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FREE RADICALS OBSERVED IN THE GRAFTING OF MALEIC ANHYDRIDE ON POLY(METHYL METHACRYLATE)†

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ABSTRACT

The ESR method was used for investigating free radicals formed during thermal decomposition of dibenzoyl peroxide in the poly(methyl methacrylate) (PMMA)–maleic anhydride (MAN) system at 400 MPa. No primary product from the addition of a polymer radical to maleic anhydride was observed, but instead a polyene radical was formed within the polymer matrix. Possibilities of the formation of polyene radicals as well as the effect of temperature and reaction time on the concentration of free radicals are discussed.

INTRODUCTION

The method of thermal decomposition of peroxide in a polymer under high pressure (described in our earlier papers) generally provides polymer radicals of rather high concentration sufficient for their measurement and characterization by the ESR method [1, 2]. The technique is based on the stabilization of polymer radicals which are formed via transfer of a radical initiator to the polymer chain under high pressure (100–1000 MPa) and at the decomposition temperature of the initiator. In the presence of a small amount of monomer (1–10 weight %), the

†Dedicated to Otto Vogl on the occasion of his 65th birthday.

distinct ESR spectra of propagating radicals belonging to the respective monomers were observed even when a foreign polymer matrix was used [2, 3].

Our aim was also to examine free radicals produced by the addition of maleic anhydride (MAN) to the polymer radical while grafting of maleic anhydride on poly(methyl methacrylate) (PMMA). It is still not quite clear under what grafting conditions short MAN chains or only individual monomer units are bound to polymer. This obscurity is underlined by the fact that maleic anhydride does not show any marked tendency to homopolymerization, and polymerizes at high concentrations of radical initiator only [4]. Gaylord et al. [5, 6] predicted the formation of shorter maleic anhydride chains during peroxide grafting of polyethylene or polypropylene in the melt. In contrast, De Vitto et al. [7], when carrying out reactions in xylene, found that the maleic anhydride units graft to ethylene/propylene copolymers. The grafting of maleic anhydride onto various polymers, polyolefins in particular, is currently important for the preparation of both polymer mixtures and composites. For this reason we have been studying radical processes accompanying polymer grafting by the ESR method, hoping to obtain a better understanding of the mechanism using this model system. Due to the high melting temperature of polypropylene, we were unable to apply this technique directly to follow the grafting of polypropylene with maleic anhydride. We had to choose another model system, viz., poly(methyl methacrylate) and maleic anhydride. There was also the possibility in this system to distinguish the free radicals of a polymer matrix.

EXPERIMENTAL

Sample Preparation for the Grafting of Poly(Methyl Methacrylate) with Maleic Anhydride

Poly(methyl methacrylate), 8.7 g, Vedril-8 type supplied by Montedison, was precipitated from chloroform solution with methanol. It was then impregnated overnight with 40 mL of a mixed solvent solution of CHCl_3 and CH_3OH (1:3 vol) which contained dibenzoyl peroxide (DBP, 0.3 g; 3 weight %) and maleic anhydride (MAN, 1 g; 10 weight %). Solvents were distilled from the disperse mixture in a vacuum drier, and the polymer residue was dried by free evaporation of the solvent residues.

ESR Spectra of Free Radicals Generated in Poly(Methyl Methacrylate) under High Pressure

Free radicals in DBP and MAN containing PMMA were generated by thermal decomposition of peroxide in a high-pressure apparatus (see Fig. 1) described elsewhere [8].

The sample (3) of PMMA containing 3% by mass of DBP or 10% by mass of MAN was inserted into a device consisting of a stainless steel cylinder (5) and a 6-mm diameter piston (2). The device was subjected to a pressure of 400 MPa produced by a hydraulic press (9). The sample was then rapidly heated to the desired temperature for the required time. The device was equipped for temperature and pressure stabilization. During this treatment the sample was blanketed in a nitrogen atmosphere which was forced into the device through port (8).

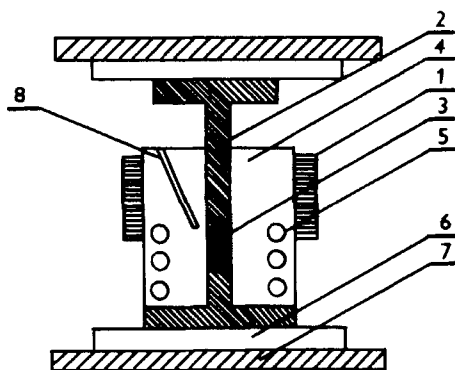


FIG. 1. Drawing of the apparatus used for high-pressure sample annealing: 1, heating element; 2, piston; 3, sample; 4, heat insulator; 5, steel cylinder; 6, cooling tube; 7, polyethylene cover; 8, nitrogen supply; 9, extension of hydraulic press; 10, resistance thermometer.

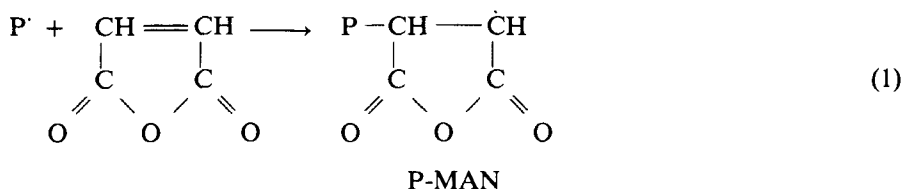
After annealing at temperatures between 90 and 120°C for 10 to 240 min and subjecting the sample to 400 mPa, it was quickly cooled to room temperature and the pressure was released. Then the sample was transferred to a cavity resonator of a Varian E-4 X-band ESR spectrometer to record the spectra.

The concentration of free radicals in the polymer samples was determined by using a commercial standard having a known spin value (standard Strong Pitch).

RESULTS AND DISCUSSION

Figure 2 shows the ESR spectrum of free radicals in PMMA formed via thermal decomposition of benzoyl peroxide in PMMA without MAN at 110°C and 400 MPa. An ESR spectrum of a mixture of free radicals produced by a transfer of the radical center from peroxide fragments to various segment sites of the PMMA chain was obtained as expected. The radicals formed were $-\dot{\text{C}}\text{H}-\text{C}(\text{CH}_3)(\text{COOCH}_3)-$, $-\text{CH}_2-\dot{\text{C}}(\text{CH}_3)(\text{COOCH}_3)$, and alkyl radicals [9].

If the reaction was carried out under similar conditions (400 MPa, 95–120°C) but in the presence of MAN, only one type of spectrum was observed; namely, a singlet with $\Delta H_p = 1.2$ mT (Fig. 3). At lower temperatures, i.e., 70 and 80°C, we observed the same shape of ESR spectrum but with a much lower intensity. This spectrum does not correspond to the expected propagating radical of MAN described by Stojachenko et al. [10]:



They report a doublet with $\Delta H_p = 1.05$ mT as observed during copolymerization of MAN with 1,3-dimethyl butadiene initiated by γ -rays at -70°C . On the other



FIG. 2. EPR spectrum of free radicals generated during thermal decomposition of BP_x (8 mass %) in a poly(methyl methacrylate) matrix deprived of monomer for $T = 120^\circ\text{C}$, 30 min, and 400 MPa.

hand, Tiño and Plaček [11] also observed a doublet spectrum with $\Delta H_p = 1.4$ mT after irradiating the methyl methacrylate-maleic anhydride copolymer. They did not, however, attribute it to the propagating radical of MAN but rather to a transferred radical on a MAN unit of the polymer chain. The singlet ESR spectrum observed by us is ascribed to polyene radicals also recorded by Tiño et al. [12] in irradiated MMA-MAN copolymer above 0°C . Their signal had the same line width of $\Delta H_{1/2} = 1.2$ mT. The formation of the polyene radical can be explained in two

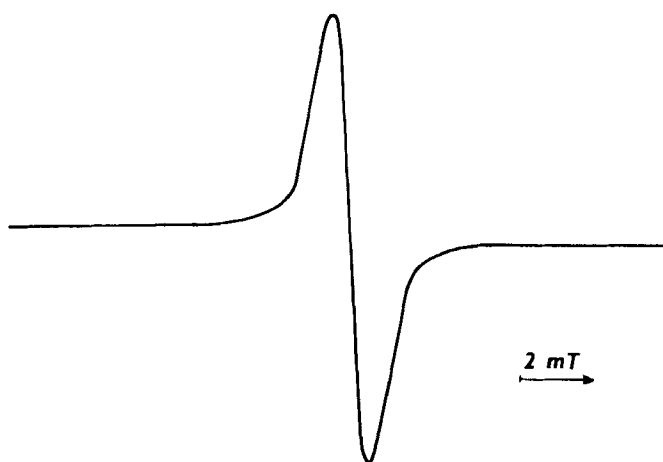
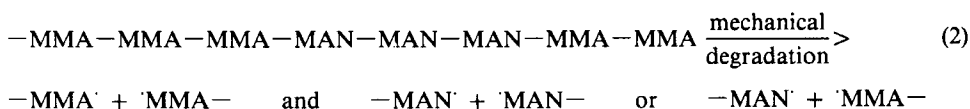


FIG. 3. EPR spectrum of free radicals generated during thermal decompositions of BP (3 mass %) in PMMA in the presence of maleic anhydride (10 mass %) at 120°C , 20 min, and 400 MPa.

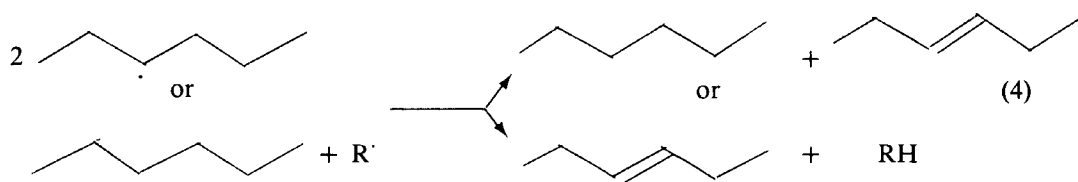
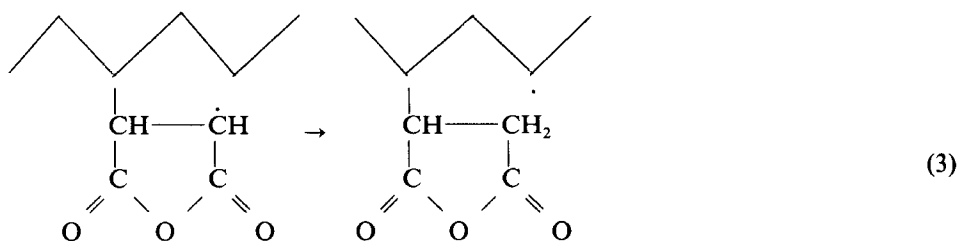
ways. The first is based on an idea that in grafting at high temperature, the shorter MAN chains are bound to PMMA under simultaneous decarboxylation and formation of polyene radicals. This idea corresponds to the proposal of Tiño et al. [12]. These authors considered formation of longer MAN sequences in the MMA-MAN copolymer. After mechanical degradation of this copolymer, they observed polyene radicals which are not the primary radicals originating from the breaking of bonds between MAN and MMA units in the chain of the copolymer. Mechanical degradation of this copolymer would be expected to produce mainly MMA· and MAN· radicals:



The observation of polyene radicals by Tiño et al. was also accounted for by decarboxylation of MAN segments under the given reaction conditions of mechanical degradation.

The second mode of production of polyene radicals is based on an idea that they need not be formed exclusively from decarboxylated MAN chains but can also be formed by elimination of ester groups on the PMMA chains. It is not possible to distinguish the ESR spectrum of the polyene radical formed on the PMMA chain from that formed on the decarboxylated MAN chain. On the other hand, the fact that we failed to trap any primary product of the addition of a polymer radical to the double bond of MAN under any experimental condition leads to the conclusion that the initial polymer radicals are responsible for the successive decarboxylation of MAN chains and possibly to elimination of ester groups along MMA chains in the present system.

The PMAN· radical appears to be much more reactive than PMMA·. We were able to observe by ESR the PMMA· radical generated under the same experimental conditions. Apparently the PMAN· is quickly lost by hydrogen transfer and also by disproportionation or recombination reactions as well as by radical-induced decarboxylation and decarbonylation.



where R· = primary radical of peroxide, propagating radical.

The observed polyene radical derived from a decarboxylated MAN chain cannot, in fact, represent the main product of maleination since analytical methods have shown that under similar conditions (at temperatures around 180°C), MAN units are bound to the polymer, e.g., to polypropylene, and the anhydride rings remain intact. One can infer from this that the observed polyene radicals are unique for the maleination reaction of PMMA. The formation of polyene systems is one of the results of the radical or nonradical processes occurring in the system studied. Also, the participation of the MAN units inside the polyene system or as the radical ends cannot be eliminated. Elimination of groups from PMMA chains seems to be more probable since PMMA tends to form polyene systems whose structures have not yet been clarified completely [13].

Figure 4 shows the time dependence of the formation of free radicals in the system PMMA-MAN-BP at 400 MPa at various temperatures. We see that at each temperature the accumulation of radicals is very slow, requiring more than 100 min to achieve a measurable level. The achievement of higher concentrations of free radicals at higher temperatures is associated with a more rapid decomposition of peroxide. On the other hand, at temperatures between 110 and 120°C, a maximum was observed in plots of the consumption of the reaction components, benzoyl peroxide and maleic anhydride. The maximum can be regarded as a steady-state condition in which the rate of formation of radicals equals that of their decay. In the region beyond the maximum, the rate of formation of free radicals decreases for the reasons specified, and therefore an overall decrease in the concentration of free radicals occurs [1, 14]. In the studies performed at 95 and 100°C, the times of radical excitation were not sufficient for us to find maximum concentrations of radicals at these temperatures.

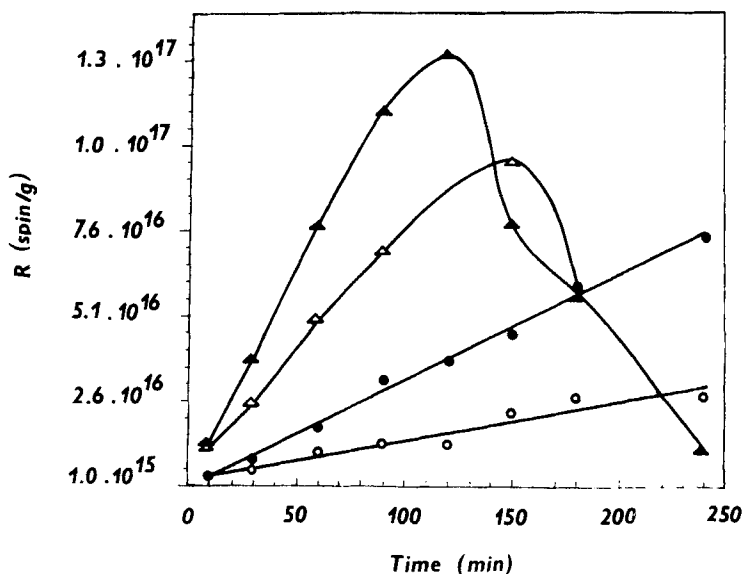


FIG. 4. Time dependence of the concentration of free radicals at 400 MPa and at various temperatures: (○) 95, (●) 100, (△) 110, and (▲) 120°C.

CONCLUSIONS

The ESR study of the grafting of maleic anhydride onto poly(methyl methacrylate) demonstrates that:

1. High pressure grafting (at 400 MPa) did not give rise to a stabilized primary radical of the type PMAN·.
2. Only a radical by-product of the grafting reaction was observed, i.e., polyene radical.
3. The PMAN· radical seems to be much more reactive than the propagating PMMA· radical. The latter radical can be observed under the same reaction conditions but in the absence of MAN.
4. The high pressure method of generation of free polymer radicals by the thermal decomposition of peroxide makes it possible to reach a high concentration of free radicals: $\sim 10^{17}$ spins/g.

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