Chemiluminescence imaging of polymer materials under thermal oxidation and stress

Satoru Hosoda*, Yoshinori Seki and Hayato Kihara
Sumitomo Chemical Co. Ltd, Chiba Research Laboratory, Anesakikaigan 5-1, Ichihara-city, Chiba, 299-01 Japan

(Received 7 December 1992; revised 13 January 1993)

Chemiluminescence imaging was successfully carried out for some polymer materials under heating or mechanical stress using a two-dimensional photoelectron detector. Oxidative degradation could be visualized for the press-moulded sheets of Nylon 6 (Ny6) and polystyrene (PS), and for the multilayered sheet composed of polyethylene (PE) and styrene–butadiene triblock copolymer (SBS) by heating samples at 50–154°C in air. The chemiluminescence intensity varied over the surface of the sample specimen; the surface trimmed with a razor blade and the cracked portion exhibited especially strong luminescence for Ny6 and PS samples. The difference in the oxidation reaction rate between the two kinds of materials could be visualized clearly for the multilayered sheet of PE and SBS. Stress-induced luminescence was observed on drawing Ny6 at room temperature, and it was found that the luminescence was remarkably strong around the stress-concentrated part of the specimen.

(Keywords: imaging; chemiluminescence; thermal oxidation)

INTRODUCTION

The degradation of polymer materials is caused by various external factors such as heat, u.v. light, ozone and mechanical stress, resulting in brittleness, cracks, colouration/discolouration, etc. The process of degradation is known to be accompanied by very weak emission of chemiluminescence[1,2]. Since chemiluminescence has a high sensitivity to oxidative degradation[3–5], chemiluminescence measurement has been used as a tool for the evaluation of the stability of polymer materials against heat[6,7], u.v. light[8–10], electron beam[11] and γ-ray irradiation[12,13].

With regard to detection, a photomultiplier may be used as a photon detector and the total number of photons emitted from the sample surface is counted in conventional instruments. Recently, a new detector system equipped with a series of multichannel plates as an intensifier has made the photon counting measurement extremely sensitive. By combining this system with a two-dimensional detector (a vidicon or a position-sensitive detecting system), the imaging of chemiluminescence has become possible as reported by Hiramatsu *et al.*[14] in studies on the real-time imaging of the permeant distribution on a polymer film surface. In order to develop the superiority of the high sensitivity and handling simplicity of chemiluminescence measurements, we have investigated the imaging of the chemiluminescence induced by heat and mechanical stress for some polymer materials with the use of the detecting system described above.

EXPERIMENTAL

Materials

Polymer samples used in this study are commercial products of Nylon 6 (Ny6, Ube Industry, $M_n = 1.4 \times 10^4$), polystyrene (PS, Sumitomo Chemical, $M_w = 21.5 \times 10^4$, $M_w/M_n = 2.1$), high-pressure low-density polyethylene (PE, Sumitomo Chemical, $M_w = 14.3 \times 10^4$, $M_w/M_n = 4.2$) and styrene–butadiene triblock copolymer (SBS, Shell, $M_w(\mathrm{St}) = 1 \times 10^4$, $M_w(\mathrm{Bd}) = 3.5 \times 10^4$, PS content = 30 wt%). Samples were hot-press moulded into a sheet 2 mm thick at 230°C for Ny6 and 200°C for PS, and a sheet 0.1 mm thick at 150°C for PE and SBS. The Ny6 specimen was slowly cooled down in a hot-press ($\sim 0.5°\mathrm{C\,min^{-1}}$) and the others were cooled in a water-cooled press. A multilayered sheet was obtained by compression moulding at 150°C using eight SBS sheets and seven PE sheets which were layered alternately. Sample specimens were cut into an appropriate size with a razor blade.

Chemiluminescence measurement

Imaging experiments were carried out with an ARGUS-100 (Hamamatsu Photonics Co.) and a quantum microscope (Charles Evans and Associates), used separately. The images were obtained using an optical object lens system. A Nikon 50 mm (F = 1.4) lens or a Chino 14 mm (F = 2.5) lens was used for ARGUS-100, and two Canon lenses of 24 and 85 mm were used in combination for the quantum microscope (an image focal plane with a diameter of 6.8 mm is represented by 256 pixel positions, so that features as small as 25 μm should be distinguishable). Plural microchannel plates were installed in both instruments to amplify the photoelectron signal by the order of 10^4–10^6. In the

---

* To whom correspondence should be addressed

0032-3861/93/224602-05

ARGUS-100, amplified photoelectrons are converted into visible light by using a low-lag vidicon and the image is observed through a CCD camera. For the quantum microscope, image acquisition is carried out using a two-dimensional resistive anode encorder with which the position of an electron-pulse can be detected electronically. The position data are digitized, accumulated and processed by a microcomputer in both instruments. A trimmed sample was heated in air at the temperature range 50–154°C.

The stress-induced chemiluminescence (SICL) was measured at room temperature with the stretcher that we had developed for the chemiluminescence measurement[15] at the drawing rate of $2.5\,\mathrm{mm\,min^{-1}}$. Stress, strain and luminescence intensity during drawing were recorded simultaneously with this instrument. The sample specimen used for the SICL measurement was 50 mm × 50 mm × 0.5 mm and the SICL imaging was obtained for a specimen 20 mm × 50 mm × 0.5 mm. The latter specimen has a hole 6 mm in diameter at the centre. The distance between the chucks was set at 40 mm.

RESULTS AND DISCUSSION

Chemiluminescence imaging under heating

Figure 1 shows the chemiluminescence image obtained at 120°C for a PS specimen trimmed to 1.0 cm × 1.5 cm at room temperature. The flat surface of the specimen did not show any emission under these conditions. However, strong chemiluminescence was observed at the edge of the specimen and in the cracked part which might have occurred during the trimming process. This result suggests that the edge and the cracked part produced by mechanical trimming are appreciably activated to an oxidation reaction compared to the flat surface which was not exposed to any stimulative mechanical treatment. This type of imaging was also reported for a sample of hydroxy-terminated polybutadiene gumstock[16], in which the cracked parts also exhibited strong emission.

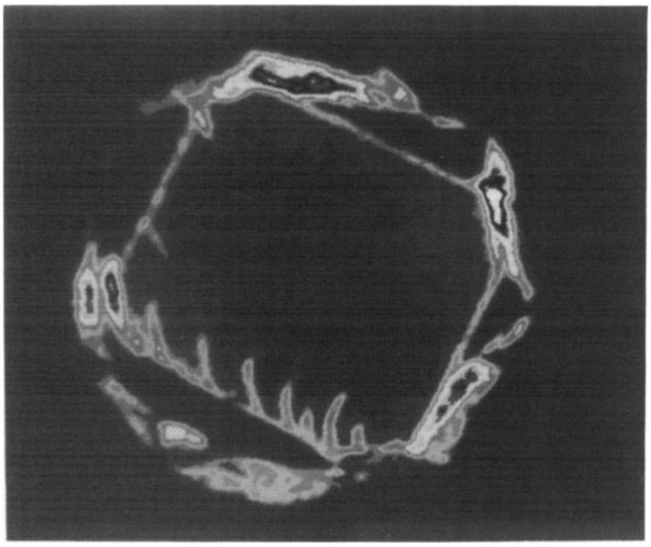

Figure 1 The chemiluminescence image obtained at 120°C for the polystyrene specimen, 1.0 cm × 1.5 cm

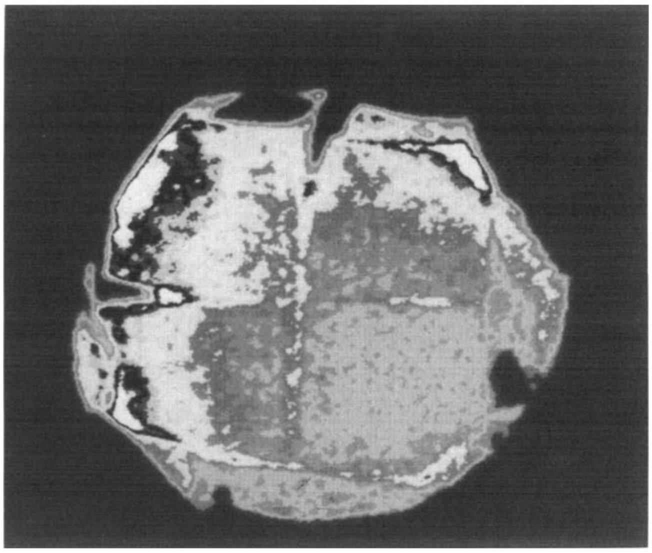

Figure 2 The chemiluminescence image obtained at 100°C for the Nylon 6 specimen, 2.0 cm × 2.0 cm. The specimen was folded a few times at room temperature so that the folded lines met at a right-angle at the centre of the specimen

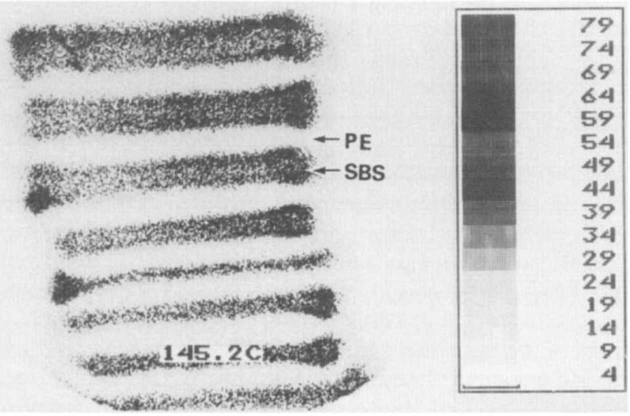

Figure 3 The chemiluminescence image obtained at 145°C for the polyethylene (PE)/SBS triblock copolymer multilayered sheet. Each individual sheet is originally 0.1 mm thick

However, Ny6 is well known to show strong chemiluminescence when heated in air[2]. Therefore, imaging of a Ny6 sample specimen 2.0 cm × 2.0 cm was tried in air at different temperatures from 50 to 145°C. At each temperature, an image was acquired for 10–20 min. Although an image was not detected below 50°C, the total image intensity increased with increasing temperature above 50°C. *Figure 2* shows the image obtained at 100°C for the Ny6 specimen which was, as a special case, folded a few times at room temperature so that the folded lines met at a right-angle at the centre of the specimen. Just like the sample of PS, the edge parts exhibited stronger chemiluminescence than the flat surface of the specimen. In addition, the crossed folded lines were clearly visible, suggesting that the stress-charged portion is significantly active in the oxidation reaction of Ny6. This might be, as discussed later, because of the increased peroxy radicals produced by chain scission under the mechanical stress in air.

The chemiluminescence of a PE/SBS multilayered specimen about 1.5 mm thick was measured at eight different temperatures from 88 to 154°C. The image was not clear below 115°C, but became clearly visible above 126°C. The image obtained at 145°C is shown in *Figure 3*, indicating that the eight SBS layers exhibit stronger chemiluminescence ($\sim 50\,\mathrm{cps\,pixel^{-1}}$) than the seven PE layers ($5\text{–}10\,\mathrm{cps\,pixel^{-1}}$) under heating in air.

Although the layers might expand to some extent at this temperature, each PE and SBS layer, which was originally 0.1 mm thick at room temperature, is quite distinguishable. Considering the clearness of the image obtained, the lateral spatial resolution with the lens system used here would be 30–50 μm. We also examined the other multilayered systems composed of 0.1 mm thick sheets of high-impact PS (HIPS)/PS and SBS/PS, in which PS has a lower chemiluminescence intensity than HIPS and SBS. The same types of images as those of the SBS/PE system were obtained above 80°C for HIPS/PS and above 136°C for SBS/PS in air. From these results, it is considered possible to visualize the difference in the rates of the oxidation reactions between component polymers of systems such as multilayer extruded laminates.

Imaging of stress-induced chemiluminescence (SICL)

Weak light emission has been reported to occur during the mechanical deformation of several kinds of polymers[17,18], and the luminescence is considered to be attributable to several processes including chemiluminescence from the bimolecular termination reaction of peroxy radicals. George *et al.*[19] reported detailed results for the SICL during the deformation of Nylon 6/6 fibres and concluded that the main part of the chemiluminescence resulted from progressive scission of taut tie-molecules in the amorphous phase. We have also measured SICL for various kinds of polymers[15,20] and found that Ny6, which was slowly cooled from the melt, showed strong luminescence during deformation while the quenched sample showed very weak emission. *Figure 4* shows the time courses of the total SICL intensity and the applied stress for the slowly cooled Ny6 specimen. Extension and relaxation were repeated a few times in a series of measurements. Strong SICL, which was detected on increasing the tensile stress, decreased with stress relaxation and increased again with the next extension, as reported by George *et al.*[19] for Nylon 6/6.

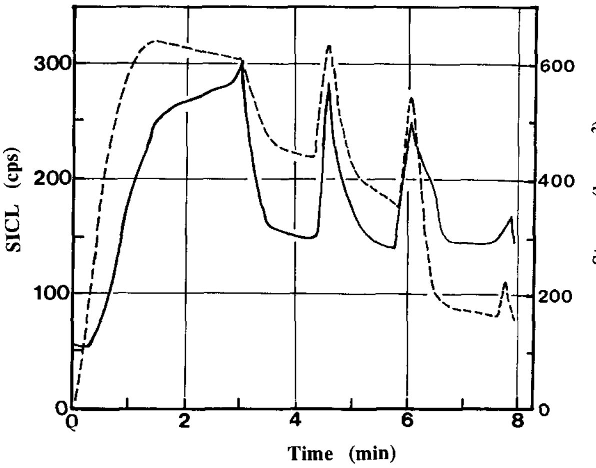

Figure 4 The time course of the total SICL intensity (——) and the applied stress (---) for a slowly cooled Nylon 6 specimen uniaxially drawn at the rate of 2.5 mm min^{-1} at room temperature

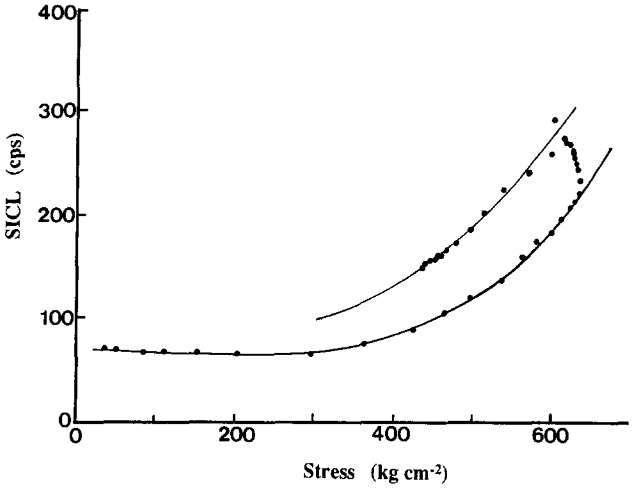

Figure 5 SICL intensity as a function of the applied stress for a slowly cooled Nylon 6 specimen. Closed circles are the experimental results and lines express the theoretical relationship obtained from equation (2) in the text

Free radical formation during the deformation of PE and nylons has been revealed by e.s.r. measurement[21] and by i.r. spectra of the oxidation products from subsequent reaction[22]. The rate of free-radical formation due to the chain scission, R, on an applied stress σ at a temperature T is given by the Zhurkov equation[23]:

$$R=n_c\omega_0\exp[-(U_0-\beta\sigma)/RT] \qquad (1)$$

where n_c is the number of chains to be cut off, ω_0 is the fundamental bond vibration frequency, U_0 is the main-chain bond strength, and β is the activation volume for bond scission. If the applied stress on the sample specimen is assumed to be the average stress on the chains, and the SICL observed is proportional to the rate of alkyl radical formation (because the reaction rate of peroxy radical formation from alkyl radical and oxygen is considered to be extremely fast, $E_{ac} \fallingdotseq 0$ kcal mol^{-1} [24]), then the intensity of the SICL can be expressed as follows:

$$I_{CL}=I_0\exp(\beta\sigma-U_0)+I' \qquad (2)$$

where I_0 is a constant including the overall efficiency of emission and I' is the intensity of emission other than SICL. SICL was plotted as a function of stress in *Figure 5* using the data shown in *Figure 4*. The experimental results show good agreement with the theoretical relationship described by equation (2), suggesting the validity of the mechanism estimated above.

Imaging of SICL was tried for a Ny6 sample specimen which possessed a hole at the centre of the specimen. By means of this hole, good reproducibility for the stress concentration in drawing the sample could be obtained. The intensity of the visual SICL became strong on increasing the extension ratio, and SICL was found to be strong especially around the hole in a transverse direction relative to the machine direction as shown in *Figure 6*, which indicates the SICL real-time image of the area around the hole of the sample drawn for 45 s (the strain is, therefore, estimated to be $\varepsilon=4.7\%$). The attached small picture roughly corresponds to the area of the image, and the arrows show the machine direction. The hole at the centre could not be distinguished in the SICL image because the luminescence intensity was very weak both at the region of less stress and at the hole space.

In order to understand the regional peculiarity for SICL, simulation by a finite element method (FEM) was carried out for the stress distribution when drawing a Ny6 specimen with the same shape factors as those of the experiment at strain $\varepsilon=5\%$, using the computer program ABAQUS (HK and S Co.). Young's modulus

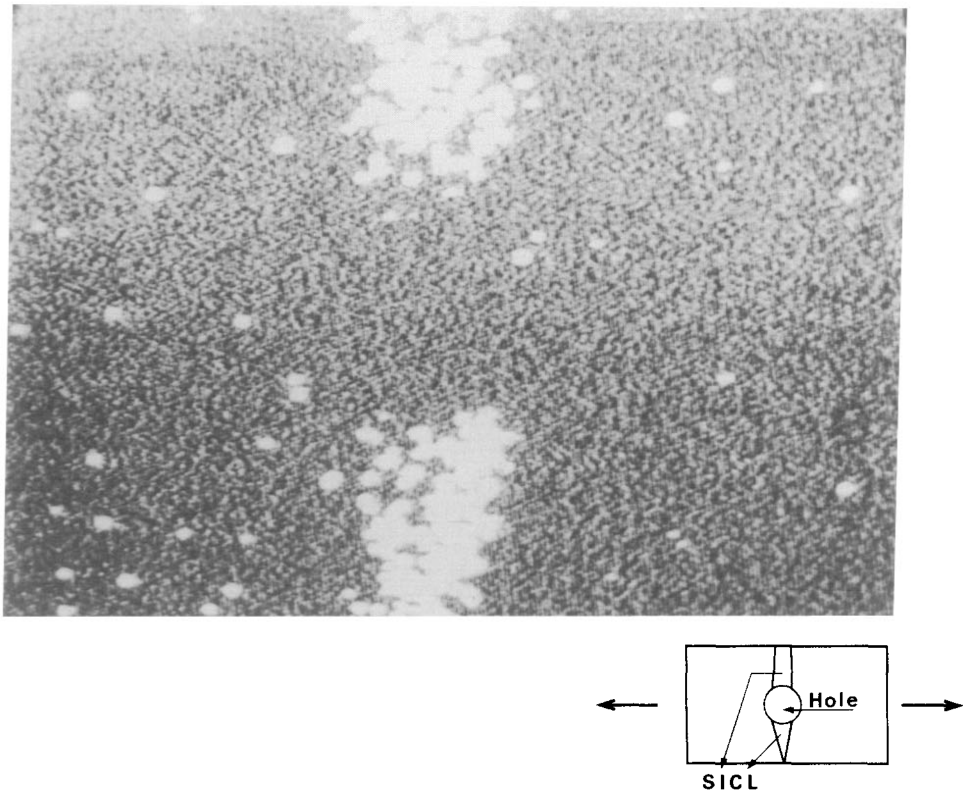

Figure 6 The real-time image of the region around the hole of the Nylon 6 specimen drawn at the rate of 2.5 mm min^{-1} at room temperature (strain; $\varepsilon = 4.7\%$). Attached small picture roughly corresponds to the region of SICL imaging, and arrows show the machine direction

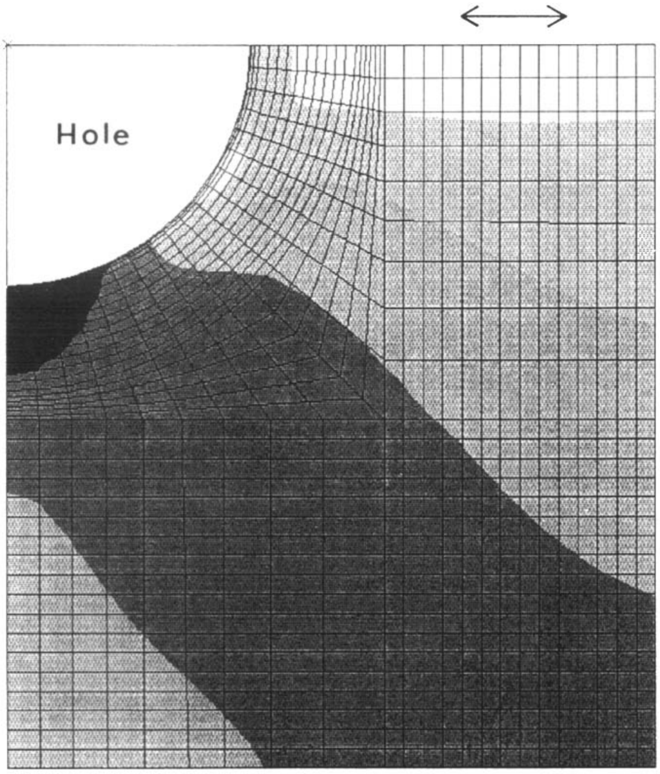

Figure 7 Simulation of the stress distribution for the drawn state ($\varepsilon = 5\%$) of a Nylon 6 specimen by a finite element method. Arrow shows the machine direction. A quarter of the whole area around the hole at the centre of the specimen is shown. The stress concentration increases with increasing darkness

and Poisson's ratio for Ny6 were taken to be 18 500 kg cm^{-2} and 0.30, respectively. The simulation indicates that the stress is concentrated around the hole in the transverse direction as shown in *Figure 7* (dark region), which is coincident with the portion of observed SICL.

In the case of crystalline polymers the crystalline phases are considered to be connected by a number of tie molecules in the amorphous phase. Chain scission of the tie molecules is considered to occur predominantly for the most strained molecules. The radical thus formed could easily react with oxygen in the air to produce peroxy radicals which are assumed to exhibit chemiluminescence through a bimolecular termination reaction. Hence it is quite reasonable that the deformation of crystalline polymers like Ny6 produces strong SICL at the area of stress concentration as a result of tie–chain scission.

Examples shown in this paper strongly suggest that chemiluminescence imaging is a promising technique for visualizing and predicting the sites of failure induced by ageing and mechanical stress in various polymer materials. Heat and mechanical deformation were demonstrated as primary causes of an increase in chemiluminescence, but it is of course possible to use other external causes such as u.v. light, γ-ray irradiation, electric stress, etc. Accordingly, chemiluminescence imaging could be developed in various fields to investigate the effects of these causes on the ageing of polymer materials.

ACKNOWLEDGEMENTS

The authors would like to thank Mr. H. Miyagi for his help in the FEM simulation and Drs A. Craig and R. Fleming of Charles Evans and Associates for helpful discussions and the imaging experiments of the multilayered sheets. Thanks are also due to Sumitomo Chemical Co. Ltd. for permission to publish this paper.

REFERENCES

1 Ashby, G. E. *J. Polym. Sci.* 1961, **L**, 99
2 Schard, M. P. and Russell, C. A. *J. Appl. Polym. Sci.* 1964, **8**, 985
3 Rychla, L. M., Fodor, Zs. and Rychly, J. *Polym. Deg. Stab.* 1981, **3**, 371
4 George, G. A. in 'Development in Polymer Degradation-3', (Ed. N. Grassie), Applied Science, London, 1981
5 Zlatkevich, L. *J. Polym. Sci., Polym. Lett. Edn* 1983, **21**, 571
6 Hosoda, S. and Kihara, H. *ANTEC* 1988, **88**, 941
7 Kihara, H. and Hosoda, S. *Polym. J.* 1990, **22**, 763
8 Osawa, Z., Konoma, F., Wu, S. and Cen, J. *Polym. Photochem.* 1986, **7**, 337
9 Cen, J., Konoma, F. and Osawa, Z. *Polym. Photochem.* 1986, **7**, 469
10 Kihara, H., Yabe, T. and Hosoda, S. *Polym. Bull.* 1992, **29**, 369
11 Yoshii, F., Sasaki, T., Makuuchi, K. and Tamura, N. *Ikigakau* 1985, **55**, 252
12 Yoshii, F., Sasaki, T., Makuuchi, K. and Tamura, N. *J. Appl. Polym. Sci.* 1986, **31**, 1343
13 Itoh, M. *Nihon Gomu Kyokaishi* 1985, **58**, 461
14 Hiramatsu, M., Muraki, H. and Itoh, T. *J. Polym. Sci., Polym. Lett. Edn* 1990, **28**, 133
15 Kihara, H. and Hosoda, S. *Polym. Prepr., Japan* 1989, **38**, 1195
16 Fleming, R. H. and Craig, A. Y. *Polym. Deg. Stab.* 1992, **37**, 173
17 Butyagin, P. U., Yerofeyev, V. S., Musalyelyan, I. N., Patrikeyev, G. A., Streletskii, A. N. and Shulyak, A. D. *Polym. Sci. USSR* 1970, **12**, 330
18 Streletskii, A. N. and Butyagin, P. Yu. *Polym. Sci. USSR* 1973, **15**, 739
19 George, G. A., Egglestone, G. T. and Riddell, S. Z. *J. Appl. Polym. Sci.* 1982, **27**, 3999
20 Kihara, H., Seki, Y. and Hosoda, S. Polymer '91, 10–14 February 1991, Melbourne, Prepr. 329
21 Kausch, H. H. 'Polymer Fracture', Springer-Verlag, Heidelberg, 1978
22 Korsukov, V. Ye., Vettengren, V. I., Novak, I. I. and Zeitseva, L. P. *Polym. Sci. USSR* 1974, **16**, 1781
23 Lloyd, B. A., De Vries, K. L. and Williams, M. L. *J. Polym. Sci. A-2* 1972, **10**, 1415
24 Reich, L. and Stivara, S. S. 'Autooxidation of Hydrocarbons and Polyolefins', Marcel Dekker, New York, 1969