Generation of free radicals with lauroyl peroxide, azobisisobutyronitrile and their mixture in polymer matrix at high pressure

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The dependence of an increase in the concentration of free radicals on the time of annealing of poly(methyl methacrylate) containing azobisisobutyronitrile, lauroyl peroxide or their mixture has been investigated by the e.s.r. method at temperatures between 70° and 150°C and pressures between 100 and 800 MPa

In our previous papers[1–4] using benzoyl peroxide (BP) for generating free radicals in a polymer matrix at high pressure we found that both in the presence and in the absence of free monomer in the polymer, thermal decomposition of BP gives rise to polymer radicals measurable by the e.s.r. method. The difference in the nature of the free radicals obtained in the two procedures consists in the fact that in the presence of monomer a growth radical is formed[2] and in the absence of monomer, a mixture of the growth radical and radicals localized inside the polymer chain is produced as a result of transfer reactions involving initiator radicals and polymer chains[1,2]. The question arises whether in the presence of residual monomer in the polymer (MMA in PMMA) propagating polymer radicals are formed by direct reaction of monomer with radical fragments from peroxide or by addition of monomer to polymer radicals created by the transfer reaction. In order to be able to answer the question, we excluded one of the possibilities of the formation of propagating polymer radicals by employing AIBN as initiator, where the transfer reaction to PMMA is negligible.

In the present paper the effects of AIBN and of LP on the generation of polymer radicals in PMMA in the presence of residual monomer and at high pressure were compared. At atmospheric pressure decomposition rate constants and initiating efficiency of LP for MMA polymerization are close to those of AIBN. The different chemical structure of AIBN and LP enables the different effect of high pressure on the cage effect and its consequences for radical generation in PMMA to be followed.

EXPERIMENTAL

Four samples of PMMA were prepared by bulk polymerization of methyl methacrylate initiated by:

(1) [AIBN] = 9.70 x 10^{-3} mol/dm^3 (13% of residual monomer in polymer, M_w = 3.1 x 10^6);

(2) [LP] = 9.70 x 10^{-3} mol/dm^3 (13.4% residual monomer in polymer, M_w = 2.9 x 10^6);

(3) a mixture of AIBN and LP, [AIBN] = 2.86 x 10^{-3} mol/dm^3 and [LP] = 9.71 x 10^{-3} mol/dm^3 (24.8% residual monomer, M_w = 3.1 x 10^6);

(4) a mixture of AIBN and BP, [AIBN] = 2.86 x 10^{-3} mol/dm^3 and [BP] = 7.77 x 10^{-3} mol/dm^3 (12.2% residual monomer, M_w = 7.2 x 10^6).

The temperature of polymerization was always 40°C and the time of polymerization 35 h. Since the half lives in solution at 40°C are 354 h for AIBN and 392 h for LP[5], we can assume that the total concentration of AIBN and LP decreased during polymerization by 5%. The loss of BP during polymerization is negligible because of its slower decomposition in solution ($t_{1/2}$ = 1 x 10^{-7} sec^{-1}). The concentration of the individual initiators was not determined after polymerization of PMMA in particular samples where the radicals were generated by thermal decomposition of peroxide at high pressure.

The generation of radicals was performed as follows: the sample was put into a steel pressure device, pressed to the required pressure and held at this pressure and constant temperature. The temperature and pressure were automatically regulated. Rapid heating and cooling of the pressure device was secured by a temperature impulse with sharp edges. On cooling the device and pressure release, the sample was transferred to a cavity resonator of an X-band Varian E–4 ESR spectrometer. The e.s.r. spectrum of the sample did not change noticeably during transfer and measurement at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the time dependence of radicals generated by

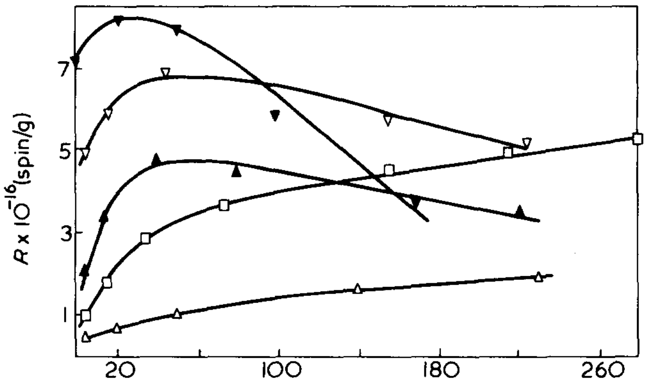

Figure 1 Variation of free radical concentration with the time of annealing during thermal decomposition of LP in PMMA at 800 MPa: △, –80°C; □, –90°C; ▲, –110°C; ▽, –130°C; ▼, –150°C

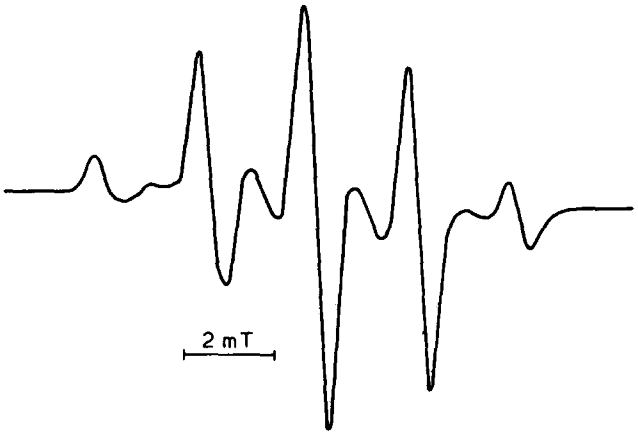

Figure 2 E.s.r. spectrum of free radicals initiated by thermal decomposition of a mixture of AIBN and LP in PMMA at 100°C and 800 MPa after 20 min annealing

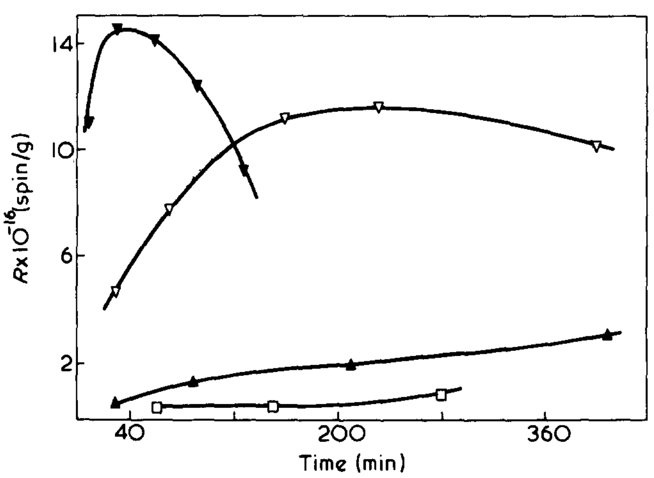

Figure 3 Variation of free radical concentration with the time of annealing during thermal decomposition of AIBN in PMMA at 800 MPa: □, –90°C; ▲, –110°C; ▽, –130°C; ▼, –150°C

decomposition of LP in PMMA at 70°–150°C and at 800 MPa.

The e.s.r. spectra in *Figure 2* show that this method of generating polymer radicals leads mainly to growth PMMA radicals. The increase in radical concentration with the time of annealing of PMMA in *Figure 1* is in fact a cumulation of polymer radicals produced by gradual decomposition of initiator and by consecutive reaction of radicals formed from initiator with residual monomer or polymer matrix[4].

This increase in radical concentration is affected also by the fact that during annealing free monomer in the polymer is gradually consumed so decreasing softening of the polymer by its monomer and the rate of termination is lowered. *Figure 1* shows maxima of radical concentration reached at temperatures between 110° and 150°C after 20–50 min annealing. A decrease in radical concentration after reaching the maximum can be attributed to a decrease in the concentration of LP.

Figure 3 shows the time dependence of radical concentrations obtained by annealing the AIBN-containing PMMA at 800 MPa. A more significant difference in the radical concentration as a function of temperature was observed. At 70°C and 800 MPa no measurable radical concentration in AIBN-containing PMMA was obtained.

The differences observed between PMMA with AIBN and PMMA with LP cannot be attributed to either the different content of residual monomer or to different molecular weight of PMMA. The former contained 13.0% of residual monomer and $M_w = 3.1 \times 10^6$ and the latter 13.4% of residual monomer and $M_w = 2.9 \times 10^6$. Differences between the AIBN and LP from the viewpoint of radical concentrations and their time dependences might be due to several causes: (a) different pressure effect on the cage effect of AIBN or LP during their thermal decomposition. Thus, the initiation efficiency of both initiators may change; (b) the greater agglomeration of LP at high conversions of polymerization (probably due to smaller compatibility of LP with PMMA matrix) compared with AIBN resulting in an induced decomposition of LP.

Dependences shown in *Figure 3* show that radicals can be generated in the polymer matrix containing residual monomer with an initiator not belonging to typical initiators of transfer reactions. In other words, polymerization in the polymer matrix takes place at high pressure by direct addition of the initiator of radicals to monomer.

When comparing LP and AIBN, the former brought about a more rapid increase in the radical concentration at all temperatures and pressures used in the initial phase of annealing of PMMA (*Figure 1*). On the other hand, the maximum radical concentration is retained much longer in the presence of AIBN (*Figure 3*). Therefore it seemed useful to find out whether AIBN and LP would retain these properties if both would be present in a mixture of PMMA and residual mono-

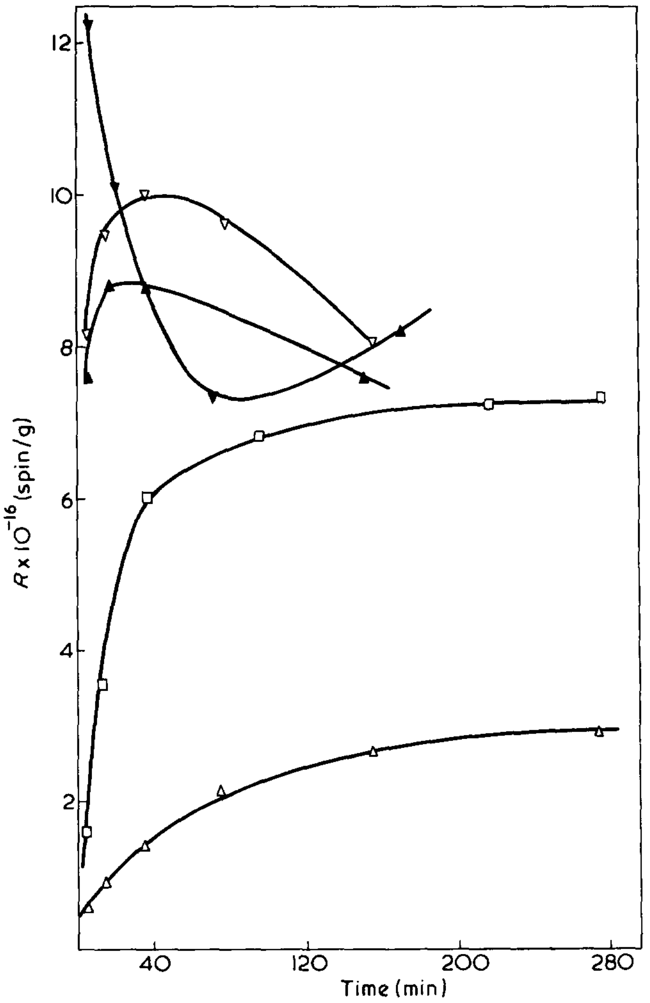

Figure 4 Variation of free radical concentration with the time of annealing during thermal decomposition of a mixture of AIBN and LP in PMMA at 800 MPa: △, –80°C; □, –90°C; ▲, –110°C; ▽, –130°C; ▼, –150°C

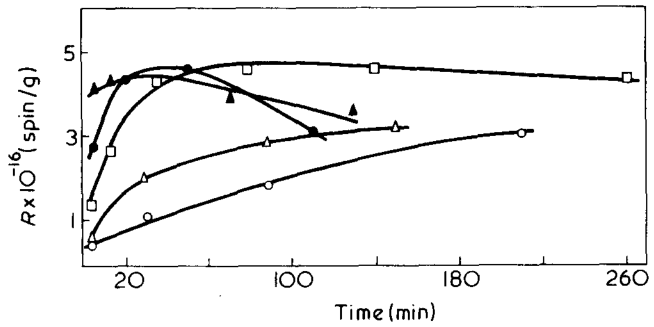

Figure 5 Variation of free radical concentration with the time of annealing during thermal decomposition of a mixture of AIBN and LP in PMMA at 200 MPa: ○, –70°C; △, –80°C; □, –90°C; ●, –100°C; ▲, –110°C

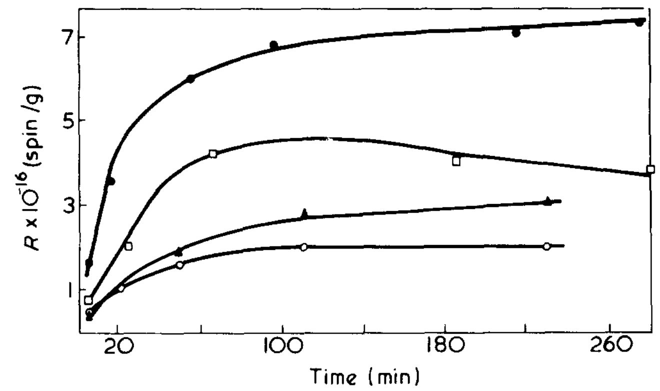

Figure 6 Variation of free radical concentration with the time of annealing during thermal decomposition of a mixture of AIBN and LP in PMMA at 90°C and pressure: ○, –100 MPa; ▲, –400 MPa; □, 600 MPa; ●, 800 MPa

mer. PMMA with AIBN and LP (initial [AIBN] = 2.86×10^{-3} mol/dm^3 in MMA before polymerization) was annealed at temperatures between 70° and 150°C and pressure 800 MPa (*Figure 4*). The total concentration of the mixture of initiators was approximately 25% higher than AIBN and LP separately. We obtained higher values for maximum concentration at 150°C, namely about 12×10^{-16} radicals/g. By employing LP the maximum radical concentration measured was about 8×10^{-16} radicals/g. Plots in *Figure 4* show that by using a mixture of initiators the specific properties of individual initiators were preserved; i.e. a rapid increase in radical concentration [LP] and a slower decrease in radical concentration [AIBN] with the time of annealing.

If LP- and AIBN-containing PMMA was annealed at 200 MPa and 80°C, the same concentrations were obtained as at 800 MPa (*Figure 5*). However, the maximum concentration of radicals measured at higher temperatures was much lower than that measured at 800 MPa.

The stabilizing effect of pressure on polymeric radicals in the PMMA matrix at 90°C is illustrated in *Figure 6*. An increase in pressure from 100 MPa to 800 MPa can lead to more than a three-fold increase in radical concentration for LP- and AIBN-containing PMMA. This is a consequence of the effect of pressure on decreasing the rate of termination of polymeric radicals.

The highest radical concentration was obtained for PMMA containing a mixture of AIBN and BP at 70°C and 800 MPa (*Figure 7*). The initial concentration of a mixture of initiators in MMA was [AIBN] = 2.8×10^{-3} mol/dm^3 and [BP] = 7.77×10^{-3} mol/dm^3. (The content of residual monomer in PMMA was 12.2%.) Since the radical concentration obtained by using AIBN in PMMA at 70°C was not measurable by the e.s.r. method, only BP should be responsible for the radicals formed in this case. The much higher radical concentration in PMMA obtained when using BP compared with AIBN is probably connected with the fact that BP radicals react also with the PMMA matrix by transfer. After diffusion of monomer to radicals in the matrix, polymerization can be initiated. During thermal decomposition of AIBN, only addition of primary radicals from AIBN to monomer can take place and transfer to the PMMA matrix can be neglected unlike the case with BP. This facilitates mutual termination reactions of primary radicals formed from AIBN leading to a lower radical concentration with AIBN.

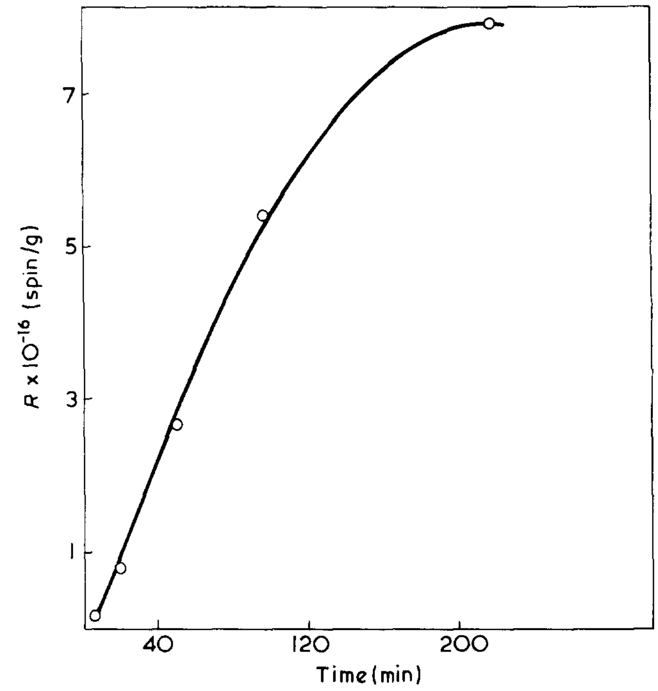

Figure 7 Variation of free radical concentration with the time of annealing during thermal decomposition of a mixture of AIBN and BP in PMMA at 70°C and 800 MPa

The results show that radicals in the polymer matrix containing residual monomer can be successfully generated also by direct reaction of primary radicals of the initiator with monomer at high pressure. However, much higher concentration of radicals is obtained when employing an initiator, the radicals of which attack also the polymer matrix. The polymer radicals formed are stabilized with respect to termination reaction compared with the low molecular weight radicals. Thus the possibility of reaching the higher total concentration of propagating radicals in the polymer matrix arises compared with the use of an initiator yielding less reactive radicals, such as AIBN, during decomposition.

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