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ORIGINAL CONTRIBUTION

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Study of the influence of physical aging on macroradical decay in poly(methyl methacrylate)

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Abstract The macroradical decay in poly(methyl methacrylate) samples with different thermal histories was investigated in the temperature interval 20-100 °C using ESR spectroscopy and the second order kinetic model. The rate constants exhibit two different regimes with the transitions at $T_{tr} = 68 \pm 1$°C which are independent of thermal treatment. For $T < T_{tr}$ and $T > T_{tr}$ the rate constants as well as the corresponding activation parameters are sensitive to history because of different physical microstructures. The compensation law, i.e., the linear relation between $\ln k_{0,eff}$ and E_{eff}, was analyzed in terms of the so-called compensation quantities k_c and T_c and a proximity between $T_c = T_{tr}$ and $T_0 = 53 \pm 3$ °C – Vogel temperature for α-segmental dynamics was found. A comparison of kinetic and dynamic data suggests that the decay of terminal macroradicals in the low-temperature region is controlled by secondary relaxations and that the α-mobility contributes to a more rapid decay at higher temperatures below T_g.

Key words Physical aging – macroradical decay – compensation law – relaxation dynamics – poly(methyl methacrylate)

Introduction

The glassy state of amorphous polymer is the nonequilibrium state of a disordered system, the physical and physico-chemical properties of which depend on formation history [1]. The physical microstructure of a glassy matrix contains information not only about formation (e.g., by cooling from the elastic state at a given rate), but also about the following thermo-mechanical history (e.g., by annealing at $T < T_g$) [2]. The phenomenon of structural relaxation sometimes called physical aging was extensively studied by classical thermodynamic methods, such as dilatometry [3] and calorimetry [4]. The decrease in volume and enthalpy with time is connected with the reduction in the overall free volume as well as with the change in conformational population. Recent microscopic investigation using positron annihilation spectroscopy [5] showed that this decrease is connected with a decreased number of holes, with mean size practically unchanged. Although there is no agreement concerning the temperature range of structural relaxation [6–8], the greatest influence on the properties is observed after annealing at temperatures in sub-T_g region, i.e., from 10° to 30 °C below T_g. The mentioned microstructural changes lead to a decrease in intrinsic mobility and to significant changes in mechanical [9], dielectric [10] and diffusion-transport properties [11].

From the theoretical point of view a quasi-punctual model of the amorphous phase [12, 13] is one of the most successful microscopic treatments for a simulation of temperature and time changes in thermodynamic and mechanical properties of glasses. This model is based on two concepts. Firstly, the amorphous phase is considered to be a close packing of segments where induced thermal fluctu-

ations of density, i.e., defects, occur. Secondly, the defect diffusion process is assumed to result from molecular motions which are strongly correlated; this correlation effect is assumed to be hierarchical, implying a series distribution of characteristic times and elementary β-mobility is the basic process of α-relaxation.

More attention has recently been paid to the study of the effect of physical aging on the processes occurring at a molecular level. The results of photochromic, fluorescence [14–16] and ESR studies [17, 18] indicate a significant influence of aging on the dynamics of these local processes. We have recently demonstrated the relations between decay characteristics of terminal macroradicals and varying thermo-mechanical history of polycarbonate (PC) [19].

Because of its commercional importance, poly(methyl methacrylate) (PMMA) is one of the well examined polymers from the point of view of the influence of structural relaxation on volume [20], enthalpy [21, 12, 22], and dynamic-mechanical [20, 12, 13] properties. Recently, phototransformational [15, 23] and spin probe reorientational [17] processes were investigated as a function of thermal history. On the other hand, the influence of physical aging on macroradical decay has not yet been examined, although the behavior of macroradicals in PMMA was studied in view of the effect of different parameters, such as pressure and cross-linking [24].

The influence of microstructural reorganization as a result of physical aging below T_g on kinetic characteristics of macroradical decay in PMMA was studied by the ESR method. The results were compared with the analogous ones obtained for PC [19] and our findings were interpreted qualitatively by comparing kinetic characteristics with literature dynamic data and applying microscopic explanation of changes in both enthalpy and dynamic-mechanical properties in PMMA obtained using a quasi-punctual defect model [12, 13].

Experimental

Poly(methyl methacrylate) (PMMA), Röhm GmbH, Darmstadt, Germany, $M_n = 6 \times 10^4$ and the polydispersity $M_w/M_n = 2$ was used. The glass transition temperature T_g of reference sample was 115 °C which indicated a rather higher content of syndiotacticity.

Three types of samples with the following thermal histories were investigated.

1) The quenched sample (q- PMMA) as reference material was obtained after elimination of the previous history by heating at 130 °C for 30 min and subsequent cooling to room temperature.

2) The aged samples (ag- PMMA) were prepared by annealing portions of the reference material at $T_a = 100$ °C and $T_a = 85$ °C for the same time of $t_a = 15$ weeks.

The DSC method was used for quantitative macroscopic characterization of samples in terms of the extent of structural relaxation by means of the relative change in excess enthalpy. A Perkin–Elmer DSC 7 instrument with a computational data station enabling the integration of difference thermograms was used.

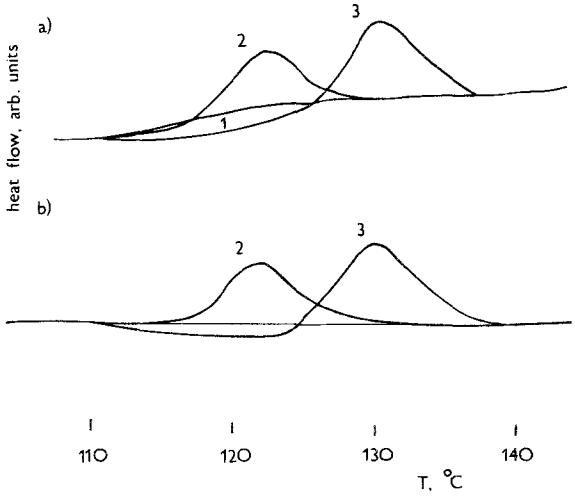
The samples were evacuated for 10 h at 10^{-4} MPa and then irradiated with a ^{60}Co source at the temperature of dry ice, the total radiation dose being 10.5 kGy. An ESR spectrometer Varian E-4 equipped with a temperature variator E-257 was connected with a computer Varian 610-100 and used for recording the spectra and for evaluating the kinetic behavior of macroradicals as a function of temperature and thermal history.

Results

DSC measurements

Figure 1 shows DSC thermograms of the reference and two physically aged samples. The peak features of annealed materials superimposed on the typical step effect of the glass transition of the reference sample reflect the accomplished structural relaxation monitored through enthalpy change in the system (Fig. 1a). Quantitative characterization was achieved by determining the relative extent of excess enthalpy relaxation. The actual enthalpy difference between reference and aged sample $\Delta H(T_a, t_a)$ was found by integration of difference thermograms (Fig. 1b)

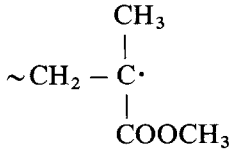
Fig. 1 DSC responses of PMMA samples with different thermal histories; a) original thermograms, b) difference thermograms; 1) reference, 2) 85 °C/15 weeks, 3) 100 °C/15 weeks



and is referred to the maximum excess enthalpy given by the relationship $\Delta H_{max}(T_a, t_a) = \Delta C_{P,g} \Delta T_a$, where $\Delta C_{p,g}$ is the difference between specific heats of elastic and glassy state $\Delta C_{p,g} = 0.30$ J/gK, which is in agreement with the published data [25] and $\Delta T_a = T_g - T_a$. The sample of ag-PMMA annealed at 100 °C has $\Delta H(100\,°/15w) = 3.7 \pm 0.05$ J/g which corresponds to the decrease in excess enthalpy equal to 82%, while the lower annealing temperature (85 °C) results in a smaller relative extent of enthalpy relaxation (by 46%).

ESR measurements

The ESR spectra of all three γ-irradiated PMMA sample's types exhibit a nine-line spectrum – Fig. 2. The nonet spectrum is generally ascribed to terminal macroradicals [24].



(I)

This signal remains constant over the whole temperature range of kinetic measurements from 20° to 100 °C except for very high temperatures of 90° and 100 °C where the relative intensities of nonet lines change slightly. This small change was attributed to a change in the distribution of conformations of terminal macroradicals [28].

The decay of terminal macroradicals (*I*) in glassy PMMA was investigated over a wide temperature interval almost up to T_g. Kinetic measurements were done using a new sample at a given reaction temperature during 30 min. Figure 3 shows the tests of the second order kinetic model at one relatively lower (40 °C) and one higher (80 °C) temperature respectively for all thermal histories examined. The linearity of plots confirms the validity of second order kinetics in the whole temperature interval:

$$\frac{1}{c(t)} - \frac{1}{c_0} = k \cdot t\,, \tag{1}$$

where c_0 and $c(t)$ are the concentrations at time $t = 0$ and t respectively and k is the decay rate constant. A more complicated kinetics of macroradical decay in PMMA has been described recently [29]. This kinetics was described by the time-dependent rate constant $k(t) = kt^{\alpha - 1}$. The coefficient α ($0 < \alpha \leq 1$) is a measure of the initial distribution of reactivity which is in operation especially at temperatures close to the glass transition point. This indicates a tight coupling of structural relaxation of the matrix with the proceeding chemical process. In our case, there is a special situation where $\alpha = 1$. This means virtually the same reactivity. The constant value of the parameter α means that the decay of centers takes place during a relatively short period measured practically under quasi-equilibrium conditions. This enables us to elucidate the influence of different thermal histories of matrices on the kinetic characteristics of macroradical decay.

Figure 4 shows the Arrhenius representation of the decay rate constants for terminal macroradicals of PMMA of various thermal histories. The effective activation

Fig. 2 Typical ESR spectra of terminal macroradicals in PMMA samples with different thermal histories 1) reference 2) 85 °C/15 weeks 3) 100 °C/15 weeks registered at room temperature

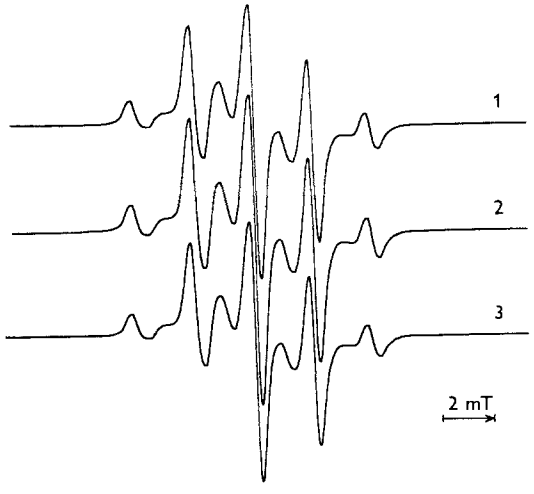
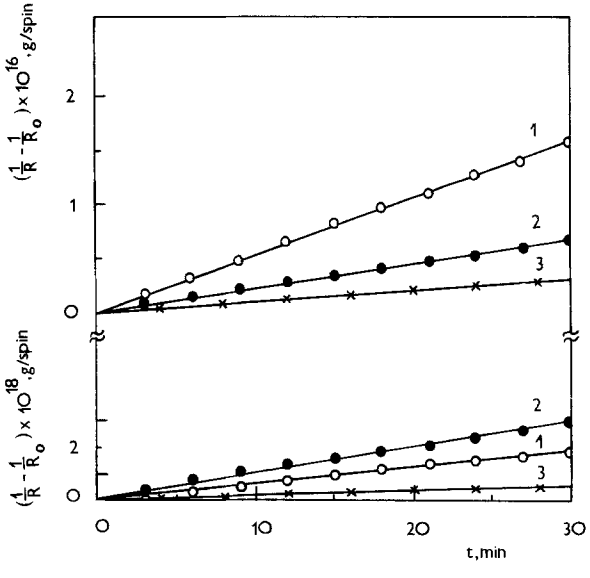


Fig. 3 Tests of the second-order kinetic model for macroradical decay in PMMA; 1) reference, 2) 85 °C/15 weeks, 3) 100 °C/15 weeks



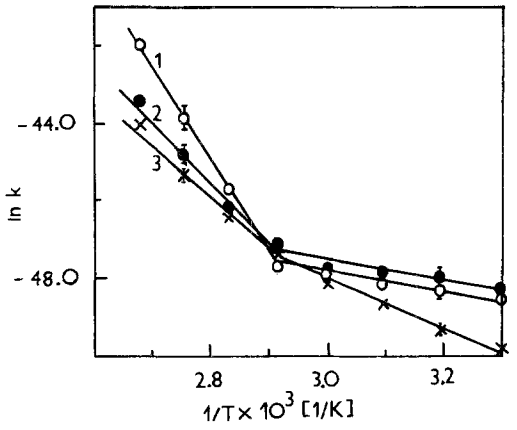


Fig. 4 Arrhenius plot of temperature dependence of the macroradical decay rate constants of in PMMA with different thermal histories; 1) reference, 2) 85 °C/15 weeks, 3) 100 °C/15 weeks

Table 1 Kinetic parameters of the Arrhenius plots for macroradical decay in PMMA samples with different thermal histories

Sample history		Temperature interval °C	$k_{0,\mathrm{eff}}$ g/spins	E_{eff} kJ/mol
Unaged		30–60	1.41×10^{-18}	19
		70–100	3.61×10^{10}	203
Aged	85 °C/15w	30–60	3.23×10^{-19}	14
		70–100	1.71×10^{0}	137
	100°C/15w	30–60	6.41×10^{-14}	49
		70–100	3.51×10^{-3}	119

parameters of decay reaction, i.e., the effective pre-exponential factors and effective activation energies, are summarized in Table 1.

Discussion

Our DSC thermograms are similar to those obtained by the Perez' group [12, 13] for variously aged PMMA samples. These were successfully simulated by using the quasi-punctual defect model [26]. The approach is based on the idea [26, 27] that the enthalpy decrease is modeled as diffusion and the following combination of the low-density and high-density defects in the matrix. Recent positron annihilation investigations [5] indicating a decrease in the number of free volume entities during sub-T_g annealing support the defect annihilation mechanism of structural relaxation in glassy materials. Accepting this idea, the order of samples according to the degree of defectness is: reference sample > sample aged at 85 °C/15 w > sample aged at 100 °C/15 w.

A common feature of the temperature dependence of the decay constants in Fig. 4 is the existence of the two temperature regions with different temperature coefficients. Transitions between these regions take place within a very narrow temperature interval and are practically independent of history: $T_{tr} = 67$ °C for the unaged sample, $T_{tr} = 68$ °C for the aged sample (85 °C/15 w) and $T_{tr} = 69$ °C for the aged sample (100 °C/15 w). The decay rate constants at temperatures above and below T_{tr} are different and reflect the fine influence of changed physical microstructural situation on chain mobility and consequently on macroradical decay.

In the low-temperature region from 20 °C to T_{tr} we observe a slightly faster decay in the aged sample 80 °C/15 w when compared with the reference material, but with the comparable effective activation energies about 17 ± 2 kJ/mol. Comparison of these values with an effective activation energy of γ-relaxation maximum 13 kJ/mol [30] indicates that the local mobility of side methyl groups controls an approach of reactants and their following decay by mutual combination. On the other hand, stronger physical aging results in a more significant decrease in decay rate constants and in an increase of the effective activation energy in the low temperature region. This fact is evidently related to an almost double decrease in excess enthalpy owing to a more extensive annihilation of microstructural defects during aging [12, 13]. This enthalpy decrease reduces the mobility of chain segments and the migration of free volume and results in slowing down the transport of macroradicals into the contact and finally their decay combination. The effective activation energy of decay of 49 kJ/mol is higher than the mean effective activation energy for γ-mobility and lower than that for β-relaxation maximum of 69–78 kJ/mol [13, 30, 31] obtained by classical relaxation experiments. However, very detailed analysis of a relative broad β-relaxation peak revealed the existence of a rather broad activation energy distribution ranging from 30 to 100 kJ/mol [32, 33]. Comparison of the decay activation energy in ag-PMMA (100 °C/15 w) with this activation energy distribution suggests that the low activation energy branch of the β-mobility may control the decay of reactants in the most densified sample.

The rate constants obtained for different starting thermal histories reach practically identical values at T_{tr} within the limits of experimental errors. This indicates an identical process which begins to control the transport and the following decay of terminal macroradicals at T_{tr} independently of the total enthalpy and thus free volume content. These transition temperatures are slightly above the so-called Vogel temperature $T_0 = 50$ °C [34] or 55 °C [20] of the empirical Vogel-Fulcher–Tamman equation for α–re-

laxation dynamics in an equilibrium state [35]:

$$\tau_\alpha = \tau_\infty \cdot e^{\frac{B}{T-T_0}}, \quad (2)$$

where τ_α is the relaxation time of α- relaxation maximum of the loss peak from relaxation spectroscopies, T is the absolute temperature and τ_∞, B and T_0 are the fitting parameters respectively. According to free volume interpretation, $T_0 < T_g$ is the temperature above which an equilibrium free volume and a mobility connected with it appears [20, 35]. This is supported by the well-known facts that in some polymers with well separated α- and β-peaks the former begins to appear already below the calorimetric T_g and that its peak has its maximum above T_g. Hence, the increased decay rate above T_{tr} may be connected with the possibility of the local course of α-segmental motion in some small regions of the otherwise glassy matrix below T_g [36].

At the reaction temperatures above T_{tr}, the rate constants are again sensitive to previous thermal treatment. The order of the rate constants is consistent with that of the relative extents of enthalpy relaxation. The activation energy decreases from 203 kJ/mol in the reference sample to 119 kJ/mol in the most aged sample. The effective activation energy for the reference sample is little lower than that of α-mobility in the non-equilibrium region below the glass transition of about 230 kJ/mol. This value was estimated from the shift factor data below T_g in PMMA [20].

An approximative activation energy agreement seems to confirm the dominant role of α-mobility in the reference sample at least. The effective decay activation energy decreases with the higher enthalpy relaxation extent. This is an opposite trend when compared with the behavior of pure α-mobility in a glassy state going from above T_g [37, 38]. The most remarkable feature of Arrhenius plots is actually their gradual leveling-off, i.e., the decrease in the difference between the effective activation energies in both the low- and high-temperature region, ΔE_{eff} with increasing extent of enthalpy relaxation. Apparently, this phenomenon represents a more general trend because we also observed it in our preceding investigations of PC [19]. In this case even the linearization of the kinetic curves to the final mean effective activation energy close to the value corresponding to the intense β-relaxation maximum was observed [19]. However, a comparison of PMMA with PC shows that complete elimination of transition does not appear for similar ΔT_a regardless of longer annealing time t_a (15 weeks vs. 12 days). This is evidently a consequence of different aging rates in PMMA as compared with PC [7]. But the confirmation of a possible approach to the mean E_β for PMMA requires verification in very time-consuming experiments. Our findings imply the shift in the character of the controlling process from more cooperative α-mobility in non-equilibrium state in the unaged sample to a more local mobility in the densified samples. Interestingly, the effective activation energy in the most aged sample of 119 kJ/mol is slightly higher than that of the high-energy branch of activation energy distribution of β-relaxation (100 kJ/mol) [31–33]. This suggests a small contribution of the cooperative mobility in the decay process.

Dynamic-mechanical PMMA measurements [13] at various stages of physical aging at two temperatures, viz. 80° and 103 °C which are very close to our annealing temperatures revealed that the mechanical spectra show a slight change in the strength of β-relaxation, but a considerable reduction in intensity in the temperature region between β- and α-relaxation maxima. The simulations of the temperature dependence of the loss tangent tan δ_m for different annealing conditions applying the idea of defects and the concept of hierarchical correlation motions indicate that these changes result from the hindrance to the course of cooperative α-mobility owing to a decrease in the matrix defectness [13]. As the decay of centers (I) in the high-temperature region is at least influenced by α-segmental dynamics, some relationship between the population of α-relaxation domains in differently annealed samples and the values of the decay rate constant could exist. In this sense our findings are apparently consistent with the microscopic picture of the quasi-punctual defect model about the mechanism of physical ageing.

The reaction system investigated is a unique case of the identical process of identical reactants in an identical matrix under different microstructural conditions. For this reason, it is suitable for testing the third kinetic law for reactions in condensed media, i.e., the compensation law. Figure 5 shows the validity of a linear relation between the logarithm of the effective pre-exponential factor and the effective activation energy:

$$\ln k_{0,\,eff} = A + B\,E_{eff}, \quad (3)$$

where A and B are the empirical coefficients equal to -47.7403 and 0.3543, respectively. The kinetic law may be discussed in terms of phenomenological parameters of compensation temperature T_c and compensation rate constant k_c [39]. According to the most general interpretation they may be regarded as characteristics of the processes having the same molecular mechanism [39]. Thus, we can write

$$k(T) = k_c \cdot e^{-\frac{E_{ef}}{R}\left(\frac{1}{T}-\frac{1}{T_c}\right)} \quad (4)$$

An analysis leads to values $T_c = 66\,°C$ and $k_c = 1.85 \times 10^{-21}$ g/spin s. It is remarkable that T_c is equal to T_{tr} which well approaches T_0 quite. A question arises about what is the common mechanism in the decay pro-

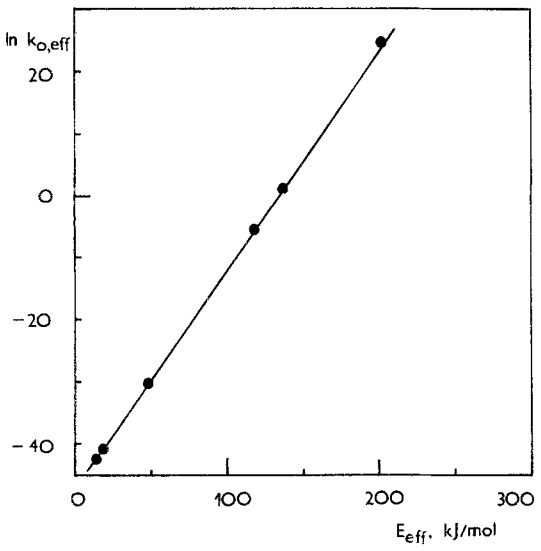


Fig. 5 Compensation graph for macroradical decay in PMMA with different histories

cesses of terminal centers below and above $T_c = T_{tr}$. Since the macroradical decay is controlled by the secondary and primary mobilities, our question can be reformulated to what is the common molecular mechanism in both movement types. Our tentative explanation is based on the above-mentioned leveling- off trend of $\ln k - 1/T$ curves with the increasing extent of enthalpy relaxation. For the most aged sample (100 °C/15 w) the broad activation energy distribution of β-mobility dominates the macroradical decay practically throughout the temperature interval with a small contribution from α-mobility at high temperatures. Johari's results show [40] that secondary relaxations in glassy materials take place in defect regions with the low local density, i.e., free volume. The localized molecular motions lead to defect diffusion through disordered matrices till the local free volume accumulation occurs at some place (in a form of a big hole or a number of small holes in a limited zone). This takes place at $T_{tr} \approx T_0$ where the cooperative α-mobility begins to appear. Our finding that T_{tr} is independent of total enthalpy and free volume level means that the temperature factor is dominant. On the other hand, at $T > T_{tr}$, not only temperature but also free volume content determines the contribution of cooperative α-mobility to the decay process. The lower the excess enthalpy and thus the free volume fraction, the lower the probability of the occurrence of local free volume regions enabling cooperative α-segmental mobility. This notion explains the observed decreasing trend in E_{eff} with the increasing enthalpy relaxation in the high-temperature region of the decay reaction.

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