E.s.r. study of radical polymerization of pentaerythrityl monoacetal dimethacrylate in polystyrene matrix at high pressure

J. Tiňo, E. Borsig and F. Szöcs
Polymer Institute, Slovak Academy of Sciences, 809 34 Bratislava, Czechoslovakia

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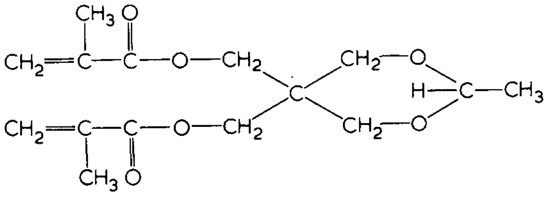
The e.s.r. spectrum of free radicals formed during polymerization of a bifunctional monomer of pentaerythrityl monoacetal dimethacrylate by thermal decomposition of benzoyl peroxide in a polystyrene matrix at 700 MPa is studied. Formation of propagating radicals of cyclopolymerization and crosslinking polymerization is discussed.

INTRODUCTION

The use of bifunctional monomer, i.e. a monomer having two vinyl groups in a molecule isolated one from another, e.g. by alkyl chains, can lead to cyclopolymerization in the presence of radical initiator. The cyclopolymerization is favoured over other reactions especially when the bifunctional monomers are 1,5- or 1,6-dienes[1]. Some authors[2,3] have succeeded in examining propagation radicals during cyclopolymerization by the e.s.r. method.

We employed the bifunctional monomer pentaerythrityl monoacetal dimethacrylate (PEDMA)



a 1,10-diene. According to the known results[1], during polymerization of a bifunctional monomer like PEDMA, branching but mainly crosslinking will occur.

It is known from the literature that in the case of 1,6-dienes, the portion of cyclopolymerization increases by diluting the monomer with an inert solvent[1].

Instead of solvent we used polystyrene impregnated with PEDMA (~10%) and benzoyl peroxide as initiator. The polymerization of PEDMA was performed in the polystyrene matrix by thermal decomposition of benzoyl peroxide at high pressure, which stabilizes propagating radicals of polymerization with respect to termination reactions[4,5]. The aim of the present study is to find out which propagating radicals are formed during polymerization of PEDMA – a monomer not typical of cyclopolymerization.

EXPERIMENTAL

Monoacetal pentaerythritol was prepared by reaction between pentaerythritol and paraldehyde in the presence of concentrated hydrochloric acid at m.p. = 104°C[6]. Reaction of pentaerythritol monoacetal with the chloride of methacrylic acid gave pentaerythrityl monoacetal dimethacrylate – PEDMA with m.p. 89°–90°C. Elemental analysis: H = 7.31%, C = 60.46%, theoretical H = 7.43% and C = 60.39%.

PEDMA (0.15 g) and benzoyl peroxide (0.125 g) were dissolved in a mixture of chloroform (7.5 ml) and methanol (10 ml) and the mixture was added to precipitated polystyrene (Vestyron N, 2.5 g) having $M_w = 3.17 \times 10^5$. Polystyrene was allowed to impregnate the mixture 24 h in the dark. Then the solvent was evaporated from the mixture at room temperature and the impregnated polystyrene dried at room temperature in a vacuum drier.

The polystyrene containing PEDMA and benzoyl peroxide prepared in this manner was used for radical generation by thermal decomposition of benzoyl peroxide at high pressure. The samples were put into a high pressure device[7], subjected to a pressure of 700 MPa, heated to the desired temperature and annealed between 110° and 140°C. After exposition the sample was cooled, pressure released and the sample was transferred into a resonator of a Varian E-4 e.s.r. spectrometer to record the spectrum. The e.s.r. spectrum was measured at room temperature and atmospheric pressure. The high pressure device consisted of a steel cylinder and a piston subjected to pressure[7]. It enables rapid heating and cooling of the sample. The e.s.r. spectra were analysed by computer simulation of the experimental spectra[8].

RESULTS

In their investigation of cyclopolymerization of *N*-n-propyldimethacrylamide Kodaira and Aoyama[2,3], found that

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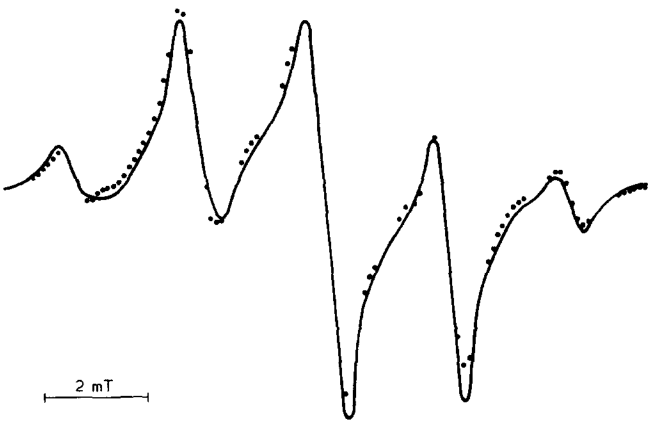
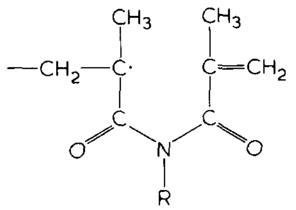


Figure 1 E.s.r. spectrum of radicals formed by thermal decomposition of benzoyl peroxide in polystyrene matrix at 700 MPa and 110°C in the presence of PEDMA measured at room temperature. ——— Experimental; . . . . . . theoretical

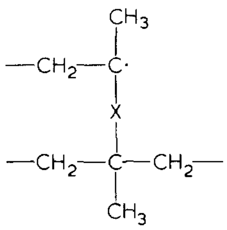
the main radical species formed in the polymerization system are radicals I:



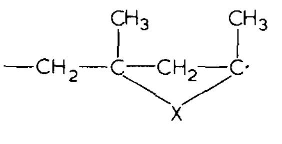
(I)

with the following hyperfine splitting constants: a^{CH_3} = 1.96 mT, a^{CH_2} (1) = 3.92 mT, a^{CH_2} (2) = 0.90 mT. These values differ considerably from those obtained by analysis of the e.s.r. spectrum of radicals trapped in irradiated PMMA[9]. On this basis it is seen that replacement of methyl in an ester group leads to a change in radical conformation. Proton splitting constants in a CH_2 group of a radical correspond to angles[2] θ_1 = 118°39′ and θ_2 = 0°, the values for these angles in PMMA[10] being: θ_1 = 63°6′, θ_2 = 56°24′.

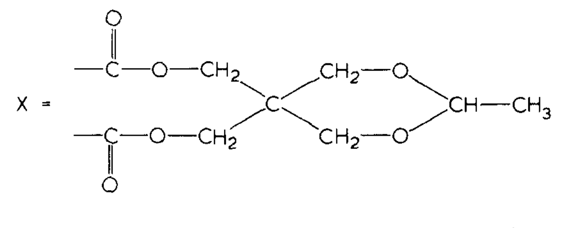
Figure 1 shows the e.s.r. spectrum of radicals formed by thermal decomposition of benzoyl peroxide in the polystyrene matrix in the presence of PEDMA.



(II)



(III)



Detailed analysis showed that the spectrum is multicomponent (asymmetrical) and can be reconstructed by spectra of the radicals II and III, having the splitting constants listed in *Table 1* and doublet spectrum with large line width (2.8 mT). We did not succeed in unambiguous assignment of the radical to this spectrum; however, its parameters indicate the presence of polyene structure – further structure IV.

The spectra with splitting constants differing (especially for β protons) from those of the PMMA radical (*Table 1*) correspond to radicals II and III. Similarly as in radical I, also here the replacement of methyl in the ester group leads to different stable conformations of the respective radicals. The spectra do not show unambiguously which of the two radicals is assigned the constants in the first and second rows of the Table.

The structure of the spectrum depends on the temperature used for radical generation. Analysis of the spectra shows that at higher temperature the radicals II and III are represented to smaller extent (*Figure 2*, spectra 2 and 3) and the structure of the total spectrum is determined by radical IV.

DISCUSSION

On the basis of the analysis of the e.s.r. spectrum we can expect the presence of mainly three radicals denoted as II, III and IV in the polystyrene matrix containing PEDMA. For answering the question what kind of polymerization reaction will proceed with PEDMA in the polymer matrix, solely radicals II and III are significant. The radical IV is formed by transferring the radicals of initiator to PEDMA polymer.

As has already been said, it cannot be determined from the analysis of the e.s.r. spectrum which of the two components of the spectrum belongs to radical II and which to radical III. However, we know that both components correspond to propagating radicals. During polymerization of

Table 1 Hyperfine splitting constants in radicals II, III and IV (mT)

Radical	a_H	$a_H^{CH_3}$	$a_{H1}^{CH_2^*}$	$\Delta H_{1/2}$
II	–	2.29	2.29	0.8
III	–	2.11	1.44	0.7
IV	1.80	–	–	2.8

* $a_{H2}^{CH_2}$ is not observed in the spectrum

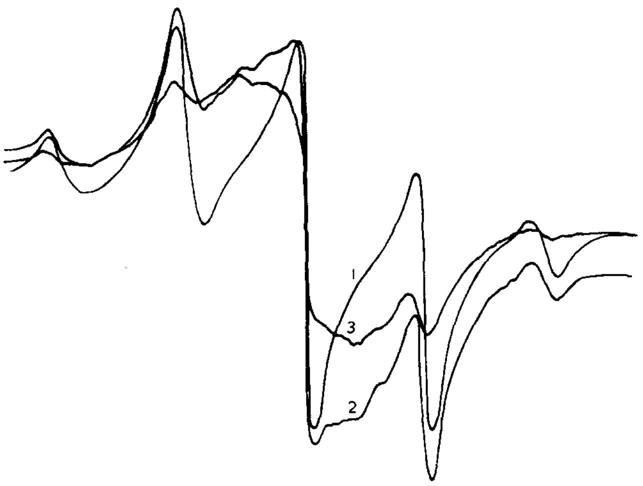


Figure 2 E.s.r. spectra of radicals forms by thermal decomposition of benzoyl peroxide in polystyrene matrix at 700 MPa in the presence of PEDMA: 1, at 110°C; 2, 130°C; 3, 140°C measured at room temperature

PEDMA, the two types of propagating radicals can be considered:

(a) radicals leading to crosslinking polymerization

(b) radicals leading to cyclopolymerization

The former type will be produced especially when greater number of molecules of the PEDMA monomer are in the neighbourhood of initiating radical centre. Taking into account the more polar character of PEDMA compared with polystyrene, one may assume inhomogeneities in the polystyrene matrix in the form of clusters of PEDMA. Therefore even at low total PEDMA concentration in polystyrene and considering the character of the monomer we can expect considerable crosslinking polymerization or an observation of the propagating radicals corresponding to such polymerization (radical II).

The type III radical is probably formed when the propagation reaction is controlled by diffusion of PEDMA to radical centre. Then formation of the conditions for cycloaddition of PEDMA to radical centre is assumed to be more probable.

The analysis of the e.s.r. spectrum also showed that one component of the two considered (i.e. radicals II and III) represents about a six-fold radical concentration with respect to the second compoennt. Of the two structures of radicals II and III considered, type II radical may be taken as more stable, especially when it is part of the polymer network; therefore it can be assumed that the radicals II will occur in higher concentration. Kodaira and Aoyama[3] achieved similar results in the study of radical polymerization of bifunctional monomer though on the basis of different arguments. Then the remaining component of the spectrum should be assigned to the propagating radical arising during cyclopolymerization, i.e. to radical III.

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