Irradiation effects of excimer laser radiation and electron beam on polypropylene and ethylene–tetrafluoroethylene copolymer films

Shunichi Kawanishi, Yuichi Shimizu, Shun'ichi Sugimoto and Nobutake Suzuki
Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, 25-1 Mii-minami, Neyagawa, Osaka 572, Japan

(*Received 11 November 1989; revised 17 April 1990; accepted 10 May 1990*)

The irradiation effects of the intense ultraviolet radiation from an excimer laser on polypropylene (PP) and ethylene–tetrafluoroethylene (ETFE) copolymer films are compared with those from electron beam studies. Irradiation of PP films with a KrF laser and an electron beam induced the degradation of the polymer, and use of an ArF laser selectively decomposed the alkyl phenol type additive contained as an antioxidant in PP instead of degrading the polymer. Irradiation with a KrF laser induced the carbonization of ETFE copolymer due to polymer degradation, and irradiation with an ArF laser and an electron beam formed –C=O and –C=C– groups in the polymer chains.

(Keywords: excimer laser; electron beam; irradiation effect; selective photodecomposition; polypropylene; ethylene–tetrafluoroethylene copolymer)

INTRODUCTION

There has been considerable interest recently in the use of intense ultraviolet (u.v.) radiation from excimer lasers for the modification of polymer surfaces to improve adhesion or to provide functionalities. Many studies on the interaction of u.v. laser pulses with solid organic materials, such as aromatic polymers and biological tissue, have been carried out since the discovery of the phenomenon of ablative photodecomposition (APD)[1,2]. Using APD the depth of the cut and the thermal damage to the substrate can be controlled[3]. Aromatic polymers which are difficult to modify because of excellent heat resistance and chemical stability can be easily and cleanly etched with the APD process.

The APD process is useful for the etching of aromatic polymers and biological materials. However, it is not available for modifying aliphatic polymers. A few studies on the irradiation effect of excimer laser radiation on aliphatic polymers have been reported[4]. The characteristic weak photoabsorption in the u.v. region of the aliphatic polymers should show the different photoreaction in the polymer matrix of the aromatic polymers. The commercial merit of the aliphatic polymers is their production at low cost. Addition of high functionalities to these polymer materials is regarded as important, and is a new application of intense u.v. radiation from excimer lasers.

The irradiation effects of laser radiation and electron beam on the photodecomposition or degradation of polypropylene (PP) and ethylene–tetrafluoroethylene (ETFE) copolymer are reported here using ultraviolet and visible (u.v.-vis.) and infra-red (i.r.) spectroscopy techniques.

EXPERIMENTAL

Samples

Commercially available polymer films of PP (25 μm thick) and ETFE (50 μm thick) were purchased from the Asahi Glass Co. Ltd. The chemical structures for these polymers are listed in *Table 1*.

Irradiation

The laser used for irradiation was a Lumonics model HE-460 excimer laser which emitted 0.1–0.5 J pulses of 15–20 ns duration at 193 nm (ArF) and 248 nm (KrF). The laser was generally operated at 1 Hz to avoid any heating effect on the polymer. The laser beam was not focused and its dimension was 8 × 33 mm^2. The fluence quoted hereafter was measured by a Gen-Tech Joule meter (Model ED-500). The samples were attached to the surface of the probe of the Joule meter keeping the incident angle normal, and the intensity of the light transmitted through the polymer films was measured and averaged over irradiation. The deviations of the fluence from the mean values were about 3.8 and 8.1% for KrF and ArF laser irradiation, respectively. The fluence of each laser radiation is given in *Table 2*. Energy absorbed into each polymer was calculated by subtraction of the transmitted intensity from the incident intensity. The values per pulse are also listed in *Table 2* and compared with the absorption coefficient measured using a spectrophotometer.

Laser irradiation was carried out in air at room temperature.

Electron beam irradiation was carried out at room temperature with a van de Graaff type accelerator operated at 1.5 MV with a beam current of 50 μA.

0032-3861/91/060979-05

Table 1 Polymer films used in this study

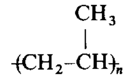
Polymer	Structure	Thickness (μm)
Polypropylene (PP)	 $-(CH_2-\underset{}{\overset{CH_3}{\overset{\vert}{C}H}})_n-$	25
Ethylene–tetrafluoroethylene (ETFE) copolymer	$-(CH_2-CH_2)_n-(CF_2-CF_2)_m-$	50

Table 2 Conditions of laser irradiation on polymer films

KrF radiation

Polymer	Intensity (J) Incident	Intensity (J) Transmitted	$\log(I_0/I)$ (–)	OD_{248}[a] (Abs.)	Absorbed energy (kJ kg^{-1})
PP	0.357	0.290	0.09	0.14	11.3
ETFE	0.357	0.283	0.10	0.13	3.7

ArF radiation

Polymer	Intensity (J) Incident	Intensity (J) Transmitted	$\log(I_0/I)$ (–)	OD_{193}[a] (Abs.)	Absorbed energy (kJ kg^{-1})
PP	0.270	0.115	0.37	0.69	26.1
ETFE	0.270	0.146	0.28	0.63	6.1

[a] Measured using a spectrophotometer

The samples wrapped with aluminium foil were placed on a metal plate temperature-controlled by circulating water, and were irradiated. The absorbed dose was measured by a cellulose triacetate film dosemeter[5]. The absorbed dose of each sample was 10^5 Gy (= 10^5 J kg^{-1}).

Measurement of spectra

Ultraviolet-visible absorption spectra were measured using a Shimadzu UV 2100 spectrophotometer.

Infra-red transmission and attenuated total reflection (ATR) spectra were measured using a Perkin Elmer Fourier transform infra-red spectrometer Type 1720X. For ATR measurement, the spectrometer was equipped with an ATR attachment and KRS-5 reflection element (Spectra-Tech Inc., 2 × 20 × 52.5 mm) with 45° facits.

Optical emission measurement was carried out using an FP-550 fluorophotometer (Japan Spectroscopic Co., Ltd).

RESULTS AND DISCUSSION

Irradiation effects on PP film

Ultraviolet-visible spectra of PP films are shown in *Figure 1*. These spectra contain the influence of reflection of the polymer. *Figure 1d* (broken line) corresponds to the part of the reflection, $\log(1 - R)$, calculated from the reflectivity R of non-irradiated PP film. When the PP film was irradiated with a KrF laser (*Figure 1a*), the absorbance was enhanced in the wavelength range 190–400 nm as compared with that of the non-irradiated film (*Figure 1b*). In contrast with this case, with ArF laser irradiation (*Figure 1c*) the absorbance decreased in the range 190–240 nm.

Differential u.v.-vis. spectra between non-irradiated and irradiated PP films are shown in *Figure 2*. The influence of the reflectivity of the films on the differential absorption spectra was negligible. The quantities of energy absorbed into the polymer films for irradiation with electron beam, KrF laser (15 pulses) and ArF laser (15 pulses) radiation were 10^5, 1.7×10^5 and 3.9×10^5 J kg^{-1}, respectively. By irradiating with a KrF laser (*Figure 2a*) and electron beam (*Figure 2b*) the differential spectra had peaks in the wavelength range below 190 nm, and at about 210 and 250 nm. In the case of ArF excimer laser irradiation (*Figure 2c*), a considerable decrease in absorbance was clearly observed at a wavelength below about 240 nm. These results indicate that there is a large difference between irradiation effects of KrF and ArF laser radiation; KrF laser irradiation induces the formation of new absorption bands and ArF laser irradiation decomposes a component contained in the polymer. The irradiation effect of electron beam is similar to that of KrF laser radiation.

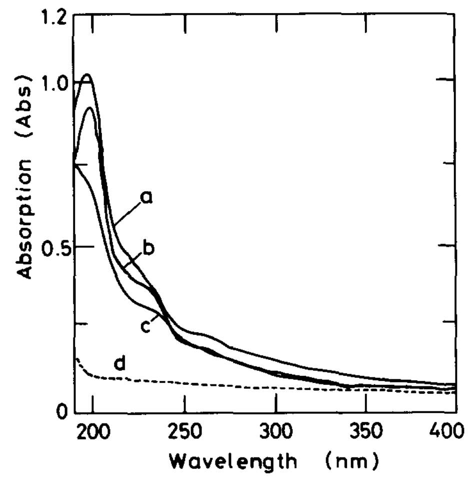


Figure 1 Ultraviolet-visible absorption spectra of PP. (a) KrF laser irradiation 15 pulses, (b) non-irradiated sample, (c) ArF laser irradiation 15 pulses, and (d) plot of $\log(1 - R)$, where R is the reflectivity of non-irradiated PP film

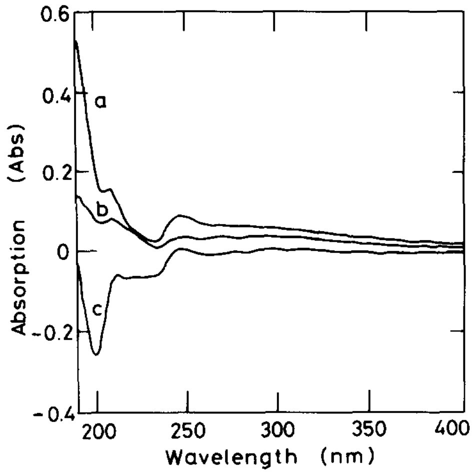


Figure 2 Ultraviolet-visible differential spectra between non-irradiated and irradiated PP. (a) KrF laser irradiation 1.7×10^5 J kg^{-1}, (b) 1.5 MeV electron beam irradiation 10^5 J kg^{-1} and (c) ArF laser irradiation 3.9×10^5 J kg^{-1}

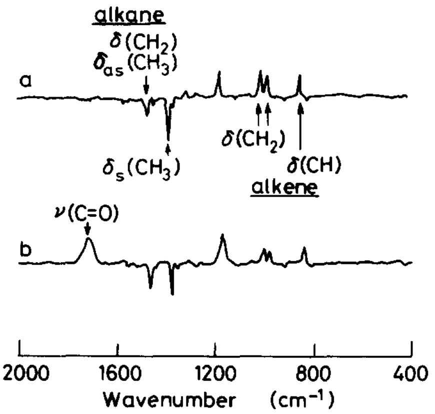


Figure 3 Differential i.r. spectra of irradiated PP. (a) KrF laser irradiation and (b) 1.5 MeV electron beam irradiation

Differential i.r. spectra between non-irradiated and irradiated PP films are shown in *Figure 3*. The observed transmission i.r. spectra of non-irradiated PP was similar to those reported earlier[6,7]. By irradiation with both a KrF laser (*Figure 3a*) and an electron beam (*Figure 3b*), the vibration bands of alkane (1300–1500 cm^{-1}) decreased and those of alkene (800–1100 cm^{-1}) increased. Furthermore, in the case of irradiation with an electron beam the increase in carboxyl group (–C=O, 1715 cm^{-1}) was observed. However, the i.r. spectrum was hardly affected by ArF laser irradiation. These results indicate that the –C–C– bonds in PP polymer chains are transformed into –C=C– bonds by irradiation with a KrF laser and an electron beam, and the oxidation of the polymer matrix chains is induced alone by electron beam irradiation.

As described above, the degradation of the polymer chains occurs by irradiation using a KrF laser and electron beam, and the oxidation products are formed by electron beam irradiation. It is assumed from the above results that the u.v.-vis. absorption bands observed below 200 nm in *Figure 2a* and *2b* are attributed to the $\pi \rightarrow \pi^*$ absorption of –C=C– and –C=O groups induced in the polymer chains by the irradiation. It is also assumed that the absorption peak at 250 nm in *Figure 2b* is due to the $n \rightarrow \pi^*$ absorption of the –C=O group. ArF laser irradiation does not produce –C=C– and –C=O groups because the i.r. spectrum was in accordance with that of the non-irradiated polymer film, and no change in absorbance at 190 and 250 nm was observed. This result indicates that the degradation of the polymer is not induced by ArF laser irradiation. Thus, the oxidation and degradation induced in the polymer matrix by irradiation can be explained by i.r. and u.v.-vis. spectroscopy.

Results of optical emission measurements are shown in *Figure 4*. The emission maximum was observed at 342 nm (λ_{em}). An excitation spectrum (*Figure 4a*) was obtained by measuring the optical emission intensity with scanning excitation wavelength when the emission wavelength was fixed at λ_{em}. The emission spectrum (*Figure 4b*) was recorded with scanning emission wavelength. Both the excitation and emission spectra are similar to those reported in earlier literature[8]. Consequently the optical emission is assumed to be fluorescence due to an alkyl phenol type additive, for example, 2,6-di-tert-butyl-4-methylphenol (BHT, see *Figure 5*) contained in PP as an antioxidant. The absorption at 198 nm may correspond to the ^{1}B band whose absorption coefficient, ε, is generally in the order of 10^4. Calculating the concentration of the antioxidant using ε and absorbance of PP film at 198 nm, it can be estimated that there is 0.1–0.5% antioxidant in PP. Irradiation using a KrF laser and electron beam slightly changed the shape of the emission spectra because of a variation in absorbance due to colouration of the polymer.

The excitation spectrum (*Figure 4a*) almost agrees with the decrease of the u.v.-vis. absorption component by ArF laser irradiation (*Figure 2c*), so the decrease in the u.v.-vis. absorption band is considered to be attributable to the decomposition of the antioxidant in the polymer. Thus, the decomposition of the antioxidant is primarily induced by irradiation using an ArF laser, and the PP matrix is not influenced by the quantity of absorbed energy, 26.1 kJ kg^{-1}.

As shown in *Figure 1*, the absorption spectrum of non-irradiated PP film at 190–400 nm consists of two components: one is due to the imperfections of the polymer, such as the –C=C– bond which is introduced

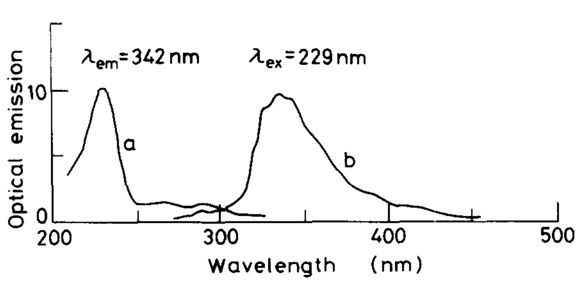


Figure 4 Optical emission spectra of non-irradiated PP. (a) Excitation spectrum. The emission wavelength, λ_{em}, is 342 nm. (b) Emission spectrum. The excitation wavelength, λ_{ex}, is 229 nm

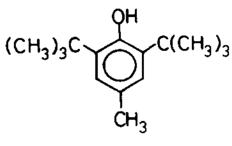


Figure 5 Chemical structure of 2,6-di-tert-butyl-4-methylphenol (BHT)

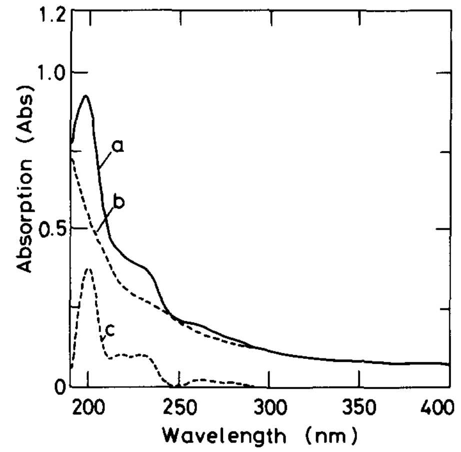


Figure 6 Measured and evaluated spectra of non-irradiated PP. (a) Measured spectrum, (b) evaluated spectrum by subtracting spectrum c from the measured spectrum a, and (c) evaluated spectrum due to the antioxidant estimated by the decrease component in *Figure 2c*

in the production of the polymer; and the other is due to the antioxidant. *Figure 6b* is ascribed to the imperfections of the polymer, and the estimated spectrum (*Figure 6c*) approximately corresponds to the absorption spectrum of the additive contained in PP as an antioxidant.

Since the wavelength of KrF laser radiation, 248 nm, differs from that of the absorption bands of the antioxidant, the radiation energy is largely absorbed into the imperfect portion of the polymer. Hence, the polymer is predominantly degraded by KrF laser irradiation without decomposition of the antioxidant, and the increase in u.v.-vis. absorbance due to the formation of $-C=O$ and $-C=C-$ groups is observed. As the absorption spectrum of the antioxidant possesses peaks at 198 and 230 nm, ArF laser radiation, 193 nm, can be largely absorbed into the antioxidant. It is therefore presumed that the selective decomposition is induced by the photon energy directly absorbed into the antioxidant. As shown in *Figure 6*, the 193 nm photon should be absorbed not only by the antioxidant but also by the imperfect portion of the polymer. However, only the decomposition of the antioxidant was observed and not polymer degradation by irradiation with an ArF laser. This suggests that the 193 nm photon energy absorbed into the imperfect portion is inactivated by the antioxidant whose energy level for the lowest excited state is lower than that of the 193 nm photon (6.42 eV), with the antioxidant acting as a stabilizer for PP irradiated with 193 nm photon. For electron beam irradiation, since the energy absorbed is proportional to the electron density of the materials, the degradation of the polymer precedes the decomposition of the antioxidant whose concentration is less than about 0.5%.

Irradiation effects on ETFE copolymer film

Ultraviolet-visible absorption spectra of ETFE films irradiated with a KrF laser (100 pulses) are shown in *Figure 7*. The contribution of the reflectivity of the polymer on the absorption spectra is shown in *Figure 7c*. The absorption spectrum of non-irradiated ETFE may be due to the imperfect portion of the polymer formed during production. A large increase in absorbance for ETFE irradiated with a KrF laser was observed in the wavelength range greater than 190 nm.

Figure 8 shows the u.v.-vis. differential spectra between non-irradiated and irradiated ETFE. The influence of the reflectivity on the differential spectra is negligible. The quantities of absorbed energy for irradiation with a KrF laser (100 pulses), an ArF laser (100 pulses) and electron beam were 3.7×10^5, 6.1×10^5 and 10^5 J kg^{-1}, respectively. In these cases, the absorption band whose peak centred at about 230 nm appeared. For irradiation with a KrF laser (*Figure 8a*), in addition to the 230 nm peak absorption band, a large increase in the absorbance at longer wavelengths was observed. This increase is considered to be due to carbonization due to the degradation of the polymer. In fact, the exposed portion of the films blackened. ArF laser irradiation only produced the 230 nm absorption band. Electron beam irradiation (*Figure 8c*) increased the absorption band spread at wavelengths less than 200 nm, overlapping the 230 nm absorption band.

The differential i.r. spectra between non-irradiated and irradiated ETFE films are shown in *Figure 9*. The ATR-i.r. transmission spectrum of non-irradiated ETFE agreed with results reported earlier[9]. In KrF laser

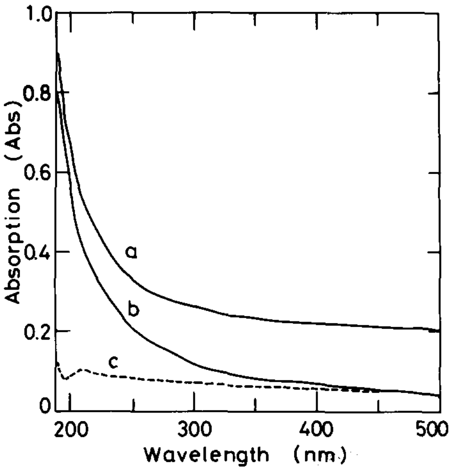


Figure 7 Ultraviolet-visible absorption spectra of non-irradiated and KrF laser 100 pulses irradiated ETFE. (a) Non-irradiated, (b) 100 pulses irradiated, and (c) plot of $\log(1-R)$, where R is reflectivity of non-irradiated ETFE film

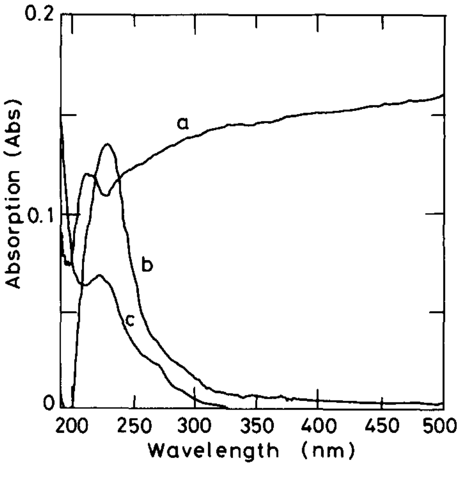


Figure 8 Ultraviolet-visible differential spectra between non-irradiated and irradiated ETFE. (a) KrF laser irradiation 3.7×10^5 J kg^{-1}, (b) ArF laser irradiation 6.1×10^5 J kg^{-1}, and (c) 1.5 MeV electron beam irradiation 10^5 J kg^{-1}

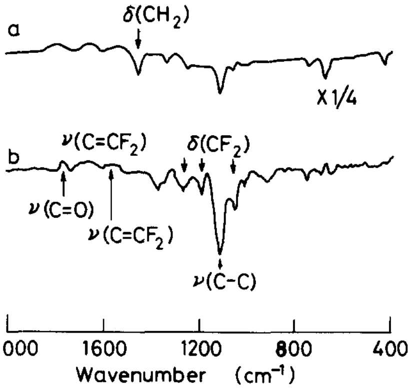


Figure 9 Infra-red differential spectra of ETFE obtained from ATR measurement. (a) 1.5 MeV electron beam irradiation, and (b) ArF laser irradiation

irradiation, the transmittance decreased as compared with non-irradiated ETFE. This is attributed to the carbonization of the polymer as mentioned above. The decrease in the absorbance ascribed to –C–C– and $-CF_2$ groups and the formation of the –C=O group (1720 cm^{-1}) and the double bonds ($-C{=}CF_2$, 1500–1700 cm^{-1}) were observed by irradiation with an ArF laser and electron beam. It has been clarified by i.r. measurement that the observed u.v.-vis. absorption bands below 200 nm and at 230 nm correspond to the $\pi \rightarrow \pi^*$ absorption of the –C=C– group and the $n \rightarrow \pi^*$ of the –C=O group, respectively. These results indicate that irradiation with an ArF laser and electron beam degrades the polymer with the formation of –C=C– and –C=O groups, and KrF laser irradiation induces much larger degradation of the polymer with carbonization.

The reason why the irradiation effects using a KrF laser differ from those using the other methods of irradiation is considered. By irradiation using a KrF laser, an ArF laser and electron beam, the –C=O group formed in the polymer matrix and the 230 nm peak absorption band appeared. Since the wavelength of KrF laser radiation, 248 nm, is close to the peak wavelength of the 230 nm absorption band, the photon can be efficiently absorbed into the polymer to induce degradation of the polymer matrix. In contrast, the wavelength of ArF laser radiation, 193 nm, has no component of this absorption band, so that photon energy is absorbed into only the imperfect portion of the polymer. The absorbed energy only induces oxidation and increases the intensity of the 230 nm absorption band. Electron beam energy is absorbed by the polymer matrix through Compton scattering and the quantities of absorbed energy are proportional to the electron density of the materials. Therefore, the chemical reactions induced by electron beam irradiation occur in the polymer matrix at random.

For only KrF laser irradiation, much larger degradation of the polymer compared with irradiation using an ArF laser and electron beam occurs through a selective excitation of the absorption band formed by the irradiation.

CONCLUSIONS

It was found that irradiation effects of u.v. radiation from an excimer laser on PP and ETFE greatly differ from those from an electron beam.

For PP film, irradiation with a KrF laser and electron beam degraded the polymer with the formation of double bonds and carbonyl groups. Degradation of the polymer was not observed using ArF laser irradiation, because of the selective decomposition of the alkyl phenol type additive contained in the polymer matrix as an antioxidant whose absorption peak is close to the emission wavelength of the ArF laser radiation.

For ETFE film, since the absorption peak newly formed by each irradiation lay near the emission wavelength of the KrF laser, the polymer was degraded more by irradiation with the KrF laser than with the ArF laser and electron beam.

ACKNOWLEDGEMENT

The authors thank Dr J. Okamoto and Dr F. Yoshii at the Takasaki Radiation Chemistry Research Establishment, JAERI for their fruitful discussions.

REFERENCES

1 Kawamura, Y., Toyoda, K. and Namba, S. *Appl. Phys. Lett.* 1982, **40**, 374
2 Srinivasan, R. and Mayne-Banton, V. *Appl. Phys. Lett.* 1982, **41**, 576
3 Srinivasan, R. *Science* 1986, **234**, 559
4 Srinivasan, R., Sutcliffe, E. and Braren, B. *Laser Chem.* 1986, **9**, 147
5 Tanaka, R., Mitomo, S., Sunaga, H., Matsuda, K. and Tamura, N. Japan Atomic Energy Research Institute Report JAERI-M 82-033, 1982
6 Carlsson, D. S. and Wiles, D. M. *Macromolecules* 1971, **4**, 174, 179
7 Pouchert, C. J. 'The Aldrich Library of FT-IR Spectra Ed. 1', Aldrich Chemical Company, Inc., Wisconsin, 1985
8 Kawanishi, S., Hagiwara, M., Katsumura, Y., Tabata, Y. and Tagawa, S. *Radiat. Phys. Chem.* 1985, **26**, 705
9 Blais, P., Day, M. and Wiles, D. M. *J. Appl. Polym. Sci.* 1973, **17**, 1895