Study of polypropylene peroxidation by ozonization using electron spin resonance and transmission electron microscopy

B. Catoire, V. Verney*, R. Hagege and A. Michel*
Institut Textile de France, BP 60, 69132 Ecully Cedex, France
*and *Laboratoire des Matériaux Organiques/CNRS, BP 24, 69390 Vernaison, France*
(Received 18 March 1991; revised 5 August 1991; accepted 6 August 1991)

Ozonization seems to be an interesting way to create reactive sites when the aim is to optimize radical grafting of vinyl monomers on polypropylene. In order to extensively follow the grafting parameters we used the spin-probe technique of electron spin resonance as well as the spin-trapping technique in conjunction with the diffraction and morphological techniques of transmission electron microscopy. The data indicate that ozonization modifies the diffusion mechanism of liquid monomers in the polypropylene matrix and suggest that grafting takes place in the amorphous phase. We also showed that a core–shell morphological structure can be observed on ozonized polypropylene (granules and fibres). Further, information on peroxide location was obtained.

(**Keywords: electron spin resonance; transmission electron microscopy; polypropylene; ozonization**)

INTRODUCTION

Ozonization is a useful tool to create peroxide groups on a polypropylene chain which are able to initiate radical polymerization of vinyl monomers. These groups operate in the temperature range of 70–180°C[1–5].

In order to use the reactivity of the material in the condensed state, parameters such as peroxide thermal decomposition kinetics, the nature of the generated radicals, the accessibility of peroxide sites, monomer diffusion and location in the ozonized matrix, and chemical and morphological structure modifications have to be well controlled and optimized.

In order to follow the thermally induced radicals and their kinetics in the polymer matrix, the spin-trapping technique of electron spin resonance (e.s.r.) was used[6,7]. The diffusion into and the location of monomers in the polypropylene were studied using the spin-probe technique of e.s.r.[8,9].

We also studied the morphological structure modifications using transmission electron microscopy (TEM) and morphological probes[10].

EXPERIMENTAL

Materials

The polypropylene used was either in powder form obtained from polymerization (average particle diameter 290 μm) or fibres (average diameter 25 μm) obtained from melt-spinning.

The polypropylene powder used contained no stabilizers and had an average molecular weight of 289 000 and a molecular weight distribution of 6.

The yarns used contained u.v. stabilizers and were made of continuous monofilaments.

Ozonization of the polypropylene powder was carried out in a fluid bed with an ozone–oxygen–nitrogen gas mixture ($O_3 = 6.2\ \mathrm{mg\ l^{-1}}$) for 5 h at 70°C.

The polypropylene fibres were treated in a reactor for 45 min at 70°C with an ozone–oxygen gas mixture.

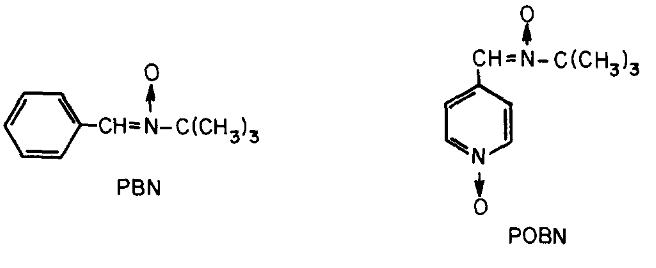
Equipment

The transmission electron microscope used was a Phillips model EM 400. The e.s.r. measurements were carried out on a Bruker 100D working in the X-band with a 10 000 G magnet. The d.s.c. apparatus was a Du Pont 990.

E.s.r. spin-trapping technique

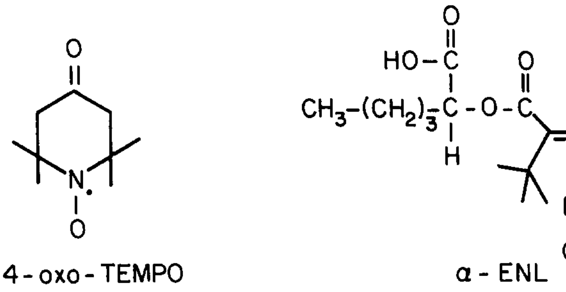
The nitrones used were *N*-tert-butyl-α-phenyl nitrone (PBN) and α-4-pyridil-1-oxide-*N*-tert-butyl nitrone (POBN) and were obtained from Jansen Chemica (*Scheme 1*).

The inclusion of spin traps was carried out as follows: Polypropylene powder or fibre, control and ozonized, were dipped for 1 h at 40°C into a solution of dichloromethane (swelling agent) containing the spin trap. The



Scheme 1 Spin-trap molecules

0032-3861/92/112307-05



Scheme 2 Spin-probe molecules

samples including the nitrone were dried at 35°C to remove all of the solvent.

E.s.r. spin-probe technique

Two nitroxide radicals with very different chemical compositions were used: 2,2,6,6-tetramethyl-4-oxo-piperidinooxy (4-oxo-TEMPO, Eastman Kodak) and a molecule containing a lipophilic group, 2,2,5,5-α-lauric acid ester-4-pyrolin-1-yloxy (α-ENL) (*Scheme 2*). The α-ENL was synthesized in the Institute Textile de France[11].

The inclusion experimental protocol is the same as described above. The samples were dried and washed twice with methanol in order to eliminate the probe molecules left on the surface.

TEM morphological probe technique

This method consists of polymerizing inside the polymer an elastomer (polyisoprene) with free double bonds and fixing these double bonds with osmium tetroxide (OsO_4)[10]. The experimental protocol is the following: Polypropylene samples (powder or fibre), control and ozonized, were put into an autoclave and subjected to isoprene vapour at 80°C for 24 h. Polymerization of isoprene inside the solid polymer was initiated either by heat for non-ozonized polypropylene (control) or by the grafted peroxides of the ozonized polypropylene. The samples including polyisoprene were then exposed at 35°C to OsO_4 vapour for 30 h. The stained polypropylene was embedded with araldite either at 70°C or at room temperature.

TEM electron diffraction technique

Electron diffraction was performed according to the selected area electron diffraction technique[12]. The selected area was a circle of 1 μm in diameter for a section with a thickness of ~0.1 μm. The low dose technique was used in order to minimize electron damage. For comparison, four prints were recorded on the same plate with identical illumination conditions.

RESULTS AND DISCUSSION

E.s.r. spin-trapping technique

The thermally induced radicals are generally too short-lived at the grafting temperature and cannot be observed by e.s.r. unless previously stabilized by molecules called spin traps.

This technique involves nitrone diamagnetic molecules (ST) able to fix the thermally induced radicals (R°) to form a more stable paramagnetic nitroxide addition product called a spin adduct (SA°):

$$R^\circ + ST \rightarrow SA^\circ$$

The nitrones used as spin traps were chosen on account of their good thermal stability.

Figure 1 shows the e.s.r. spectrum of ozonized polypropylene powder or fibre including PBN or POBN heated for 15 min at 115°C. Such spectra were recorded after cooling to room temperature. The three wide and asymmetrical lines with a total width of 60 G are characteristic of a generated nitroxide spin adduct molecule strongly immobilized in a highly viscous medium in the accessible zones (amorphous interlamellar zones) of the polypropylene. Conversely under similar conditions of inclusion and heat treatment no significant response with the non-ozonized polypropylene (powder and fibre) is observed.

The area located under the absorption curve is proportional to the number of free radicals. If the line shapes of the two samples are quite similar, then measurements of the derivative lines will permit correlation.

As long as the spectra are recorded after cooling to room temperature similar line shapes are observed. In order to follow the variations of generated nitroxide radicals we chose to measure the height of the peak marked 1 on the spectrum, other things being equal.

The variations in intensity values (arbitrary units) *versus* time at various temperatures reach asymptotically a constant value. Below 75°C the content of induced nitroxide radicals is too weak for significant measurements to be done. Identical phenomena are observed irrespective of the spin trap used.

It was possible to measure initial decomposition rates and to calculate the activation energy of the thermal decomposition of the peroxides[7]. The value found was 100 kJ mol^{-1} and is in good agreement with literature values[13,14].

E.s.r. spin-probe technique

The spin-probe technique for e.s.r. was used to study the influence of the molecular structure on the diffusion of a molecule into the polypropylene matrix. This method involves a very stable nitroxide molecule as a spin probe. Such radical molecules are very sensitive to their submicroscopic environment and give information about

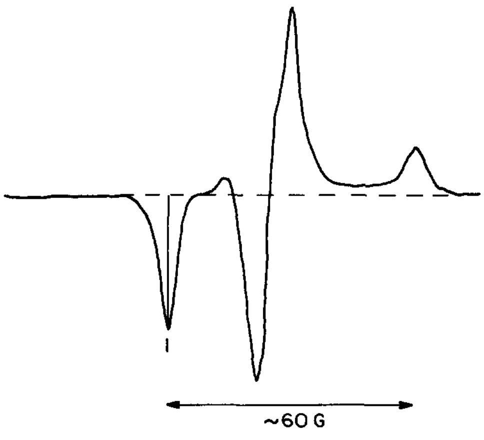


Figure 1 E.s.r. spectrum recorded, after cooling to room temperature, of ozonized polypropylene (powder or fibre) including PBN or POBN and heated for 15 min at 115°C

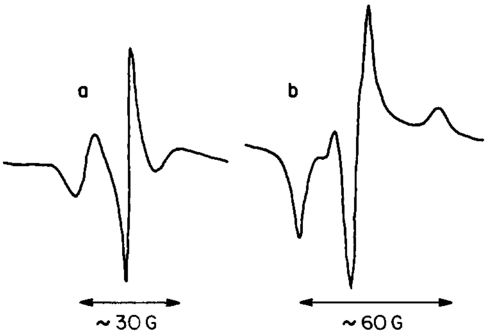


Figure 2 E.s.r. spectra obtained from ozonized polypropylene fibre: (a) 4-oxo-TEMPO as spin probe; (b) α-ENL as spin probe

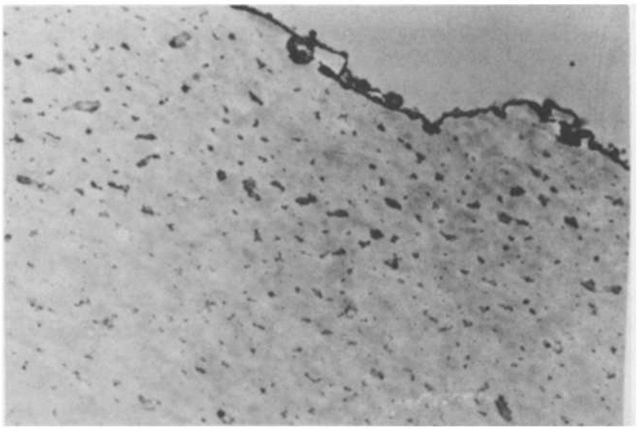


Figure 3 TEM cross-section of the edge of a non-ozonized polypropylene granule including polyisoprene and stained with OsO$_4$ (×4150)

their location and degree of dispersion in the polymer matrix. The radical rotational motions reflect its environment via the shapes of the spectra.

Figure 2 shows the spectra obtained with ozonized polypropylene fibre or powder including 4-oxo-TEMPO and α-ENL. *Figure 2a* shows that the probe has diffused at a supramolecular level where the nitroxide molecules retain some freedom of motion (anisotropic spectrum with three lines and with a total linewidth of 30 G). *Figure 2b* shows that α-ENL has deeply penetrated into the accessible zones of the polypropylene structure at a macromolecular level and has dissolved in it, forming a so-called quenched solution (three wide and asymmetrical lines with a total linewidth of 60 G[15].

These results show that long aliphatic groups (such as lauroyl groups) favour the miscibility of a molecule into the polypropylene matrix and suggest that they will favour the homogeneous dispersion of any bonded monomer (such as lauroyl methacrylate) which should lead to homogeneous grafting[3].

TEM morphological probe

Figure 3 is a TEM cross-section of the edge of a non-ozonized polypropylene granule including polyisoprene and stained with OsO$_4$. The darker zones correspond to the location of OsO$_4$. The micrograph shows that the polyisoprene is dispersed in domains which are 200–2000 Å. This is due to the existence of pores in the polypropylene powder. Conversely, in *Figure 4*, the ozonized granules show a peripheral zone darker than the core which is due to a greater quantity of included polyisoprene in the skin structure, which is in addition to the stained elastomer observed on the control polypropylene. The thickness of the skin is $\sim$20 μm. This micrograph clearly shows that ozonization treatment modifies the diffusion of a monomer (such as isoprene) into the polypropylene through peroxide decomposition, carbonyl group formation and chain scission[3]. *Figure 5* shows the skin structure at higher magnification. Dark areas can be seen surrounded by lighter zones which may be spherulites.

A similar skin–core morphology was also shown in the case of grafting α-chloromethylstyrene onto ozonized polypropylene using scanning electron microscopy and X-ray energy dispersive analysis of chlorine atoms[16].

The same behaviour is observed with ozonized polypropylene fibres although a more marked skin–core morphology is obtained. *Figure 6a* shows a cross-section of polyisoprene stained fibres. The dark regions are located in the amorphous accessible zones surrounding clear zones with a lighter electron density. These clear

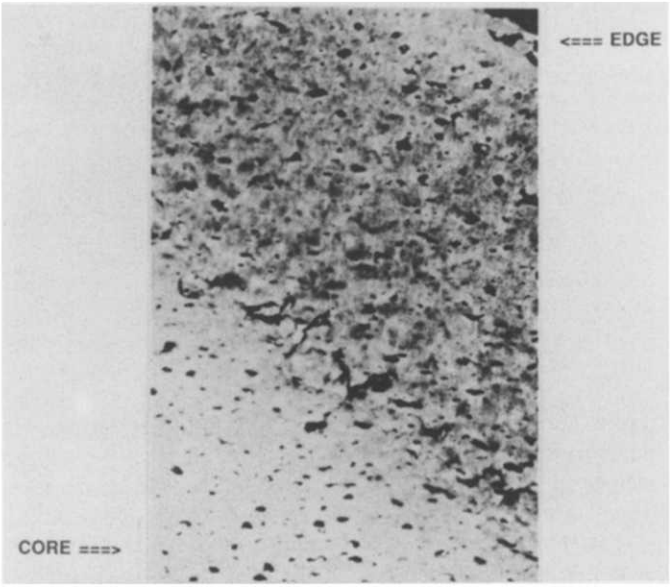


Figure 4 TEM cross-section of the edge of an ozonized polypropylene granule including polyisoprene and stained with OsO$_4$ (×3700)

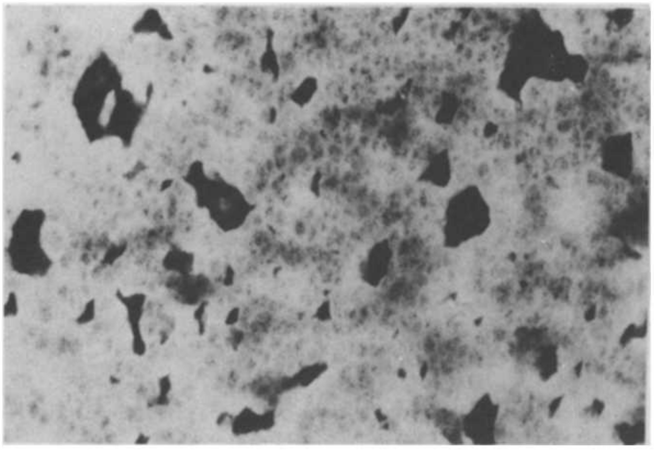


Figure 5 TEM cross-section of the skin structure of an ozonized polypropylene granule including polyisoprene and stained with OsO$_4$ (×14940)

regions would be macrofibrillar elements with crystalline tendency. The fibrillar crystalline zones appear smaller in the skin region than in the bulk of the fibre. Moreover one can notice that the skin is also of a bicomponent morphology. At the very edge of the fibre an homogeneous darker ring with no fibrillar elements is observed and, further in, layers with crystalline tendency can be observed. Some cracks due to ozone treatment are also observed; this is a well-known phenomenon in the oxidation of polymeric materials.

Figure 6b shows the control polypropylene fibre (non-ozonized) under the same experimental conditions.

These results confirm that ozone treatment modifies isoprene diffusion and that ozonization causes chemical and physical modifications which are more important in the skin than in the core of either polypropylene powder or fibres.

Microdiffraction

Figure 7 shows the structure observed by TEM and the microdiffraction spectra obtained from ultrathin sections of ozonized polypropylene granules without any staining.

Figure 7a shows an ozonized granule without any staining and embedded at room temperature. No difference is seen between the skin and the core of the granule. Likewise, the resolution of the skin and of the bulk crystalline rings on the microdiffraction spectra is similar. If the ozonized powder is annealed in an oven at 75°C or 115°C, as is the case for grafting, a very different situation is observed.

Figure 7b shows a micrograph after annealing at 75°C and shows a 20 μm thick skin. This skin presents a lighter electron density than the core. The microdiffraction spectrum of the edge of the granule shows better resolution of the crystalline rings compared with the bulk. *Figure 7c* shows a micrograph after annealing at 115°C. The same behaviour is observed but the contrast between the skin and the core is much greater. The 20 μm skin is much less electron dense (clearer) and more crystalline.

Figures 8a and *b* are micrographs of non-ozonized powder annealed at 75°C and 115°C, respectively. Irrespective of the annealing temperature no morphological crystalline difference is observed between the core and the peripheral zone.

The same structural behaviour is observed in the case of fibres. Annealing allows recrystallization of the skin.

To study the skin–core structure in more detail the samples were treated with polyisoprene and then stained.

Figures 9a and *b* show at high magnification the skin and the core of a granule annealed at 75°C. In the peripheral zone (*Figure 9a*) a very clear lamellar morphology can be seen (white regions, 50 Å thick). The

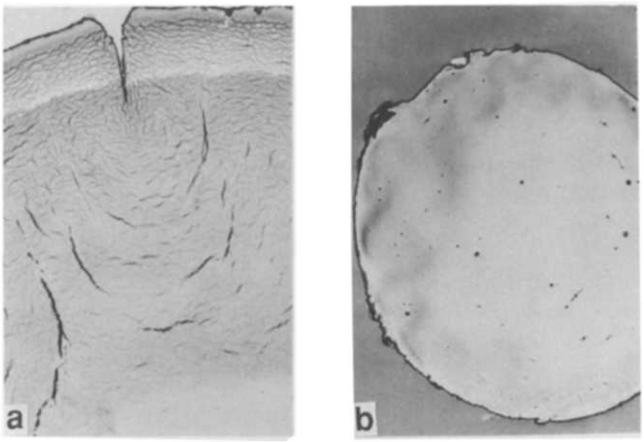


Figure 6 TEM cross-section: (a) ozonized fibre including polyisoprene and stained with OsO_4 (×10080); (b) non-ozonized fibre including polyisoprene and stained with OsO_4 (×2800)

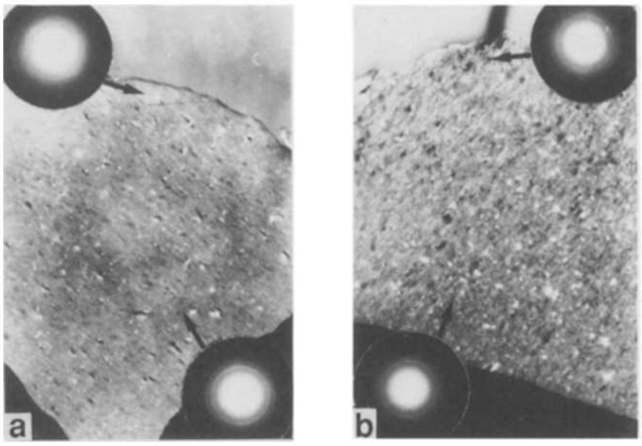


Figure 8 TEM microdiffraction spectra: control non-ozonized polypropylene granule annealed at (a) 75°C and (b) 115°C (×1008)

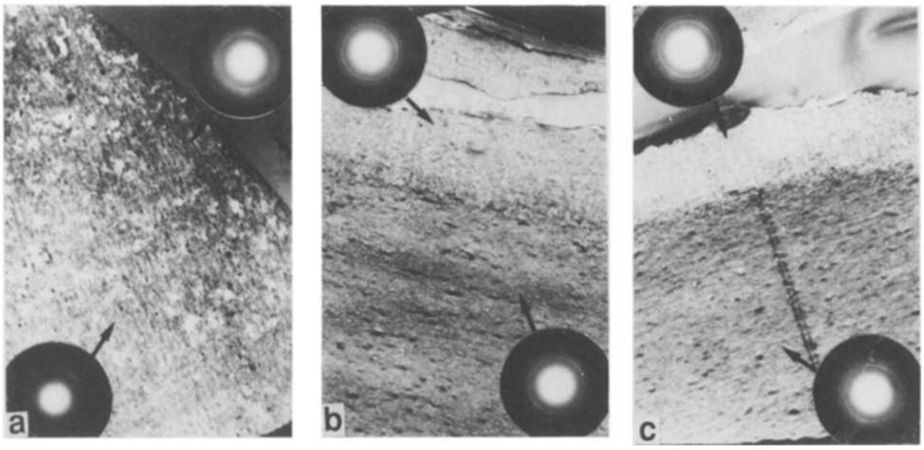


Figure 7 TEM microdiffraction spectra: (a) ozonized polypropylene without staining and embedded at room temperature; (b) as for (a) but with annealing at 75°C; (c) as for (a) but with annealing at 115°C (×1008)

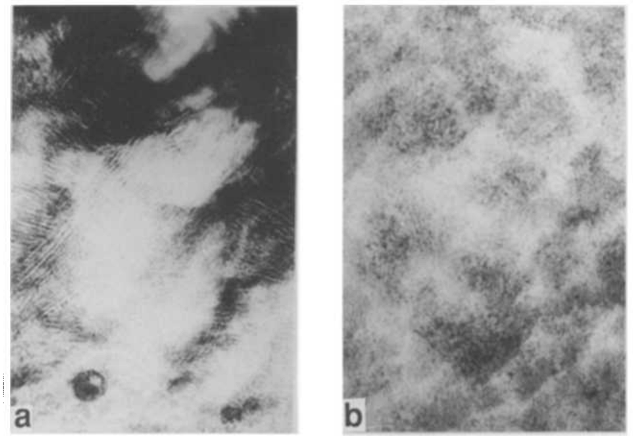


Figure 9 TEM microdiffraction spectra: (a) peripheral zone and (b) core of an ozonized polypropylene granule annealed at 75°C (× 112 000)

stained polyisoprene is located between the lamellae. Conversely, in the core (*Figure 9b*) the lamellae are present but poorly resolved. In the same experimental conditions no lamellae were observed on the control polypropylene granules. It can be said that heating has 'polarized'[17] the lamellar ozonized granule structure with amorphous interlamellar zones. This permits a better amorphization of the interlamellar zones enabling the reactive sites to diffuse more freely within them.

These results confirm that ozonization modifies the diffusion mechanism of liquid monomers in the polypropylene matrix and suggest that grafting takes place in the amorphous phase.

CONCLUSIONS

The spin-probe technique is a powerful tool to follow the diffusion and location of monomers in a solid polymer matrix, such as polypropylene, and it contributes to a better understanding of radical grafting in the heterogeneous phase.

The morphological probe technique in TEM as well as the microdiffraction technique also appear to be powerful tools to localize radical grafting in a polymer matrix. These techniques shed light on peroxide location after ozonization through morphological modifications. In the case of polypropylene ozonization, a core–shell structure is observed equally well for polypropylene powder as for polypropylene fibres.

REFERENCES

1 Popov, A. A., Blinov, N. N., Krisyuk, B. E., Karsova, S. G., Privalova, L. G. and Zaikov, G. E. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 1017
2 Smets, G., Veinand, G. and Deguchi, S. *J. Polym. Sci., Polym. Chem. Edn.* 1978, **16**, 3077
3 Verney, V., Koerper, E. and Michel, A. *Makromol. Chem., Macromol. Symp.* 1989, **25**, 187
4 Mukherjee, A. K. and Gupta, B. *J. Macromol. Sci.* 1983, **A19**, 1069
5 Citovicki, P., Mikulasova, D., Chrastova, V. and Benc, G. *Eur. Polym. J.* 1986, **13**, 655
6 Janzen, E. G., Anderson Evans, C. and Nihsi, Y. *J. Am. Chem. Soc.* 1972, **94**, 8236
7 Catoire, B., Verney, V. and Michel, A. *Makromol. Chem., Macromol. Symp.* 1989, **25**, 199
8 Berliner, L. J. 'Spin Labelling, Theory and Applications', Academic Press, New York, 1976
9 Catoire, B., Bouriot, P. and Hagege, R. *Bull. Sci. ITF* 1977, **6**, 21
10 Catoire, B., Hagege, R. and Meimoun, D. *Bull. Sci. ITF* 1969, **23**, 143
11 Catoire, B. and Roncin, J. personal communication, 1982
12 Hagege, R. *Am. Chem. Soc. Symp. Ser. 17* 1979, **270**, 301
13 Zolotova, N. V. and Denisov, E. T. *J. Polym. Sci.* 1971, **A1**, 3311
14 Iring, M. *Polym. Degrad. Stab.* 1980–81, **3**, 371
15 Catoire, B., Tassin, C., Oueslati, R., Prost, C., Verney, V. and Michel, A. *Polym. Proc. Eng.* 1986, **4**, 2
16 Polednick, C., Widdecke, H., Bodrero, S., Revillon, A. and Guyot, A. *J. Polym. Sci., Polym. Chem. Edn.* 1990, **28**, 261
17 Hearle, J. W. S. and Greer, R. *Textile Progr.* 1970, **2**, 4