLASS TRANSITION OF POLYMER

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Abstract

The idea of two miscellaneous amorphous fractions in one polymeric system is under consideration. A new factor influencing the glass transition and α relaxation observed in polymers exhibiting different supermolecular structures is discussed. In order to clarify the specific arrangement of backbone chains two types of polymers were taken under investigation: semicrystalline poly(4-methyl-1-pentene) and a liquid-crystalline poly(norbornene) derivative. In both cases, it was possible to find two well separated glass transitions. Differential scanning calorimetry and dynamic mechanical thermal analysis were used to study the effect of thermal history on the assignment of the glass transition event associated with two miscellaneous amorphous phases. The problem of molecular arrangement in the amorphous phases is discussed.

Keywords: α relaxation, glass transition, supermolecular structure

Introduction

Concepts on the molecular morphology in polymers of different supermolecular structures (semicrystalline, liquid-crystalline and amorphous) have been theoretically discussed and confronted with experimental evidences. The widely accepted model in which each chain traverse a crystalline lamella in regular folded array was revised many times in order to explain experimental facts. Basically, that was a discussion on certain aspects of restricted randomness and an existence of lamella in application to long chain polymer ([1] and references therein). It seems to be acceptable, that in structures showing long-range order, a chain must emanate from an ordered area, e.g. lamella, and goes into an ordered area. Such a supermolecular structure consisted of lamellae separated by amorphous regions can be reached in semicrystalline polymers. As was concluded earlier [2], 70% of the chains must fold back into the same lamellae from which they have emerged. The same should be true for liquid-crystalline polymeric systems, especially in a smectic one, where mesogens build ordered layers separated by amorphous areas. Because, in the later case, the degree of polymerisation is usually much lower, the spherical restriction and the problem of overcrowding of the interlayer are more seldom.

One of the most important factors determining the possibility of creation of a necessary supermolecular structure is a chemical composition of macromolecule. This purpose requires an adequate number and a proper type of moieties. However, it does not mean that the proper effect will be obtained at all, because the chemical structure is a necessary but not a sufficient condition for the creation of the crystalline or liquid-crystalline structure in polymer samples. It is worth noticing that the thermal history of polymeric material is so important as the chemical composition. It is well known that the thermal treatment of samples, especially those samples, which can create the ordered phases, influences the arrangement of chains very strongly. Any non-random arrangements would entail substantial alternations of the chain configuration. Partial ordering of any kind must increase the free energy for a system of flexible chains [3]. Only for chains of limited flexibility an ordered arrangement is preferred. Supermolecular structures frozen as a result of quenching or slow cooling exhibit different glass transition temperatures (T_g) and changes of the specific heat at T_g ($\Delta C_p(T_g)$). Moreover, molecular motion occurred in such structures (e.g. α relaxation) is activated with different enthalpies. Some experimental facts, concerning the glass transition, give evidence of an existence of a state of 'total' disorder or 'partial order' of an amorphous phase [4, 5]. One can conclude that the existence of the partial order is now undisputed. Controversies are not related to the existence or non-existence of chains folding, to reach crystalline or liquid-crystalline structures in polymeric systems, but to its nature and mechanism of its creation. The problem is whether the moieties mobility allows the chains to fold on the time scale in question?

Dynamic mechanical (DMTA) and dielectric thermal analysis (DETA), if obtained over a wide enough frequency range, reveal most polymers exhibit a small number of broad loss peaks in the glass transition zone, which presumably arises from different modes of molecular motion [6]. Two main transitions, melting (T_m) and glass transition (T_g), are readily found by all types of thermal analysis, e.g. differential scanning calorimetry (DSC). Step-wise transition at T_g is observed in DSC traces for quenched polymers whereas an endothermal peak can be recorded for polymers under slow cooling regime [7]. A bulk amorphous structure unperturbed by the presence of crystalline or liquid-crystalline domains exhibits typical stepwise transition (DSC) and a single discrete peak (DMTA). When a crystal-amorphous interphase exists, e.g. in semicrystalline polymers, the main consequence of such situation is that the thermodynamic parameters of the chains located in the interphase differ as compared with these of a bulk amorphous state. In this case macromolecule fluidity is restricted. It might result in T_g -distribution or existence of two well-separated T_g , depending on how pronounced the interaction between the crystalline and the amorphous phases can be. In dielectric and mechanical spectroscopies the aspect of the extended glass transition in polymers is reflected either as broadening of the α relaxation peak or as appearing of two α relaxation peaks, consisted of the adequate T_g values. The main consequence of the interphase existence is that some part of amorphous material is rubbery, other part is glassy that might produce special properties [8]. Such behaviour can be sometimes undesirable.

The glass transition is not limited to special types of materials. It is a central problem of condensed matter physics. Unfortunately, there is no generally accepted theory which could give the explanation of the nature of this transition. But the idea that glass and crystal structures can be closely related has been supported by recent investigations [9]. Every class of material can be transformed in an amorphous solid (without or partially amount of crystallinity) if the experimental parameters are adjusted to the dynamics of the system. The question is whether a general rule able to explain the behaviour and properties of glasses exists? Moreover, can we apply the rules and the mathematical formulae worked out for low mass molecular substances to macromolecules, especially to polymers? Most likely all amorphous polymeric materials should be divided into two subclasses: one including polymers to be able to crystallise, and the second one including polymers to be unable to reach such thermodynamically stable state. The role of the crystal–amorphous interphase was already discussed in 1962. The theoretical considerations led to the conclusion that such a situation allows the dissipation of the order existing on the crystal surface [10]. The concept of two amorphous structures has been successfully used in theoretical works concerning the description of the kinetic of phase transition in lipid membranes. For that purpose, two time scales of the process have been proposed: the first one, ‘integral’, resulting in Debye relaxation and the second one, ‘non-integral’, making the process slower [11]. Also, the models of the process of crystallisation from solution and the process of the cylindrolite growth (two-dimensional) in the amorphous system include the idea of different amorphous phases [12, 13].

In a present work it is postulated to distinguish two types of the amorphous phase. The first one, self-existed, will be called ‘real’ and the second one, co-existed with crystalline or liquid-crystalline phase, will be called ‘semi-ordered’ amorphous phase. Their thermodynamic parameters were easy to modify in the preparation processes of the samples. It will be seen below that the thermal treatment of the polymeric material led to the miscellaneous supermolecular structure creation.

Experimental

Sample preparation

Semicrystalline poly(4-methyl-1-pentene) (PMP) and liquid-crystalline poly(norbornene) derivative (CK(11)) were the same as used in previous works [14–19]. In the case of PMP, opaque and transparent films were prepared from the carbon tetrachloride solutions by casting on different type of substrates: glass (g); metal (m); teflon (t). Polymer concentration in solutions was 2, 3 and 5 mass%, that is pointed out in parentheses. For example: PMP(g/5) means that the sample was cast on the glass substratum and the concentration of PMP in solution was 5 mass%. Dissolution was achieved at room temperature or by heating at the boiling temperature of the solvent used. One sample was prepared from melt PMP(melt). The samples were cut from the obtained films.

In the case of CK(11), the samples were melted at 160°C and they were held at this temperature for about 40 min. Different cooling regimes were applied from slow to very fast (quenching) one. In that way bars with different perfection of smectic phase were obtained: CK(11/I) – good smectic phase ; CK(11/V) – completely amorphous structure. Some part of the polymer exhibiting smectic phase was stored at ambient temperature over one, CK(11/II), and seven, CK(11/IV), days. The other part of this polymer exhibiting the smectic structure was drawn over one h, CK(11/III). The samples were prepared as bars of nearly the same size.

Methods

Dynamic mechanical thermal analysis was carried out with a Polymer Laboratories DMTA Mk III system. Loss tangent and E' curves were obtained in tensile mode. A frequency range was 0.03–100 Hz and the heating rate of 0.2°C min⁻¹ of the poly(norbornene) samples measurement, CK(11), within a temperature range from 10 to 80°C was applied. The same frequency range and the heating rate of 2°C min⁻¹, within a temperature range from 10 to 200°C, were applied for the PMP samples.

Thermal characterisation of the samples by DSC was performed using a Perkin Elmer DSC7 type and the first heating run (20°C 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. The melting temperature (T_m) was defined as the maximum of the melting endotherm. The analyses were performed under the following conditions: environment – nitrogen atmosphere; flow rate – 50 mL min⁻¹; sample pan – aluminium, reference – empty aluminium pan; sample size – about 10 mg; heating rate – 20°C min⁻¹; calibration procedure – done with indium standard.

Results and discussion

The results of the thermal histories of the samples are reflected in change of the following parameters: $\Delta C_p(T_g)$, T_g and Young's modulus (E' , E''). Thermal treatment influences macromolecule arrangement giving, in many cases, an additional order. The presence of the ordered phase, that is the crystalline or liquid-crystalline one, in polymeric materials implicates a very important consequence. In order to study the effect of such structures two kinds of polymers were taken under investigation: semi-crystalline poly(4-methyl-1-pentene) (PMP) and liquid-crystalline poly(norbornene) derivative (CK(11)). Examples of DSC traces collected in two groups are presented in Figs 1a and 1b. Thermal analysis (Fig. 1a) was performed for the opaque and transparent PMP films cast from solutions (see experimental part). A wide range of conditions applied for the sample preparation made possible to obtain the samples of different morphology, which was deduced from X-ray results [20]. By comparison the X-ray patterns of all samples investigated and those reported [21], it was possible to assign each solution-cast PMP films to one of the crystal modifications. As was shown earlier, the different crystal unit and the miscellaneous structural forms like spherulites or dendrites were found. Some forms were similar to the one we can ob-

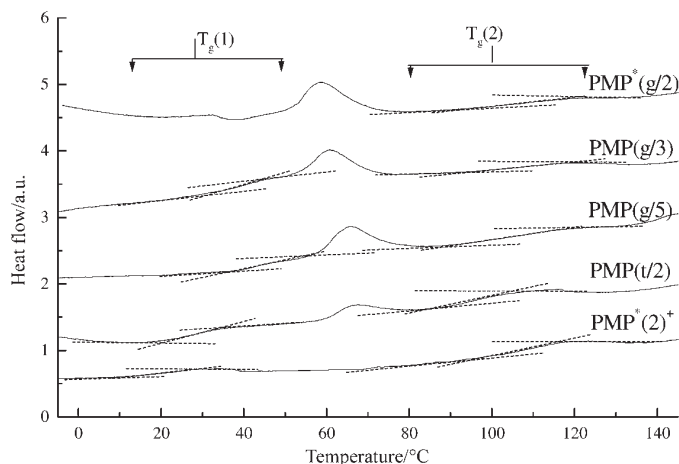


Fig. 1a Original DSC traces of the PMP films obtained under different thermal history as described in the experimental part. PMP*(2)⁺ – sample casted from cyclohexane, data taken from [18]. The description of the samples is done in the Table 1a

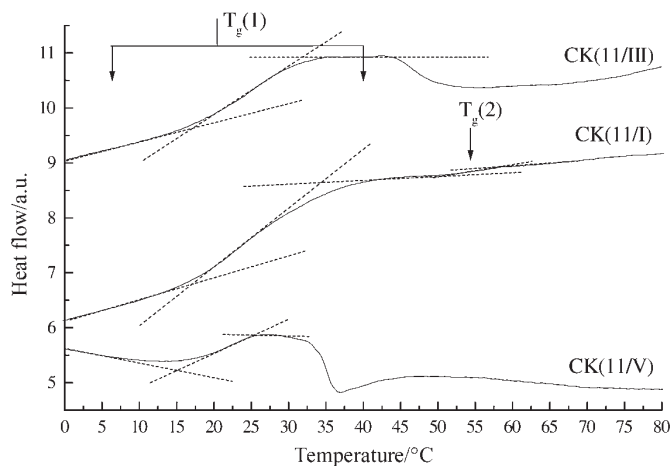


Fig. 1b Original DSC traces of the CK(11) samples obtained under different thermal history as described in the experimental part. The description of the samples is done in the Table 1b

tain in the numerical experiment using a computer simulation technique or even analytically [22]. The calorimetric results are summarised in Tables 1a and 1b. They distinctly show the influence of PMP concentration in solution on thermodynamic parameters. Lower T_g gives evidence that the amorphous phase is less stress. Also, the lower T_m indicates the worse crystalline phase existence. The degree of crystallinity was calculated from an endotherm area of each trace taking 61.9 J g^{-1} as the value of heat fusion for the 100% crystalline polymer [17]. These values should be approxi-

mately taken into account due to PMP polycrystallinity. However, the influence of the different crystal forms on the second glass transition is distinct. When the same crystallinity percent, the same size and the perfection of the crystal forms are observed, the second glass transition temperatures, $T_g(2)$, for the PMP samples are equal. In other cases, which the X-ray patterns exhibited the different crystal modifications in [20], $T_g(2)$ values are different and the DSC traces of this transition present different shapes. According to the postulate concerning the existence of two kinds of amorphous structures in polymeric materials and the method developed by Wunderlich's group [23], one can find that the ratio between two amorphous fractions contributed to the first and the second glass transition is different in all cases. Most likely not only the amount of amorphous phases is important but also the arrangement of chains in both fractions. Some deeper insight into the nature of such structures would give small angle X-ray scattering or neutron scattering. Free volume studies, successfully applied to polymer investigation [24], would also be helpful on the problem of two amorphous fractions existence.

Table 1a Transition temperatures ($T_g(1)$, $T_g(2)$, T_m), enthalpies (ΔH_m) and the change of specific heat ($\Delta C_p(T_g)$) of the opaque (*) and the transparent PMP films cast from carbon tetrachloride (+ – caste from cyclohexane, data taken from [18])

Samples	$T_g(1)/^{\circ}\text{C}$	$\Delta C_p(T_g)/\text{J}(\text{g}^{\circ}\text{C})^{-1}$	$T_g(2)/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$\Delta H_m/\text{J g}^{-1}$	Crystallinity/%
PMP(m)	45.7	0.12	125.5	228.6	14.6	23.6
PMP(2) ⁺	26.9	0.12	116.4	226.5	38.8	62.7
PMP ⁺ (2) ⁺	19.8	0.09	123.5	225.7	25.9	41.8
PMP(g/2)	35.1	0.12	103.8	226.1	32.5	52.5
PMP(m/2)	39.4	0.08	103.1	225.6	32.3	52.2
PMP(t/2)	29.2	0.04	103.2	225.1	31.8	51.2
PMP ⁺ (g/2)	×	×	109.0	228.6	40.9	66.1
PMP(g/3)	37.1	0.08	107.3	226.9	29.0	46.8
PMP(m/3)	41.6	0.06	107.1	226.5	28.8	46.5
PMP(t/3)	32.3	×	107.0	226.3	28.7	46.4
PMP(g/5)	45.0	0.07	104.0	227.9	17.5	28.3

× – no data

One can find two glass transitions for liquid–crystalline polymer similar to the situation observed for the semicrystalline samples (PMP). Disubstituted poly(norbornene) of *cis* configuration with the number of methylene units into the side-chain 11 was studied. Unfortunately, the stability of the structures was not as well as for the PMP material. Moreover, the creation of smectic phase, which is required to the second glass transition existence, was only possible under special conditions [14–16]. These restrictions narrowed the number of samples useful to this study. The examples of DSC traces are presented in Fig. 1b and the thermodynamic parameters are listed in Table 1b. Although the reason for the existence of two T_g is different from that of PMP, the behaviour of both macromolecules shows some similarity. In both cases, two fractions of the amorphous phase of different arrangement were detected. Also, the driving force for the adoption of the structure with microphase separation of two

amorphous fractions was confirmed [16]. Because the smectic phase (CK(11)) requires a partial positional order of the main-chain, two amorphous fractions exhibit different fluidity. The side alkylene chains, rather flexible, contribute to the lower transition, $T_g(1)$, whereas the norbornene main-chains, with restricted fluidity due to the smectic order in the sample, contributed to the higher transition, $T_g(2)$. This system is more complicated due to more numbers of moieties existed in the monomer. Therefore, it must be noticed here, that the transition, which is postulated as two glass transitions, should be deconvoluted into three transitions, likely, including that one concerned with mesogens fluidity (transition of the mesogens from the glass to the smectic state). However, such an idea requires further structural investigations, e.g. neutron or X-ray scattering measurements.

Table 1b Transition temperatures ($T_g(1)$, $T_g(2)$, T_i - temperature of isotropisation), enthalpies (ΔH_i) and the change of specific heat ($\Delta C_p(T_g)$) of the polynorbornene derivative CK(11)

Samples	$T_g(1)/^{\circ}\text{C}$	$\frac{\Delta C_p(T_g)}{\text{J}(\text{g}^{\circ}\text{C})^{-1}}$	$T_g(2)/^{\circ}\text{C}$	$T_i/^{\circ}\text{C}$	$\Delta H_i/\text{J g}^{-1}$
CK(11/I)	25.4	0.385	54.5	150.9	7.27
CK(11/II)	25.1	0.508	43.3	150.2	6.98
CK(11/III)	21.5	×	×	150.8	9.68
CK(11/IV)	23.5	0.329	37.0	149.8	6.92
CK(11/V)	20.4	0.397	×	149.1	8.15

× – no data

Frequency (temperature) dependent mechanical spectroscopy is very important because some relaxations in complex systems are stronger dielectrically than mechanically. The studied polymers exhibited peaks in mechanical spectra, which were not detected by dielectric measurements [25, 26]. DMTA spectra are shown in Figs 2a and 2b for PMP (with peaks assigned α_g , α_c , δ) and CK(11) (with peaks assigned α_{Sc} , α_{Mc} , SMA), respectively. In both cases the origins of α -relaxations differ but there is one common point. The features of the α relaxations reflect some difference in the restrictions of the chain mobility. It means that the chains must be located in the miscellaneous fractions of the amorphous areas. DMTA spectra at 3 Hz for the films cast from carbon tetrachloride solution of different PMP concentration are presented in Fig. 2a. The same tendencies can be observed as compared with the opaque and transparent films cast from other solutions [18]. The temperature range can be divided into three subranges (I, II, III) accorded with the DSC data. In the first one α_g relaxation occurs, corresponding to the molecular motion of the chain building the 'real' amorphous structure whereas the second one reveals α_c relaxation connected with the semi-ordered amorphous structure. δ relaxation is activated in the third subrange, the initial temperature of which is the beginning temperature of the melting process (approx. 140°C). α_g relaxation is modified depending on the used substratum, which the solution is cast on (Table 1a and [18]). The supermolecular structure of PMP films is also sensitive to both the PMP concentration and the temperature of PMP dissolving. The higher PMP concentration is the lower intensity of loss peaks

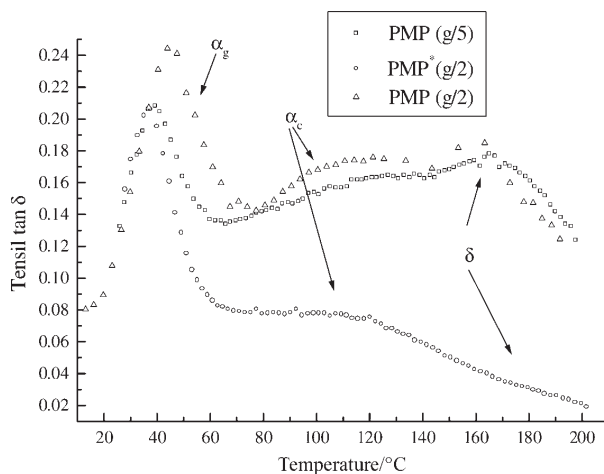


Fig. 2a DMTA data of loss tangent of the samples PMP prepared under different conditions. The presented curves were obtained for 3 Hz

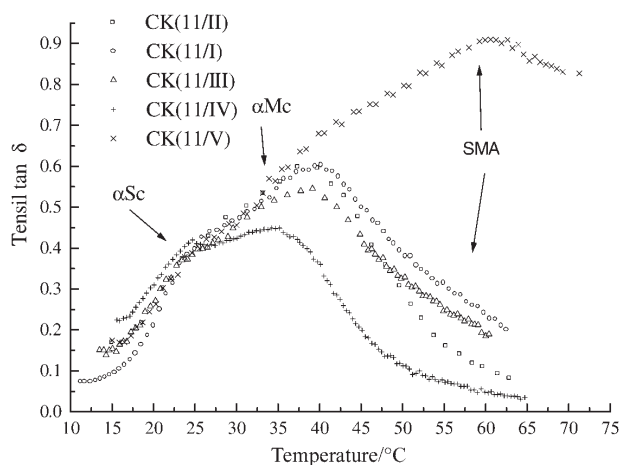


Fig. 2b DMTA data of loss tangent of the samples CK(11) prepared under different conditions. The presented curves were obtained for 3 Hz

for both amorphous fractions is. Because the lower degree of crystallinity was found in the case of PMP(g/5), it would mean that the fluidity of the backbone in the 'semi-ordered' amorphous structures is less restricted as compared with PMP*(g/2). The maximum of the tangent loss is shifted, with PMP concentration, towards to higher temperature about 7°C for α_c relaxation. This relaxation occurs at the lowest temperature in the case of the opaque PMP films. Most likely, the vicinity of the crystalline domains (showing a characteristic shape [19]) from one side and the presence of completely disordered amorphous phase from the second side makes this region less dense (more porous). Moreover, the specific arrangement of the crystal forms in

the opaque films, makes this region less stressed that results in easier activation of α_c relaxation (occurs at lower temperature). As was shown previously [18, 26], curves or straight lines could represent both α_g and α_c relaxation in Arrhenius plots. Also for the samples described in this paper both tendencies were observed.

Three molecular motions were detected for the poly(norbornene) derivative in a studied temperature range. Their origin was explained earlier based on SAXS, DETA and DMTA studies [14, 16, 25]. In this work only two of them will be discussed, those defined as side-(α_{Sc}) and main-(α_{Mc}) chain α relaxation. They are connected with methylene groups and norbornene chain motions, respectively. DMTA method was applied in the frequency range from 0.03 to 100 Hz and the temperature range covering the glass transition zone. Thermal history of the samples was chosen in such a way that the fluidity of chains decrease or increase due to structural changes. For detailed description of the thermal history of the CK(11) samples see experimental parts and [14–16]. The recorded dynamic mechanical spectra are complex. The peaks are rather broad and overlap themselves. The relaxations, most likely, do not occur with one relaxation time. No mathematical fitting procedure was applied to deconvolute such spectra. The curves, $\tan\delta \rightarrow f(T)$, vary a little as compared with each other. One can suppose that it is a result of different thermal regimes applied to the sample preparation. In the system of layered structure (smectic A phase [14]), fluidity of the norbornene main chains is rather big and the peak connected with α_{Mc} relaxation is the highest, CK(11/I), Fig. 2b. The lowest peak of the α_{Mc} relaxation was recorded when the distance between smectic layers increased, CK(11/IV). According to the model [16], the fluidity of the norbornene backbone is more restricted now because it must adopt its conformation to the arrangement of mesogens. The backbone chain is more stretched. The peak reflected α_{Sc} relaxation is a little higher for this supermolecular structure although the side-chains should be stretched, that would decrease methylene groups fluidity. Most likely, when the distance between smectic layers increases the amount of methylene groups building the amorphous layers increases, too. That would be a reason for such a recorded peak rise. This explanation is supported by the relaxation behaviour of the sample drawn over one hour, CK(11/III). Although the sample showed a smectic structure before the drawing procedure, the layered structure was completely demolished. In that case some recrystallisation occurs in a temperature range from 27 to 72°C (DSC curve, Fig. 1b). The peak represented α_{Mc} relaxation is higher as compared with the CK(11/IV) sample. The model of the structure and the problem of mesogens and main-chain interaction were discussed in detail earlier [14, 16].

One may not give a rule, which would be proper to describe α relaxations. When the line of Arrhenius' plot exhibits some curvature, it means that the molecular motion depends on a free volume in a polymer system. It should be true for the motions in which chains or their longer fragments take part, e.g. micro Brownian motions. There is no definition of α relaxation but one can treat this process just in this way. We can find in literature a lot of dielectric and mechanical data showing different Arrhenius plots, however, the problem of the relationship between the ordered (crystalline or liquid crystalline) and unordered phases has not been addressed. Most likely

this is a reason for different representations of α relaxations in Arrhenius plot. Two miscellaneous fractions of amorphous phase reflected by different chains fluidity should be taken into account in mathematical descriptions. Probably, if we used a parameter of order in a mathematical formula, which would reflect an arrangement of chains in amorphous fractions, we would find a proper description expressed only by one equation. This mathematical description, together with the results of free volume studies, will be proposed in a separate paper, which is in progress.

Conclusions

Thermal analysis is a useful tool to study oriented materials. The orientation induced by semi- or liquid-crystallinity results in the appearance of constrained and unconstrained amorphous structures. We should distinguish both types of amorphous fractions that would give better descriptions of relaxations. One fraction behaves as if it were a bulky amorphous material ('real') whereas the other one ('semi-ordered') behaves as if it were a partially ordered structure. It results in two types of loss peaks interspersed along the temperature scale. This peak reflected the mobility of the 'semi-ordered' fraction appears to arise from any of several causes: motion of defects in crystal domains; motion of folds or chain ends at the surface crystals. α relaxation in the 'real' amorphous structure reveals micro-Brownian motions. The heights of both loss peaks are quite sensitive to the amount of free volume, which is increased by quenching and decreased by annealing. The 'semi-ordered' amorphous fraction peak height is also very sensitive to the type of the ordered phase (crystal or liquid crystal) and the morphology of the crystallites (opaque or transparent films). The molecular motion related to α_c relaxation might be treated as a precursor for melting transition. It must be emphasised that the co-existence of the amorphous and crystalline phases or the amorphous and liquid-crystalline phases, e.g. in the case of semicrystalline or liquid-crystalline polymers, results in different properties of the amorphous phase. Therefore, it is supposed that the co-existed amorphous phase could be treated as a 'fingerprint' of the ordered phase, crystalline or liquid crystalline. Most likely, it would be possible to classify the co-existed amorphous phases according to their origin. It means that each crystalline structure would possess its own characteristic amorphous interphase.

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