

# Microscopic dynamic aspects of the free radical decay acceleration in sub- $T_g$ region in atactic poly(propylene)

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Free radical decay in  $\gamma$ -irradiated atactic poly(propylene) (a-PP) and microscopic chain dynamics in the same polymer have been studied by electron spin resonance and quasi-elastic neutron scattering simultaneously. It was found that an acceleration of the decay at the first acceleration temperature  $T_{acc,1} = 190$  K in the sub- $T_g$  region correlates not only with the literary values of the Vogel temperature  $T_0$  for  $\alpha$ -segmental dynamics, but also with the onset temperature of the so-called fast motion at  $T_f$ . The other acceleration temperature  $T_{acc,2} = 250$  K agrees not only with the macroscopic glass transition temperature  $T_g$  from DSC measurement, but also with the course of conformational transitions as evidenced by the recent two-dimensional  $^{13}\text{C}$  NMR study on the same sample. The relationships between  $T_{acc,1}$ ,  $T_f$  and  $T_0$  both for a-PP as a typical polymer with the simple chemical structure and for the more complex polymers studied previously, where  $T_{acc}-T_0$  correlation is present but  $T_{acc}-T_f$  correlation absent, are discussed. © 1997 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

In general, the stability and reaction behaviour of the free radical species in solid polymers depend on the structural and dynamic properties of the matrix<sup>1,2</sup>. In studies of the most representative process, i.e. free radical decay, in some cases correlations were found between its kinetic parameters such as the rate constants and transition and/or relaxational characteristics from traditional thermodynamic and relaxation techniques [calorimetry (DSC), dynamic-mechanical and dielectric spectrometries<sup>3</sup> or spectroscopic methods such as NMR]. A connection of the global decay with phase transitions at the melting temperature  $T_m$  in semicrystalline polymers or with glass transitions at the glass transition temperature  $T_g$  in amorphous phase of amorphous and semicrystalline polymers is rather trivial; the situation in the glassy state below  $T_g$  is due to the absence of temperature or/and activation-energy correlations which are still unclear. It may mean that some other motional modes, undetectable by classic methods, can participate in an approach of the decaying free radicals. For these reasons, an application of other techniques monitoring microscopic dynamics such as neutron scattering methods<sup>4,5</sup> may be useful.

In the previous paper<sup>6</sup> we have found for a series of five amorphous thermoplastics—poly(vinyl)acetate (PVAc), polyethyleneterephthalate (PET), polymethylmethacrylate (PMMA), polystyrene (PS) and polycarbonate (PC)—a new correlation between the change of the temperature coefficient of rate constant at the so-called acceleration temperature<sup>†</sup>  $T_{acc}$  in the sub- $T_g$  region and the so-called

Vogel temperature  $T_0$  from the empirical Vogel–Fulcher–Tamman–Hesse (VFTH) equation describing the  $\alpha$ -segmental dynamics in the amorphous phase:

$$\phi_\alpha = \phi_{\alpha\infty} e^{-\frac{B}{T-T_0}} \quad (1)$$

Similar acceleration of the decay can be traced at the decay of photolytically generated end-chain macroradicals in PMMA<sup>7</sup>. The existence of this correlation independent of the detail chemical structure of the reacting macroradicals indicates that the acceleration of the decay process has the physical nature and that it is connected with the onset of segmental dynamics already in the glassy state below the thermodynamic glass transition temperature  $T_g$ . However, the newly found correlation has two relative shortcomings. First, it has only been found up to now for plastics, so it is unclear whether it is valid for elastomers also. Secondly, the particular  $T_{acc}$ s have been compared with the literary data on  $T_0$ .

Recent research of the microscopic chain dynamics in amorphous polymers with simple chemical structures around  $T_g$  using neutron scattering (NS) revealed the onset of the so-called fast motion at  $T_f$  slightly near  $T_0$ <sup>8–10</sup>. We expect that combined investigations of the chain microdynamics and of the free radical decay reactivity will contribute to a better understanding of the microscopic aspects of the transport stage and consequently, the combination aspect of the free radical decay.

The subject of the present paper is to carry out on suitable chosen amorphous elastomer—atactic poly(propylene)—both the kinetic study of the free radical decay by electron spin resonance (ESR) and the dynamic study of the microscopic chain mobility by quasielastic neutron

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† We prefer to use the more suitable term of acceleration temperature  $T_{acc}$  instead of the original transition temperature  $T_r$ <sup>6</sup>

scattering. The aims of this work was to verify the validity of the  $T_{acc}-T_0$  correlation for a typical elastomer as well as to reveal some molecular aspects of the decay acceleration in sub- $T_g$ - and  $T_g$ -regions. Finally the presented findings on this simple polymer will be compared with the results obtained so far on structurally more complicated polymers<sup>6</sup>.

## EXPERIMENTAL

### Sample

Amorphous atactic poly(propylene) (a-PP) with a molecular weight  $M_w = 1.02 \times 10^6$  and polydispersity  $M_w/M_n = 2.4$  was used. The glass transition temperature  $T_g$ , determined by differential scanning calorimetry using a Perkin-Elmer DSC-7 instrument with a heating rate of  $20^\circ\text{C min}^{-1}$ , is 259 K.

### ESR measurements

Free radicals in a-PP were generated by  $\gamma$ -irradiation with a  $^{60}\text{Co}$  source with a dose rate  $0.8 \text{ kGy h}^{-1}$  in vacuum at liquid nitrogen temperature. The total radiation dose was 4.8 kGy.

ESR spectra in dependence on temperature and time were registered with an X-band ESR spectrometer Varian E-4 equipped with a temperature controller E-257. The free radical concentrations and their time evolutions were obtained using the strong-pitch standard and utilizing an IBM PC. To obtain the so-called decay curve, ESR spectra were monitored as a function of temperature; the temperature was increased in a stepwise fashion at intervals of 10 K in the range 123–263 K and at each step the sample was kept for 9 min. To obtain the rate coefficients of free radical decay, an experimental set-up was similar with two differences, one in the temperature range investigated, i.e. from 173 to 263 K and in the time interval of 36 min at each temperature stage of the kinetic measurements.

### Neutron scattering measurements

Quasielastic neutron scattering measurements were carried out with inverted geometry time-of-flight (TOF) spectrometers LAM 40<sup>11</sup> and LAM 80ET<sup>12</sup> installed at the pulsed spallation cold neutron source in the National Laboratory for High Energy Physics, Tsukuba, Japan. The energy resolutions are  $\delta\epsilon = 0.2$  and  $0.02 \text{ meV}$ , respectively. The energy windows are below 10 and  $0.5 \text{ meV}$ , respectively. The length of the scattering vector  $\mathbf{Q}$  at the elastic position ranges from 0.2 to  $2.6 \text{ \AA}^{-1}$  for LAM-40 and from 0.2 to  $1.64 \text{ \AA}^{-1}$  for LAM-80ET. The measurements were performed in the temperature range from 18 to 330 K.

The observed TOF spectra were converted into dynamical scattering law  $S(\mathbf{Q}, \omega)$  after correcting for empty can scattering, counter-efficiency, self-shielding and the incident neutron spectrum.

In order to see the characteristic features of the fast process of a-PP, the excess scattering spectra due to the fast motion were analysed following the curve-fitting method to extract the spectra widths, which correspond to the inverse of the characteristic time of the motion. In the present work we assumed that the density of vibrational states above  $T_g$  would be damped to be represented as a frequency-independent component below  $\sim 3 \text{ meV}$ , so that the observed spectra were fitted with the following model function convoluted with the resolution function of the

spectrometer<sup>13</sup>:

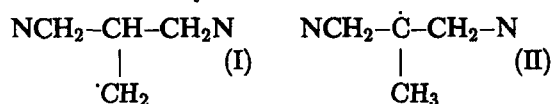
$$S(\mathbf{Q}, \omega) = C(\mathbf{Q}) \{ [1 - A_f(\mathbf{Q})] \delta(\omega) + A_f(\mathbf{Q}) L(\Gamma_f, \omega) \} + B(\mathbf{Q}) \quad (2)$$

where  $C(\mathbf{Q})$  is a constant,  $B(\mathbf{Q})$  represents the damped vibrational density of states,  $A_f(\mathbf{Q})$  is a fraction of the fast process, and  $\delta(\omega)$  and  $L(\Gamma_f, \omega)$  are a delta-function and a Lorentzian with the half-width at half-maximum (HWHM)  $\Gamma_f$ , respectively.

## RESULTS AND DISCUSSION

### Spectral features of free radical

The ESR spectrum of a-PP  $\gamma$ -irradiated at 77 K and registered at the lowest accessible temperature of our experimental set-up (123 K) is in good agreement with published data<sup>14,15</sup> [Figure 1(a)]. The main feature is a sextet signal with a somewhat pronounced central quartet part with the total width of 13 mT. This signal is a superposition of two alkyl macroradicals<sup>15–17</sup>:



The sextet form of the spectrum is preserved throughout the whole temperature interval of our measurements. The relative intensities change with increasing temperature: the extreme peaks are intensified with respect to the central part of spectrum; the total spectral intensity is decreased (Figure 1(b)–(e)). These changes result from the simultaneous decay of methyl side-groups and of tertiary alkyl macroradicals as well, as from the transformation of less stable side-group centres (I) to more stable ones (II), so that the sextet from II dominates at higher temperatures<sup>15</sup>.

### Decay curve

Figure 2 shows the so-called decay curve of free radicals in a-PP in the temperature range from 123 K up to global disappearance in the vicinity of room temperature. Each point of the decay curve represents a free radical

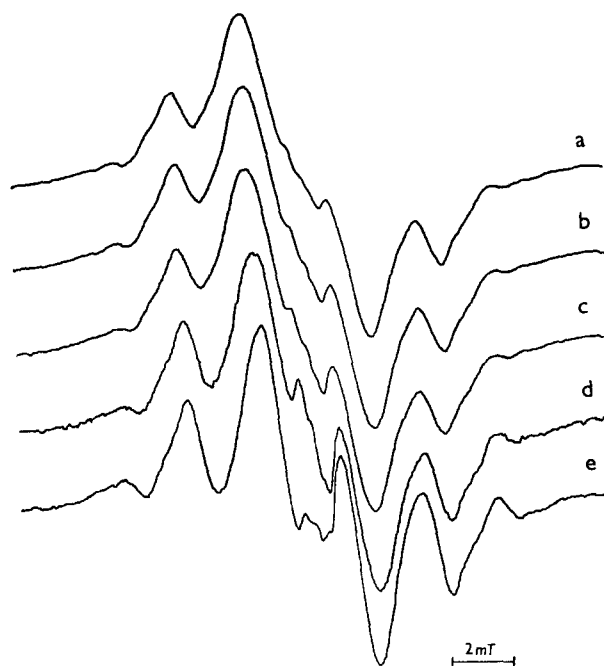


Figure 1 ESR spectra of a-PP  $\gamma$ -irradiated at 77 K and measured at (a) 123 K, (b) 183 K, (c) 203 K, (d) 243 K and (e) 263 K

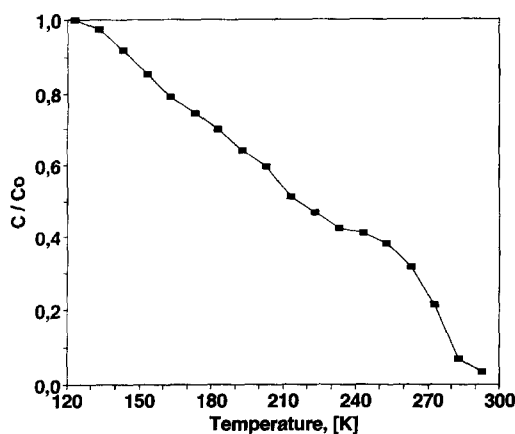


Figure 2 Decay curve of the free radicals for a-PP  $\gamma$ -irradiated at 77 K as measured from 123 K up to almost total decay at about room temperature

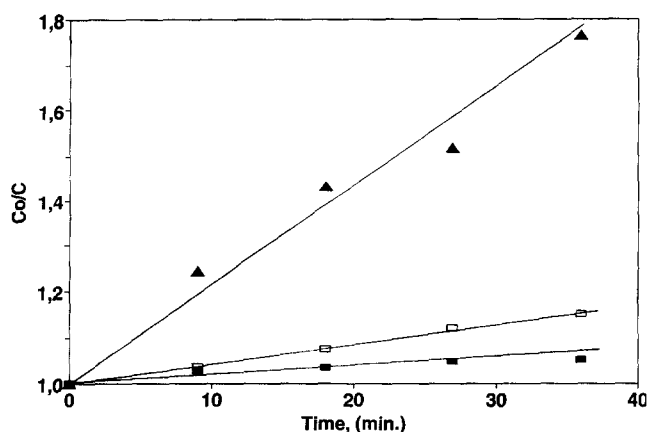


Figure 3 Tests of a second-order kinetic model for the macroradical decay in  $\gamma$ -irradiated a-PP at 183 K (■), 223 K (□) and at 263 K (▲)

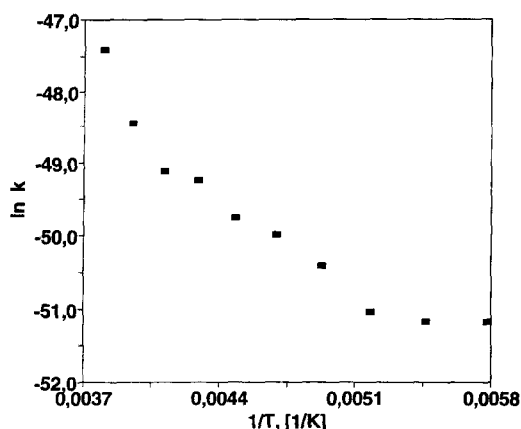


Figure 4 Arrhenius plot for the macroradical decay rate constants in  $\gamma$ -irradiated a-PP

Table 1 The results of Arrhenius analysis of the macroradical decay rate constants in  $\gamma$ -irradiated a-PP

Region	$\Delta T$ (K)	$k_0$ (g spin s <sup>-1</sup> )	$E$ (kJ mol <sup>-1</sup> )
1	173–193	$(2.3 \pm 0.2) \times 10^{-22}$	$2 \pm 0.2$
2	203–243	$(4.1 \pm 0.4) \times 10^{-19}$	$14 \pm 0.5$
3	253–263	$(5.6 \pm 0.2) \times 10^{-10}$	$57 \pm 1$

concentration in the relative expression with respect to  $C_0$  (123 K) =  $(3.3 \pm 0.05) \times 10^{17}$  spin g<sup>-1</sup> after thermal treatment with a temperature increment  $\Delta T = 10$  K for time  $\Delta t = 9$  min. Approximately three regions of different behaviour are evident. The first, up to about 230 K, is characterized by almost linear decrease in the relative concentration  $C/C_0$  with temperature. After the following second region of slowly decaying range between 230 and 250 K, the third region of very rapid decay takes place. This temperature region is characterized by the global disappearance of alkyl macroradicals which is in good agreement with the glass-liquid state transition at  $T_g^{\text{DSC}} = 259$  K.

#### Free radical decay kinetics

Information on the reaction behaviour of free radicals in solid polymers can be obtained from detailed kinetic measurements in a wide temperature interval. The results of such kinetic investigations are in Figures 3 and 4. Figure 3 shows a test of a second-order kinetic equation for the decay of alkyl macroradicals in the relative coordinates:

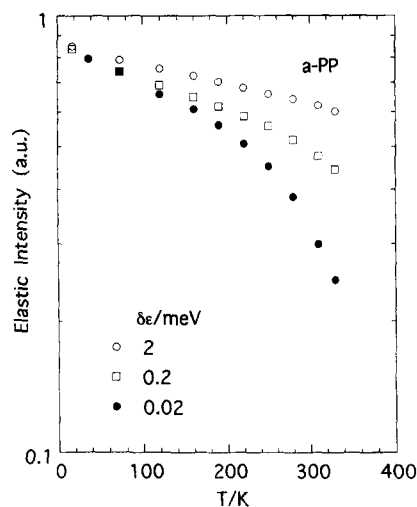
$$\frac{C_0}{C} - 1 = kC_0t \quad (3)$$

where  $C$  and  $C_0$  are the total free radical concentrations at time moments  $t = 0$  and  $t$ , respectively,  $k$  is the effective decay rate constant. Linearities these dependences confirm the validity of bimolecular character of the decay process. An Arrhenius plot in Figure 4 indicates the existence of three temperature regions of different kinetic behaviour between 173 and 263 K (see also Table 1). These regions can be characterized by two acceleration temperatures:  $T_{\text{acc},1} = 190$  K and  $T_{\text{acc},2} = 250$  K, which were obtained as the intersection points by solving two particular Arrhenius equations with respect to temperature.

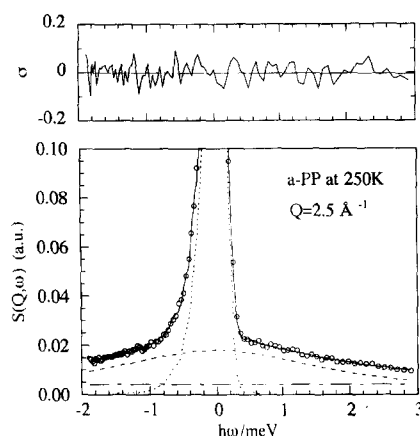
#### Microscopic dynamic properties

Most of the results of dynamic study on the same polymer by neutron scattering in a wide temperature interval from 18 to 330 K is presented elsewhere<sup>18</sup>. For this reason we mention the most important findings briefly and present some new results important in the context of our decay reaction investigation.

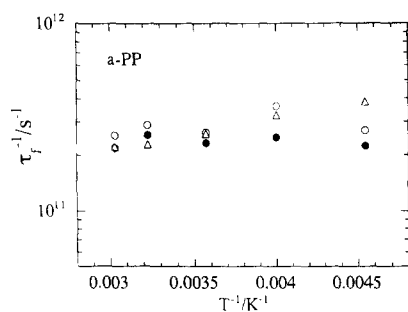
The dynamic scattering laws  $S(\mathbf{Q}, \omega)$  as a function of temperature exhibit typical features for amorphous polymers, i.e. a sharp central peak from elastic scattering decreasing with the increasing temperature and inelastic and quasi-elastic parts, which increases with the elevated temperature<sup>18</sup>. The temperature dependences of the elastic scattering intensity  $I_{\text{el}}(\mathbf{Q})$  observed at a scattering vector  $\mathbf{Q} = 1.64 \text{ \AA}^{-1}$  as a function of energy resolutions  $\delta\epsilon$  are in Figure 5. Logarithms of  $I_{\text{el}}(\mathbf{Q})$  for the lower energy resolutions (2 and 0.2 meV) decrease practically linearly in the whole temperature interval. On the other hand, for the highest energy resolution  $\delta\epsilon = 0.02$  meV  $\log I_{\text{el}}(\mathbf{Q})$  decreases linearly with increasing temperature up to 190 K. These findings show that besides the vibrational motion of hydrogen scatterers, the deviation from the linearity above 190 K indicates the onset of the so-called fast motional process. This onset temperature  $T_f$  is a quite in the vicinity of the Vogel temperature  $T_0$  ranging from 192 to 205 K<sup>19,20</sup>. On the basis of this agreement it has been concluded that the high frequency fast motion is a precursor of the lower frequency  $\alpha$ -segmental dynamics<sup>18</sup>. Similar results were found for further amorphous polymers with a



**Figure 5** Temperature dependence of the elastic intensity  $I_{el}(Q)$  at  $Q = 1.64 \text{ \AA}^{-1}$  for various energy resolutions  $\delta\epsilon = 0.02 \text{ meV}$  (●),  $0.2 \text{ meV}$  (□), and  $2 \text{ meV}$  (○)



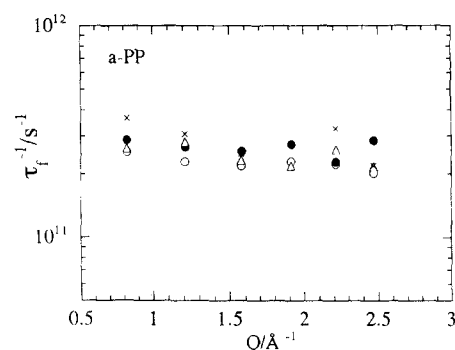
**Figure 6** An example of the results of curve-fit to LAM 40 spectrum of a-PP with equation (2). Elastic component (· · ·), quasielastic Lorentzian (fast process) (- - -), and flat background (damped vibrational density of states)(- · - ·).  $T = 250 \text{ K}$ ,  $Q = 2.5 \text{ \AA}^{-1}$



**Figure 7** Temperature dependence of inverse of the characteristic time  $\tau_f^{-1}$  of the fast process for a-PP evaluated from the curve-fit.  $Q = 2.5 \text{ \AA}^{-1}$  (○),  $1.9 \text{ \AA}^{-1}$  (●),  $1.2 \text{ \AA}^{-1}$  (Δ)

simple chemical structure such as polybutadiene and polyisobutylene<sup>8-10</sup>.

An example of the fit of the scattering spectrum using the model equation (2) is shown in *Figure 6*. The resulting characteristic time of the fast motion  $\tau_f = 1/\Gamma_f$  is almost independent of temperature, see *Figure 7*, suggesting that the fast process is a localized motion. The idea that the fast process is a localized motion is also supported by the



**Figure 8**  $Q$  dependence of inverse of the characteristic time  $\tau_f^{-1}$  of the fast process for a-PP evaluated from the curve-fit.  $T = 330 \text{ K}$  (○),  $310 \text{ K}$  (●),  $280 \text{ K}$  (Δ),  $250 \text{ K}$  (×)

fact that the characteristic time  $\tau_f$  is almost independent of scattering vector  $Q$ , see *Figure 8*. It is worth pointing out that the fast process does not include a motional passing over a potential barrier because the activation energy of  $\tau_f$  is almost zero. In other words, the fast process is a motion within a potential well, i.e. a cage motion. Therefore, the fast process is not related to conformational transition of polymer bonds, which requires an activation energy of a single bond C–C rotation ( $8\text{--}24 \text{ kJ mol}^{-1}$ ) from molecular-mechanic simulations of a model compound of a-PP<sup>21</sup>.

#### Correlation between kinetic and dynamic temperature characteristics for a simple polymer: a-PP

Having the kinetic characteristics of the free radical decay and the dynamic characteristics of microscopic dynamics, we can confrontate both phenomena and obtain a better understanding of molecular causes of the change in the decay reaction behaviour with temperature.

Good agreement between the first acceleration temperature  $T_{acc,1} = 190 \text{ K}$  and the Vogel temperature  $T_0 = 192$  and  $205 \text{ K}$ <sup>19,20</sup> confirms previously found empirical correlation for plastics<sup>6</sup> for typical amorphous vinyl elastomer, at least. Moreover, a good agreement between the acceleration temperature  $T_{acc,1}$  and the onset temperature of the fast motion  $T_f$  indicates direct connectivity of both processes. This is, the free radical decay acceleration above  $190 \text{ K}$  is directly linked to the appearance of the fast motion in a-PP. The question arising now is: what is the nature of this link? At present, the precise origin of the fast motion observed in many low-molecular substances as well as polymer substances around the glass transition temperature is still unclear. The fast process exhibits two typical relaxational features: (i) a quasielastic spectral shape; and (ii) a strong intensity increase with increasing temperature. In contrast, its apparent quasielastic width is found to be essentially temperature independent, contrary to the expectation for a thermal activated process and indicating a localized cage character of this motion. As for the decay reaction, this process is on a rather larger scale and certainly slower than one with fast mobility. Our idea on the mutual link of both processes is similar to that on the relationship between the fast motion and the  $\alpha$ -segmental relaxation<sup>9</sup>. According to this notion, the fast motion is a precursor of the glass transition by forming suitable conditions for the course of the larger scale and slower segmental dynamics. By analogy, some segmental motion must govern a mutual approach of the free radical reactants into their contact and consequently their combination interaction. One possibility may be outlined in terms of a free volume model<sup>22,23,6</sup>.

According to this idea, any molecular motion can take place when the accumulation of free volume leads to formation of voids with a size comparable to that of the moving units. An original version of this model for a disordered system of hard spheres implicitly assumes that free volume is redistributed without energy change<sup>22</sup>. In an extended version for more realistic systems with a Lennard–Jones potential, this free volume is similarly defined as part of the total free volume<sup>23</sup>, but without any specification of elemental motional source causing this redistribution. Because the fast process is a local cage motion with the characteristic time  $\tau_f$  independent of temperature, it may be a suitable candidate for such a free volume reorganizer. Thus, the fast motion works as a free volume reorganizer, allowing the migration of very small free volume entities through the matrix and subsequently their occasional local accumulation required for the course of the more obvious spatial and energy segmental motion. Such a picture seems to be supported by the fact that while the fast process is practically barrierless, the activation energy of the decay in the second region slightly exceeds the value of one-barrier transition in a-PP<sup>21</sup>. In addition, recent investigation of the same sample of a-PP from a free volume point of view by positron annihilation spectroscopy (PALS) revealed that the mean free volume hole size at 200 K is about  $80 \text{ \AA}^3$ , i.e. 1.5 times the van der Waals volume of the basic structural unit of a-PP- $\text{CH}_2\text{-CH}(\text{CH}_3)\text{-}$ <sup>24</sup>. This fact suggests that the free volume situation enables the local participation of segmental mobility of conformational type in the second decay region, at least.

As the temperature is increased, the second acceleration in the decay occurs above 250 K. This  $T_{\text{acc},2}$  is in good agreement with  $T_g = 259 \text{ K}$  from the DSC measurement. It indicates that the decay of more distant centres is influenced by a global segmental dynamics in an elastic state, at least. Recently, it was evidenced on the same sample by two-dimensional <sup>13</sup>C NMR that this segmental dynamics is characterized by the change of conformational state of bonds<sup>25</sup>. A PALS investigation leads to the mean free volume hole size of about  $95 \text{ \AA}^3$  at  $T_{\text{acc},2}$ , i.e. about two monomer units<sup>24</sup>. These findings are quite consistent, because there is a sufficient free volume fluctuation for the course of conformation-segmental motion above  $T_g$ . Thus, we conclude that in the third temperature region the global free radical decay is connected with the course of conformational transitions of bonds in chains.

#### *Correlation between kinetic and dynamic temperature characteristics for amorphous polymers of the complex chemical structure*

In the previous section we have confirmed the existence of  $T_{\text{acc}}-T_0$  correlation for a typical amorphous vinyl elastomer. Moreover,  $T_{\text{acc}}-T_0-T_f$  correlation in a-PP revealed a microscopic cause of the free radical decay acceleration in the sub- $T_g$  region. Thus, the enhancement of the decay rate constant with temperature above  $T_0$  is associated with the segmental dynamics which is closely connected with the onset of the fast motion. Originally,  $T_{\text{acc}}-T_0$  correlation has been found for a series of five amorphous thermoplastics: PVAc, PET, PS, PMMA and PC<sup>6</sup>, so that one may also expect similar  $T_{\text{acc}}-T_f$  relationships for these polymers. However, such a situation is not as straightforward as it initially appears. For two polymers of this series, PS<sup>13,26,27</sup> and PC<sup>28</sup>, it was found that the fast motion sets in at the far lower temperatures than a particular  $T_0$  for the  $\alpha$ -segmental mobility. Because a

common feature of these polymers is the presence of bulk side groups or many internal degrees of freedom it was suggested that these factors are the source of the fast motion<sup>28</sup>. Indeed, very recently in the case of PS it was evidenced that the origin of the fast motion consist in a libration motion of side phenyl groups and that a dynamic coupling between side groups and main chain takes place just below  $T_g$ <sup>13,27</sup>. On the basis of these facts we can understand why for the structurally complex polymers  $T_{\text{acc}}-T_f$  correlation in the sub- $T_g$  region is absent, although the  $T_{\text{acc}}-T_0$  relation is still present. The reason is that the decay of more distant free radicals just below  $T_g$  requires the larger scale segmental dynamics. Thus,  $T_{\text{acc}}-T_0-T_f$  correlation appears to be a feature of simple polymers with small side groups. In future studies we will concentrate on the confirmation of this prediction on further suitable model polymers. The results will be presented elsewhere.

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