Study of the influence of physical ageing and rejuvenation on macroradical reactivity in polycarbonate

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Amorphous polycarbonate with various mechanical and/or thermal histories was investigated via macroradical decay in the temperature interval between −30°C and 100°C by e.p.r. spectroscopy. The decay of end macroradicals was found to take place at low temperatures more rapidly in anisotropic drawn samples than in isotropic materials. The rate constants of both samples show breaks at ~20°C and 70°C and coincide at higher temperatures. After heating in the region below the glass transition temperature, the order of the rate constants is maintained but the decay is more rapid in aged samples compared to unaged materials. The concentration and kinetic characteristics are correlated with previous small-angle X-ray scattering results and the dynamic-mechanical relaxation results presented here and interpreted in terms of changes in free volume characteristics after cold deformation and/or annealing of polycarbonate.

(Keywords: physical ageing; rejuvenation; macroradical decay; polycarbonate)

INTRODUCTION

The non-equilibrium character of glassy amorphous and semicrystalline polymers becomes evident through processes such as physical ageing and physical rejuvenation. The former phenomenon involves the spontaneous recovery of thermodynamic quantities such as volume[1] and enthalpy[2] as well as dynamic properties such as mechanical and dielectric relaxations[3] during annealing at temperatures below the glass transition temperature (T_g). The latter process is a partial or complete elimination of the effect of ageing by mechanical treatment on a glassy polymer[3–6].

Various aspects of the thermomechanical history of glassy polymers have been extensively studied using common methods such as dilatometry[1,5], calorimetry[2,4] and mechanical and dielectric spectroscopy[3,6]. It is considered that the features of the glassy transition and the glassy state such as non-linearity, non-exponentiality, asymmetry and memory effects are connected with the distribution of the relaxation times and thus in the framework of the free volume concept of mobility not only with total free volume but also with the free volume distribution. This is why some non-traditional techniques have recently been used for measurements of these free volume characteristics. These methods include small-angle X-ray scattering (SAXS)[7–9], photoisomerization[10–12], fluorescence spectroscopy[13], positron-annihilation spectroscopy[14] and e.p.r. spectroscopy[15,16]. The results revealed that during ageing and rejuvenation not only does the total volume change but in some cases the distribution also changes.

In our previous paper[16] we have studied both processes in polycarbonate (PC) by means of the e.p.r. technique using stable radicals, i.e. the spin-probe method. It was found that the rotational mobility of these probes depends not only on the mobility of the matrix but also on the level of the free volume and its distribution. On the basis of the above-mentioned results[9,10,16] we may expect that the structural-dynamic modification of a glassy polymer might also influence other chemical properties. The aim of this report is to demonstrate this on macroradical reactivity in amorphous PC with various mechanical and/or thermal histories.

EXPERIMENTAL

The experiments were performed with PC (PC Macrolon 3100, Bayer, Germany) in plate form with the following basic characteristics: $M_n = 3.2 \times 10^4$, $\rho = 1.2\,\mathrm{g\,cm^{-3}}$ and $T_g = 150°\mathrm{C}$. The sample was pretreated before processing to remove internal stress and humidity. Four types of samples were studied:

1. isotropic, unaged (i,u)
2. isotropic, aged (i,a)
3. anisotropic, unaged (a,u)
4. anisotropic, aged (a,a).

The first type of sample was prepared by quenching from above T_g to room temperature. The third type of sample was obtained via so-called cold drawing at room temperature on a tensile testing instrument. The relative elongation was ~20%. The second and fourth groups of samples were prepared by annealing the first and third types at 125°C for 12 days.

All samples were evacuated and then subjected to γ-radiolysis at liquid nitrogen temperature to generate macroradicals. The total radiation dose was 3.6 Mrad. The structural–chemical and reaction–kinetic behaviour of the macroradicals was studied by means of a Varian E-4 e.p.r. spectrometer with a temperature variator

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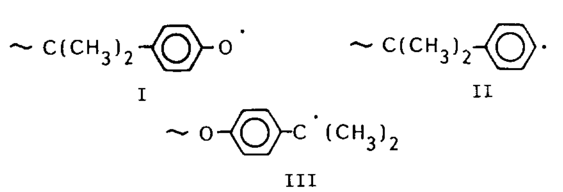
E-257. The total concentration was determined with a Varian computer.

The dynamic-mechanical properties were measured on an automatic torsion pendulum Myrenne ATM 3 in automatic mode with the following parameters: frequency 2 Hz, heating rate 3°C min^{-1}. Shear moduli (G', G''), loss coefficient ($\tan \delta_G$) and relative change in length were evaluated as a function of temperature.

RESULTS AND DISCUSSION

Decay curves and kinetic behaviour of macroradicals

All PC samples γ-irradiated at 77 K *in vacuo* gave identical e.p.r. spectra. The temperature dependence of all spectra was also very similar. According to detailed spectral analysis[17], γ-radiolysis of PC at 77 K leads to free-electron formation and chain scission resulting in the formation of end macroradicals only. The low temperature spectrum is a superposition of the signals from trapped free electrons [phenoxy(I), phenyl(II) and alkyl macroradicals(III)], the main portion being assigned to radical species I and II with I being dominant.



This work also shows that sample heating from the irradiation temperature of 77 K leads to the step-wise decay of all radical species in the region of intensive local small-scale β-relaxation at ~ −100°C[18]. The trapped free electrons decay in this region and so measurements were carried out at temperatures at which the presence of trapped electrons did not cause complications.

Figure 1 shows the decay curves for all the samples obtained during gradual heating from −30°C up to total decay at about 130°C for temperature increments of 10°C and for time increments of 13 min. It can be seen that the extent of macroradical decay and its change depends on sample treatment. The following tendencies were observed: both unaged samples show a slightly larger decay in comparison with the corresponding aged samples but a relatively less steep decrease at higher temperatures. Further, there is a smaller extent of decay in isotropic samples in comparison with the anisotropic material regardless of the following heat treatment. These trends in the decay curves suggest a relatively strong influence of structural reorganization in the glassy state on macroradical decay reactivity.

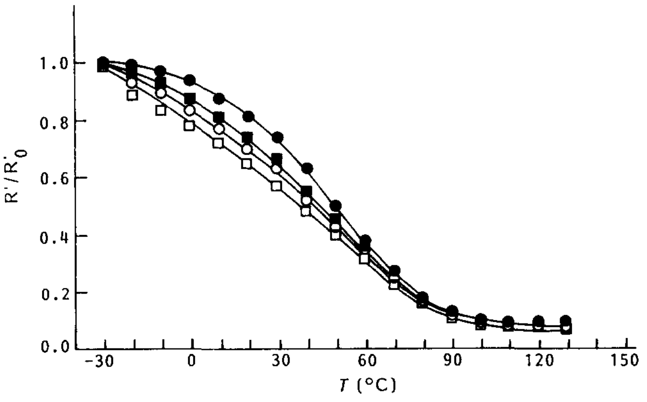


Figure 1 Decay curves of PC with various mechanical and/or thermal history: (○) i, u; (●) i, a; (□) a, u; (■) a, a

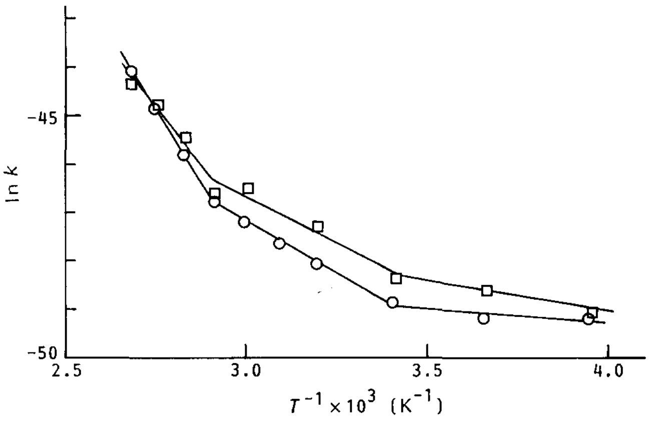


Figure 2 Arrhenius plot for the decay of end macroradicals in unaged samples: (○) i, u; (□) a, u

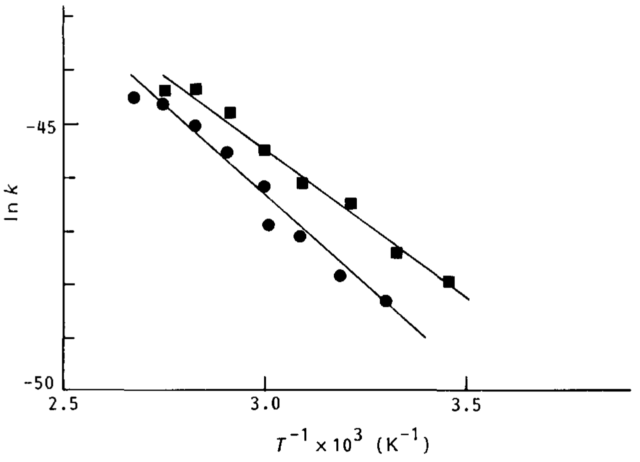


Figure 3 Arrhenius plot for the decay of end macroradicals in aged samples: (●) i, a; (■) a, a

Detailed information on the influence of mechanical and/or thermal treatment on the macroradical reactivity in amorphous PC is provided by kinetic investigations. The decay of the end macroradicals in all types of samples generally obeys the second-order kinetic equation.

Figures 2 and *3* give the results from kinetic analysis in an Arrhenius representation. The corresponding activation parameters are listed in *Table 1*. It is evident that the structural-dynamic modification of glassy amorphous PC has a pronounced effect on the decay of end macroradicals.

In the case of the unaged samples the macroradical decay takes place more rapidly in the deformed anisotropic material than in the reference sample except at very high temperatures near T_g. Their common feature is the existence of three temperature regions of different reactivity: (1) from low temperature up to room temperature; (2) from 20 up to 70°C; and (3) above 70°C. On the other hand, at low temperatures the aged samples show a very slow, barely detectable decay. A linear increase in the rate constants is observed above room temperature without any break at ~70°C, with the decay being a little more rapid in the anisotropic sample than in the corresponding isotropic material.

Table 1 Arrhenius parameters for macroradical decay in amorphous PC with various thermomechanical histories

Sample history	Temperature interval (°C)	$k_{o,eff}$ (g spin^{-1} s^{-1})	E_{eff} (kJ mol^{-1})
Isotropic, unaged	−20 to 20	7.1×10^{-21}	6.0
	20 to 70	2.8×10^{-15}	37.9
	70 to 100	2.6×10^{-6}	96.6
Isotropic, aged	20 to 90	5.3×10^{-12}	56.5
Anisotropic, unaged	−20 to 20	8.8×10^{-20}	10.9
	20 to 70	5.4×10^{-16}	32.0
	70 to 100	7.2×10^{-9}	78.9
Anisotropic, aged	20 to 90	2.6×10^{-13}	45.7

Correlations between structural-dynamic characteristics and macroradical reactivity

The structural-dynamic situation in a polymer generally determines the reaction behaviour of its macroradical species. For this reason it is useful to discuss the relationship between the structure of a matrix and its mobility as measured by SAXS[9,16] and dynamic-mechanical spectroscopy, respectively.

Previous studies on the phenomenon of plastic flow in glassy polymer showed that cold drawing, which is induced by collective motions of chain segments[19,20], leads to an increase in the free volume as well as to an extension of the free volume distribution[9,16]. The relative stability of the thermal density fluctuation, i.e. the free volume fluctuation in drawn sample as evidenced in the course parallel with the isotropic material up to ~40°C (Figure 9 in ref. 16) indicates the quasi-static character of the free volume distribution at relatively low temperatures. The following relaxation of thermal density fluctuations above 40°C[16] correlates with the β'-relaxation maximum and also with the change in length of the sample as seen in the dynamic-mechanical spectrum in *Figure 4*. In other words, cold deformation of PC at room temperature leads to formation of a frozen deformed network of entangled macromolecules[21] which is connected to the strong free volume redistribution. The onset of small-scale co-operative β'-mobility causes the release of this stressed network and results in the observed relaxation of the extended free volume distribution to the value for the reference sample[16]. The kinetic behaviour of the end macroradicals in the unaged PC samples shows two regions of different reactivity. These are connected with the above findings. More rapid decay in the cold sample in the temperature range from −20 up to 70°C relates to an extended free volume distribution i.e. weaker cage effect of the surrounding medium on the approach of the end macroradicals into a contact situation. This means that the structural aspect of the glassy matrix is a primary factor in the decay reactivity at relatively low temperatures up to ~70°C. The mobility plays a secondary role, i.e. β'-relaxation modulates the various free volume conditions in the neighbourhood of the reactants only. The second break at ~70°C correlates with the temperature parameter $T_o = 76$°C from Vogel's equation describing α_a-mobility in amorphous PC in the elastic state[22]. Its value is much below T_g for PC and represents formally the so-called divergence temperature at which the large-scale co-operative α_a-mobility disappears. From the free volume point of view[23] this corresponds to the zero equilibrium free volume connected with segmental mobility. However, actual amorphous PC with relatively stiff chains in the glassy state contains a relatively large portion of the frozen free volume, so that at sufficient thermal activation the α_a-mobility might locally take place well below T_g. This local course of the α_a-mobility probably removes all differences between the drawn and original unaged samples above 80°C in the SAXS[9] and present e.p.r. results. Thus, it seems that the mobility aspect is dominant in the control of free volume distribution as well as the decay reactivity in the high temperature region.

In both aged samples an elimination of the structural modification takes place[9,16]. The total volume and also the total free volume are reduced in comparison with the corresponding unaged samples. The values of the thermal density fluctuations in the aged samples are identical and also identical with the undeformed, unaged sample[9]. As for the dynamic behaviour, we find practically an identical level of mobility in both aged samples but a great reduction in comparison with the undrawn materials (*Figure 5*). The reactivity of the radical centres in the aged samples is quite different when compared with the unaged samples. Their stability below room temperature as manifested by an almost undetectable decay may be related to more compact aged matrices. On the other hand, the decays occur above room temperature somewhat rapidly without the break at ~70°C. These findings correlate with the onset of β'-mobility, which persists in both samples (*Figure 5*). In addition, the end macroradicals decay more slowly in the aged, undrawn material than in the aged, drawn sample. This fact seems to suggest a role for the fine local structural conditions on the macroradical decay for apparently the same overall structural and dynamic situation as measured by SAXS and dynamic-mechanical techniques.

Comparison of macroradical reactivity and radical mobility

This paper provides information on macroradical reactivity in PC with various thermomechanical histories. From detailed kinetic studies, i.e. the validity of second-order kinetics, follows the bimolecular decay mechanism for the end macroradicals I–III. For chemical

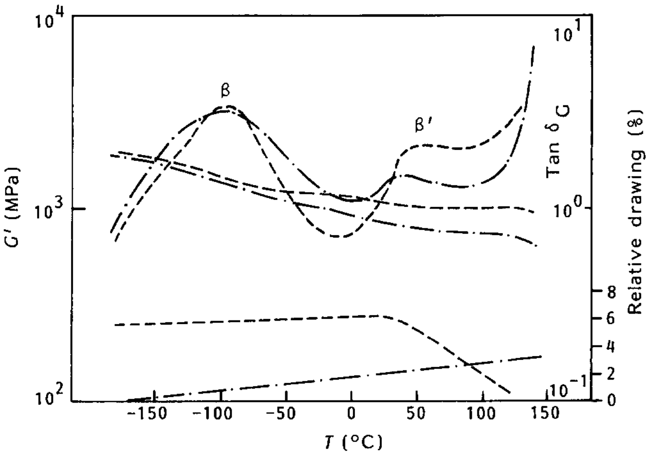


Figure 4 Temperature dependence of the shear modulus (G'), the loss tangent (tan δ_G) and the relative change in length for unaged samples: (—·) isotropic; (– –) anisotropic. The anisotropic curve is vertically shifted with respect to the isotropic curve

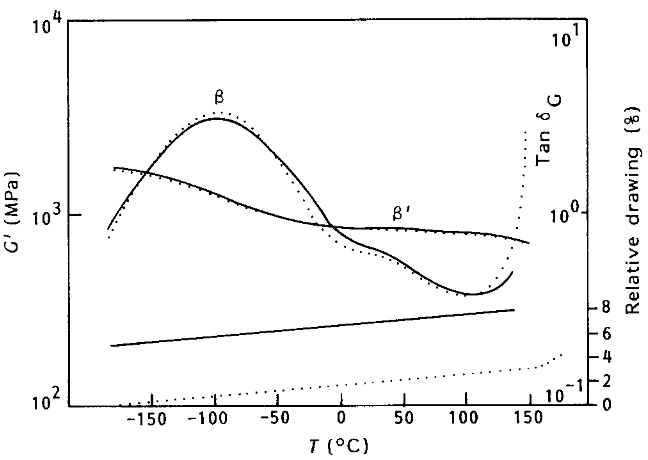


Figure 5 Temperature dependence of the shear modulus (G'), the loss tangent ($\tan \delta_G$) and the relative change in length for aged samples: (—) isotropic; (···) anisotropic. The anisotropic curve is vertically shifted with respect to the isotropic curve

reasons these end macroradicals can only decay after physical migration, i.e. an approach of the end macroradicals by some motion of the end segments of macromolecules.

In our previous paper[16] we obtained information on the rotational as well as the translational–rotational mobility of the probe TEMPO and the dependence on various thermomechanical histories of PC. It is interesting to compare both groups of e.p.r. results from the point of view of their sensitivity to various structural-dynamic situations in the same polymer matrix.

In the case of stable radicals it was found that the rotational correlation times depend strongly on the free volume characteristics and that the translations from the slow to the rapid motional regimes take place in a relatively narrow temperature interval correlating with the onset of β'-mobility. An analogical situation is also valid for the unstable macroradicals. These facts indicate the similar influence of both factors on the corresponding motional processes, i.e. reorientation of the spin probe and the approach of relatively close end macroradicals through the small-scale motion of the end segments into a contact position in the low temperature region.

On the other hand, significant differences were observed in the high temperature region. So, the break in the course of the rapid correlation times for the probe takes place at a $T_g = 150°\text{C}$. This break indicates the change of the mechanism of reorientation from rotational to the translational–rotational regime which requires the global co-operative segmental mobility of the macromolecular segments in the polymer. Finally, the rate constants in both unaged samples of PC change at ~70°C indicating a change in the mechanism which controls, or at least influences, the end macroradical decay. This means that an approach of the relatively distant end macroradicals in the unaged samples requires the local course of the co-operative α_a-mobility. Similar correlations were also found for the other polymers so that macroradical decay may be considered as a suitable tool for monitoring the local onset of the co-operative segmental mobility in the glassy state of a polymer.

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