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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

DYNAMIC MECHANICAL CHARACTERIZATION OF MOLECULAR MOTION IN A WIDE TEMPERATURE RANGE OF VARIOUS POLYMERS CONTAINING PROPYLENE UNITS

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Abstract

The temperature transitions for a series of flexible polymers containing propylene units were studied by dynamic mechanical spectroscopy. It was found that the gradual activation of the local motion of different structural units involved in polymers occurs with increasing temperature. Initially, the rotation of the side groups, such as side methyl groups, is activated and on further heating the main chain structural units show their local motions. It is important that the temperature interval of the appearance of the local motion of each structural unit is almost independent of the presence of other structural units. Accordingly, the polymers investigated can be divided into two groups. The activation of the local motion of the most rigid structural unit determines the glass transition in the first group of polymers. The glass transition of the polymers of the second group takes place at a higher temperature which depends on the content of side methyl groups and the intermolecular interaction. The increased influence of both these factors on the cooperative amorphous motion of polymers of the second group leads to their increased T_g values.

Keywords: dynamic mechanical properties, flexible polymers, glass transition, molecular mobility

Introduction

The relaxation spectra of flexible amorphous polymers, which show the changes in their molecular mobility with temperature, include the local motions of small group of atoms and cooperative motion in the temperature range of glass transition [1, 2]. The relaxation spectra of crystallizable polymers of low crystallinity (<30%) are characterized well and the reported spread of T_g is small for these polymers because of a minimal influence of the crystallites on the molecular mobility in the amorphous regions. The T_g values are also relatively unambiguous for the semi-crystalline polymers with the crystallinity in the range of 30–60%. Normally, these polymers are capable of being quenched to various levels of crystallinity to estimate T_g a function of fractional crystallinity.

However, there is some controversy in the literature concerning T_g of highly crystalline polymers without bulky side groups, in particular, linear polyethylene (PE) [2–6], and poly(oxymethylene) (POM) [2, 7–9]. Normally, these polymers can-

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not be quenched to a low level of crystallinity because of their high crystallization rates. The strong constraining effect of crystallites on the molecular motion in the amorphous region makes the interpretation of the thermal transitions observed for such polymers difficult.

The following classification of the temperature transitions in crystalline polymers is now generally accepted [1, 8]:

1. transition at $T<T_g(L)$ which is associated with local motion;
2. transition at $T_g(L)$ which is the glass transition of unconstrained amorphous regions;
3. transition at $T_g(U)$ which is associated with glass transition in amorphous region constrained by crystallites;
4. transition at $T_{\alpha c}$, corresponds to motion in crystalline regions associated with premelting.

Some empirical relationships such as $T_g(L)/T_m=0.5$; $T<T_g(L)/T_g(L)=0.75$; $T_g(U)=F(\alpha)$ may help to resolve the uncertainties in the assigning transitions for highly crystalline flexible polymers [8].

Using the concept of the double glass transitions we have analyzed the relaxation transitions in solid POM [9]. However, in our analysis instead of the empirical relationships, we suggested another criteria. Based on comparison of POM with other oxide polymers, such as poly(ethylene)(oxide),poly(trimethylene)(oxide), poly(tetramethylene)(oxide), and poly(propylene)(oxide) (PPO), we found some general features of the development of molecular mobility in solid oxide polymers with temperature. It has been established that the activation of the local motions of two structural units involved in the oxide polymer, namely CH_2-groups and the ether bond (–O–), takes place, at –120 and –80°C, respectively. The appearance of the local motion of the ether bond (–O–) which is the most rigid structural unit of these polymers determines the temperature interval of their glass transition T_g=–70°C. Moreover, we have suggested that POM has two glass transitions because of its high crystallinity: 1. $T_g(L)$ which is equal –70°C; 2. $T_g(U)$ which is characterized by a broad temperature interval (–30 – +70°C).

However, even keeping in mind this mechanism it is still difficult to compare the molecular mobility of these oxide polymers and polymers of other chemical structure. In particular, it is difficult to explain a considerable difference between T_g of PPO, which is an oxide polymer, and T_g of polypropylene (PP) which is polyolefin.

The object of this work is to study the temperature dependences of the dynamic mechanical characteristics for various flexible polymers containing propylene units together with other different structural units, in particular ether bond –O–, ketone carboxyl group –(C=O)–, and carbonate carboxyl group –O–(C=O)–O–. The detailed discussion of the relaxation transitions of these polymers reveals the correlation between the chemical structure and molecular mobility in solid flexible polymers.

Experimental

The chemical structures of the polymers in this study are given in Table 1. The polymers (except for PPO) have a low degree of crystallinity or are amorphous (we used PP with a low degree of isotacticity). Table 1 also shows the data obtained from analyses of DSC heating traces for these polymers (Fig. 1). Based on the DSC data we estimated that crystallinity of the studied polymers is below 25%(crystallinity of PPO is about 60% [12]).

Table 1 Chemical structure, DSC, and X-ray data for studied polymers

Polymer	Monomer unit	T_g/°C	T_m/°C	Q_m/J g^{-1}	a/%
Polypropylene (PP)	$-CH_2-CH(CH_3)-$	–10	145	11.0	6*
Poly(propylene ketone) (PCO)	$-CH_2-CH(CH_3)-(C{=}O)-$	20	70	12.0	22**
Poly(ethylene-propylene ketone) (EPCO)	$-\{CH_2-CH_2-(C{=}O)\}_x-$ $\{CH_2-CH(CH_3)-(C{=}O)\}_y-$ (x:y=1:1)	9	50; 90	13.0	23**
Poly(propylene carbonate) (PPC)	$-CH_2-CH(CH_3)-O-(C{=}O)-O-$	33	–	–	–
Poly(propylene oxide) (PPO)	$-CH_2-CH(CH_3)-O-$	–70	70	12.5	60*

*DSC data; Q_m^{*}=188 J g^{-1} for PP [10] and Q_m^{*}= 144 J g^{-1} for PPO [11]; ** X-ray data [13]

The dynamic mechanical properties were studied using a version of the resonance method related to transverse oscillations of a vertically positioned polymer film of the cross-section 0.2×0.5 mm^2 and 30 mm in length in the temperature range from –160 to 200°C. The resonance oscillation frequency (f_r) was varied from 400 to 40 Hz. Modulus E was calculated according to the formula

$$E = 4\pi^2 lmf_r/S$$

where l and S are the length and cross-sectional area of the polymer film, and m is the weight of the load.

The error in E is determined by the error in the measurements of geometric dimensions of the film and f_r. We assumed that the dimensions of the polymer film did not change through the whole temperature range examined. Therefore, the error of values of E was primarily due to the error in measuring f_r which was rather small (±0.1 Hz). Hence, the transitions in temperature dependences of E were identified with high accuracy. The mechanical loss tangent (tanδ), was calculated from the width of the resonance curve Δf at the $1/\sqrt{2}$ of the maximum

$$\tan\delta = \Delta f/f_r$$

The error in the determination of tanδ does not exceed 2%.

Calorimetric characterization of the polymers were carried out using a Perkin Elmer DSC-7 analyzer in an atmosphere of helium at the temperature range –150 – +200°C at a scanning rate of 20°C min^{-1}. The polymer sample weights were 10–15 mg.

Results and discussion

The temperature dependences of *E* and tanδ for PP are given in Fig. 2a. The broad transition at –100°C usually reported for PP [2, 14–16] is shown by broken line. Instead of this single transition we observe two transitions at –120 and –80°C designated by I and II, respectively. Both these transitions have a small intensity. The most intense transition III is observed at –10°C, where the DSC heating trace of PP (curve 1 in Fig. 1) shows a jump in heat capacity associated with the glass transition.

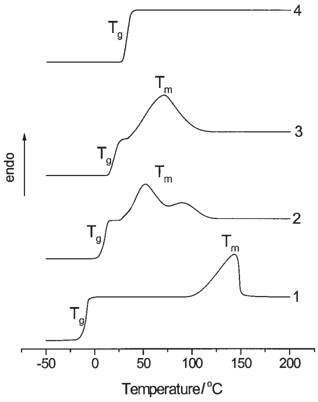

Fig. 1 DSC heating traces for (1) PP, (2) PCO, (3) EPCO, and (4) PPC (heating rate 20°C)

According to the mechanism of the molecular mobility in oxide polymers [9], transition I at –120°C is associated with the activation of the local motion of CH_2-group. We supposed that transition II can also be related to the activation of the carbon atom with side methyl group. According to [2], initiation of the rotation of the side methyl groups occurs only above –200°C. Therefore, one can suggest that the molecular mobility of the PP amorphous chains with temperature includes:

1. the rotation of the side CH_3-groups which appears at –200°C;
2. the activation of the local motion of CH_2-group and $CH(CH_3)$-group which occurs at –120 and –80°C, respectively;
3. the cooperative amorphous motion at –10°C;
4. premelting of PP crystallites at 110°C.

Figures 2b and 2c show the temperature dependences of *E* and tanδ for two flexible polyketones containing, except propylene units, ketone carboxyl groups. There

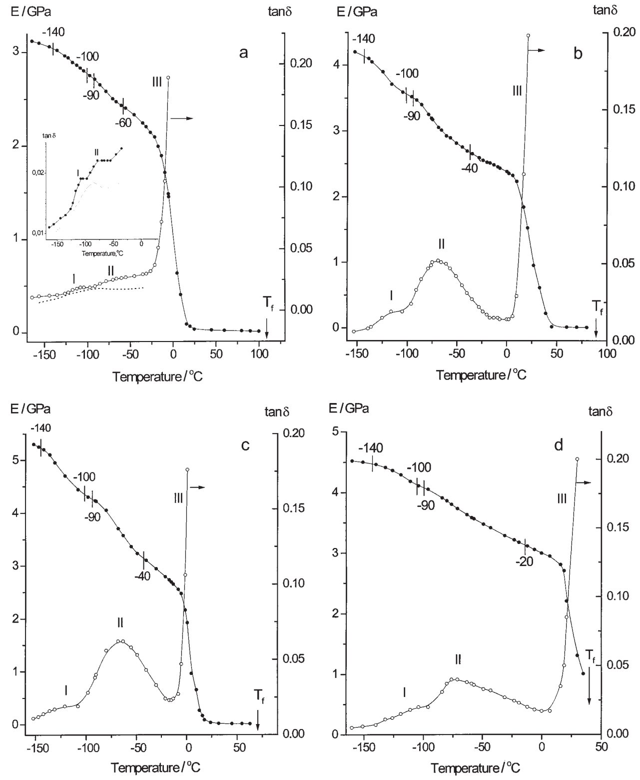

Fig. 2 Temperature dependences modulus E and mechanical loss tangent (tan δ) for (a) PP, (b) PCO, (c) EPCO, and (d) PPC

are three transitions in the mechanical spectra of both polyketones. Transition I at –120°C is associated with the appearance of the local motion of CH_2-groups. According to [2], carboxyl group involved in the main chain of flexible polymers shows its motion in the temperature range from –90 to –40°C. The appearance of the local motion of $CH(CH_3)$-group takes place in the temperature range from –90 to –60°C. Therefore, transition II at –60°C can be related to the simultaneous appearance of the local motions of $CH(CH_3)$- and (C=O)-groups. Transition III is associated with the glass transition of polyketones. The difference between the T_g of PCO (20°C) and EPCO (9°C) will be explained below. DSC data show that melting in both polyketones begins above 50°C, while their flow temperature T_f, is 70 and 90°C, respectively.

Figure 2d shows the temperature dependences of E and tanδ for aliphatic polycarbonate with propylene and carbonate carboxyl groups. The relaxation spectra of this polycarbonate is characterized by the existence of three transitions. The transition at –120°C is associated with the appearance of the local motion of CH_2-groups. The transition at –60°C can be related to the simultaneous activation of the local motions of $CH(CH_3)$- and –O–(C=O)–O-groups. Finally, the transition at 33°C is associated with the cooperative amorphous motion. The sample of polycarbonate begins to flow at 40°C.

The reported relaxation spectra of PPO is characterized by the existence of two transitions at –120 and –70°C [2]. According to the suggested mechanism of the molecular mobility in oxide polymers [9], the transition at –120°C is associated with the appearance of the local motion of CH_2-groups while the transition at –70°C is related to the simultaneous activation of the local motions of $CH(CH_3)$-groups and ether bond –O– which determines the glass transition temperature of PPO. Moreover, a very small mechanical transition at –185°C is found for PPO [2], which, similar to the transition at –200°C for PP, is associated with the rotation of side CH_3-groups. Similar behavior is not obtained for other studied polymers containing propylene units. Nevertheless, it may be assumed that the rotation of their side CH_3-groups also begins at –200°C. Table 2 summarizes the temperature intervals of the appearance of the local motions of various structural units involved in the studied polymers.

Table 2 Temperature intervals (°C) of the activation of the local motion of the structural units involved in the studied polymers.

CH_3–	–CH_2–	–$CH(CH_3)$–	–(C=O)–	–O–(C=O)–O–	–O–
–200	–140–100	–90–60	–90–40	–90–20	–90–40

According to the experimental data the studied polymers can be placed in the following row on the increasing T_g: PPO, PP, EPCO, PCO, and PPC. One can see that only the glass transition for PPO is associated with the local motion of the most rigid structural unit. The cooperative amorphous motion of the other polymers activates at a higher temperature. The explanation of this difference can be obtained by the comparison of polymers containing propylene units with oxide polymers.

Due to a small polarity of the ether bond oxide polymers are characterized by a low level of the intermolecular interaction. As a result of the absence of side groups and the weak intermolecular interaction, the cooperative amorphous motion in oxide polymers is determined by the appearance of the local motion of the most rigid structural unit, namely the ether bond.

The macromolecules of PPO contain one side methyl group per three main chain bonds. This content of side methyl groups seems to be not enough to influence considerably the cooperative amorphous motion. Hence, the glass transition of PPO is determined by the appearance of local motion of ether bond, which is its most rigid structural unit.

PP has one side methyl group per two main chain bonds. The increase in the content of side methyl groups leads to the fact that the amount of the free volume which is needed for the cooperative amorphous motion may be reached for PP only at –10°C while its most rigid structural unit, $CH(CH_3)$-group, shows mobility at –80°C.

It is interesting to compare PP with polyacetaldehyde, $[–CH(CH_3)–O–]_n$ with T_g about –20°C [2]. Similar to PP, the macromolecules of this oxide polymer contain one side methyl group per two main chain bonds and, similar to PP, its glass transition also occurs at higher temperatures than the activation of the local motion the ether bond.

PP is followed by polyketones in the studied polymer row. It is known that the polarity of a ketone carboxyl group is higher than the polarity of an ether bond. As a result of the stronger intermolecular interaction, the value of the free volume, which is needed for the glass transition, may be reached for polyketones at higher temperature in comparison with PP, in spite of a smaller content of side methyl groups (contrary to PP, there is one side methyl group per three main chain bonds for PCO and six main chain bonds for EPCO). On the other hand, because the content of methyl side groups for EPCO is less than that for PCO the T_g value for EPCO is 9°C while this value for PCO is 20°C. However, the T_g for EPCO does not reduce to the temperature of the activation of the local motion of ketone carboxyl group (–30°C) which is the most rigid structural unit of polyketones. These results seem to indicate that the strong polarity of ketone carboxyl groups exceeds the influence of the steric factor associated with the existence of side methyl groups.

The carbonate carboxyl group in PPC shows higher polarity than the ketone carboxyl group. Therefore, the $T_g = 33°C$ of PPC is higher than T_g of polyketones.

In summary, the flexible polymers in this study containing propylene units can be divided into two groups. PPO in which the glass transition is determined by the activation of the local motion of the ether bond (the most rigid unit) is related to the first group. The other polymers belong to the second group. The glass transition of the second group takes place at a higher temperature, which depends on both the content of methyl side groups and intermolecular interaction. The increase in the influence of both these factors on the cooperative amorphous motion of the second group of polymers results in increases in their T_g. The picture emerging from the dynamical mechanical behavior of the series of polymers containing the propylene units and comparison of these data with oxide polymers can be used to explaning the thermal motion in the whole class of flexible polymers.

The gradual activation of the local motions of different structural units involved in macromolecules occurs on increasing the temperature. At first, the rotation of side groups is activated, while at further heating the main chain structural units show their local motions. The temperature interval of the appearance of the local motion of each structural unit is almost independent of the presence of other structural units.

According to this scheme the activation of the local motion of the most rigid structural unit is closely related to the glass transition of polymers of the first group. Both oxide polymers and linear PE belong to this group. In accordance with this scheme, the glass transition of PE is determined by the appearance of the local motion in non-constrained amorphous regions of its only structural unit, CH_2-group, which occurs at –120°C.

The concept of the double glass transitions for highly crystalline polymers can be applied to polymers of the first group. In this case, the most rigid structural unit in the unconstrained amorphous chains and that in the amorphous chains with different restraints from the crystallites show their motions in the same temperature interval. However, this motion in the amorphous chains constrained by crystallites at this temperature is only local, while the glass transition of such constrained amorphous chains occurs at a higher temperature, which, in turn, depends on the degree of restriction.

The majority of flexible polymers such as PMMA, PVC, PS PET, aliphatic polyamides and polyurethanes are related to the second group. The cooperative amorphous motion in these polymers takes place at a higher temperature than the appearance of the local motion of the most rigid structural unit. The increase in the content of side groups and intermolecular interaction leads to the increase in the T_g values of polymers of the second group.

It is also important to emphasize that any addition of plastisizers can, as a rule, reduce the T_g values only of polymers of the second group due to the decreasing of the intermolecular interaction, while, according to this concept, polymers of the first group can hardly be plastisized.

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