

50 MeV lithium ion beam irradiation effects in poly vinylidene fluoride (PVDF) polymer

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Abstract. Irradiation effects of 50 MeV ${}^7\text{Li}^{+3}$ ion beam induced in bulk PVDF polymer have been studied with respect to their optical, chemical, structural and electrical behaviour by using UV-visible, FT-IR spectroscopy, XRD technique and electrical frequency response using LCR bridge. The ion fluences ranging from 1.27×10^{11} to 2.15×10^{13} ions cm^{-2} have been used to study dose effects of irradiation in PVDF. The recorded UV-visible spectra clearly shows five characteristic peaks at 315, 325, 360, 425 and 600 nm. Due to irradiation, the optical absorption initially decreases but then increases with higher fluences. In the FT-IR spectra, no appreciable change has been observed after irradiation, indicating that this polymer is chemically stable. There is exponential increase in admittance with log of frequency but the effect of irradiation is not quite appreciable. The value of $\tan d$ and relaxation frequency are changed appreciably due to irradiation. The diffraction pattern of PVDF indicates that this polymer is in semi-crystalline form; a decrease in the crystallinity and crystallite size has been observed due to irradiation.

Keywords. PVDF polymer; lithium ion irradiation; UV-visible and FT-IR spectroscopy; X-ray diffraction; a.c. frequency response.

1. Introduction

The importance of polymers has increased very rapidly during the last few decades because of their low cost, easy processability and low weight. However, polymers do not exhibit such a broad range of properties as inorganic materials in view of their poor electrical conduction. The wide band gap, which results from the covalent bonding, is at the origin of the intrinsic insulating properties of polymers which are optically transparent. Many efforts have been made in order to produce new molecular arrangements, which will ensure a long range electronic delocalization (Davenas *et al* 1989). Ion beam treatment of polymers has been found to produce, under appropriate conditions, useful improvements in their physical properties. Increase in hardness, strength, wear resistance (Lee *et al* 1993; Ochsner *et al* 1993; Pivin 1995; Swain *et al* 1997), electrical conductivity (Wang and Ho 1993; Rao *et al* 1994; Schiestel *et al* 1994) and improvements in the optical transmission properties of polymers (Vorcik *et al* 1993; Lessard and Manivannan 1995) have been reported; such improved polymers may be used as substitutes for metals, alloys and glasses, while retaining the inherent advantages of polymers such as light weight, moldability, and corrosion resistance.

Concerning the high energy ion irradiation of polymers, the energy transferred onto the electrons related to the so-called electronic energy loss of the incident particle is released into: (i) radiative decay, (ii) production of new reactive species (radicals, gases) and defects (unsaturations, scissions, crosslinks), and (iii) heat (Chailley *et al* 1995). The radial expansion of the energy by the ejected electrons around the ion path is responsible for chemical modification of polymers. In the low dose regime, the radiation chemistry of the PVDF $[\text{CH}_2\text{-CF}_2]_n$ or PVDF has been extensively studied under electron and gamma rays irradiation (Seguchi *et al* 1972; Galperin and Kosmynin 1973; Lovinger 1984; Komaki 1986; Pae *et al* 1987; Zhen 1990; Makuuchi *et al* 1996) and more recently under high energy ion irradiation (Guzman *et al* 1985; Mole *et al* 1998; Said and Balik 1988; Balanzat *et al* 1994; Betz *et al* 1994). The decrease in crystallinity has been reported under electron irradiation (Lovinger 1984) and after low-energy ion implantation (Guzman *et al* 1985; Said and Balik 1988). The loss of crystallinity has also been reported after 26 MeV/u Xe irradiation (Mole *et al* 1989) and 9 MeV/u C irradiation (Calcagno *et al* 1994). However, an increase in the crystallinity is also reported under 175 keV electron irradiation (Lovinger 1984). But the detailed study of change in crystallinity under high energy ion irradiation is not much reported, when dense electronic energy loss is responsible for polymer modification.

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2. Experimental

The semi-crystalline PVDF polymer specimens in the form of flat, polished sheet of thickness 250 μm and density of 1.79 $\text{g}\cdot\text{cm}^{-3}$, having upper working temperature of 135–150°C, were imported from UK (Goodfellow Co.). When heated above 400°C, PVDF can decompose to give highly toxic fumes of HF & F. The samples for irradiation were prepared in the size of 1 \times 1 cm. They were used in as-received condition without any further treatment. Three identical samples were mounted on a vertical vacuum shielded sliding ladder and irradiated in general purpose scattering chamber by using 50 MeV ${}^7\text{Li}^{+3}$ ion beam available from the 15 UD Pelletron at the Nuclear Science Centre (NSC), New Delhi. The ion beam fluence was varied in the range 1.27×10^{11} to 2.15×10^{13} ions cm^{-2} . In order to expose the whole target area, beam was scanned in the x - y plane. The ion beam energy and thickness of the target were chosen so that only the modification due to the electronic energy loss affected the exposed sample. The nature of optical, chemical, electrical and structural modifications was analyzed by using UV-visible, Fourier transform infrared (FTIR) spectroscopy, electrical frequency response using LCR bridge (4284A) and X-ray diffraction techniques. All the measurements were carried out at the ambient temperature between 20 and 22°C.

3. Results and discussion

The projected range of 50 MeV ${}^7\text{Li}^{+3}$ ion beams in the poly(vinylidene fluoride) was calculated to be 351.26 μm , using the SRIM-97 code (Ziegler 1997), which is 1.4 times the thickness of PVDF samples. The energy lost by the ions in a solid is mainly dominated by two mechanisms known as electronic and nuclear stopping. The electronic energy loss is dominant for ions with high energy and involves the energy transfer to atoms in the target due to inelastic electron–electron interaction. Collisional processes produce lattice vibration and the displacement of the target atoms. Displacement damage is usually considered to be the most important cause of material modification in solids. The SRIM-97 code (Ziegler 1997) indicates that 99.95% of energy lost by 50 MeV ${}^7\text{Li}^{+3}$ ion in 250 μm thick PVDF is electronic in nature. The electronic stopping power of the beam, $(dE/dx)_e$, is 8.387 $\text{eV}/\text{\AA}$ and the energy deposited in the medium comes out to be 40.8 MeV. The irradiation doses deposited in PVDF at three different fluences, 1.27×10^{11} , 1.45×10^{12} and 2.15×10^{13} ions cm^{-2} , are 0.82, 9.4 and 140.25 J, respectively.

3.1 Optical properties

The results of optical absorption studies with UV-visible spectrophotometer on virgin and irradiated samples are illustrated in figure 1. The optical absorption spectrum of

the virgin sample (figure 1a) shows five constant absorption regions between 190 and 310, 330 and 335, 365 and 415, 425 and 590, and 600 and 790 nm. In between these constant absorption regions, five distinct characteristic peaks have been observed at 315, 326, 360, 425 and 600 nm, respectively. The maximum absorption is found at 360 nm, and these characteristic absorption peaks may be correlated with the electronic transition occurring in fluorocarbon (CF). It is well known that many molecules contain electrons that are not directly involved in bonding, e.g. the compounds containing fluorine, chlorine, nitrogen and oxygen etc are capable of showing these types of characteristic absorptions due to the transition of non-bonding electrons.

Figures 1b–d show the optical absorption spectra of irradiated samples at three different fluences of 1.27×10^{11} , 1.45×10^{12} and 2.15×10^{13} ions cm^{-2} , respectively. It is observed that due to irradiation up to the dose level of 1.27×10^{11} ions cm^{-2} , there is a symmetric decrease in the optical absorption along the whole wavelength range. However, a reversal effect in optical absorption has been observed when dose is further increased to a value of 1.45×10^{12} ions cm^{-2} ; the characteristic absorption also shows an increase but retains the original nature of spectra. However, a very interesting change has been observed when dose is further increased to 2.15×10^{13} ions cm^{-2} ; its optical absorption increases asymmetrically along all the wavelengths. It is also observed that the flatness of region is lost due to constant

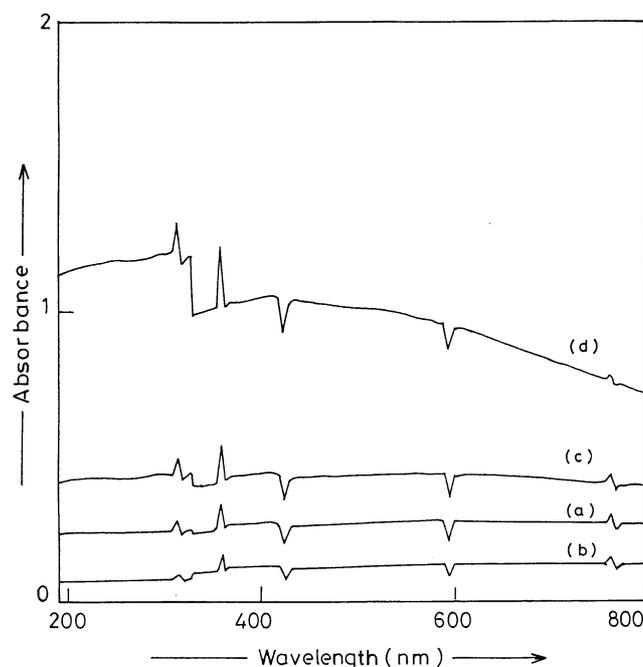


Figure 1. Optical absorption spectra of (a) virgin sample, and (b–d) of the sample irradiated with a 50 MeV ${}^7\text{Li}^{+3}$ ion beam at the fluences of 1.27×10^{11} , 1.45×10^{12} and 2.15×10^{13} ions cm^{-2} .

absorption to irradiation, but an increasing slope towards the higher wavelength after 400 nm is introduced in the spectrum. This observation indicates that the original pattern of optical absorption of this polymer is changed due to irradiation, the position of maximum absorption is shifted towards the lower wavelength from 360 nm to 315 nm. It may be concluded on the basis of this observation that optical absorption increases with the irradiation dose.

3.2 Chemical properties

Figure 2 shows the FT-IR spectra of the virgin and 50 MeV Lithium ion beam irradiated PVDF polymer samples in the range 4000–600 cm^{-1} . A very strong absorption band corresponding to the asymmetric and symmetric stretching vibrations of the CH_2 group in the PVDF sample is observed at 3025 cm^{-1} and 2985 cm^{-1} ,

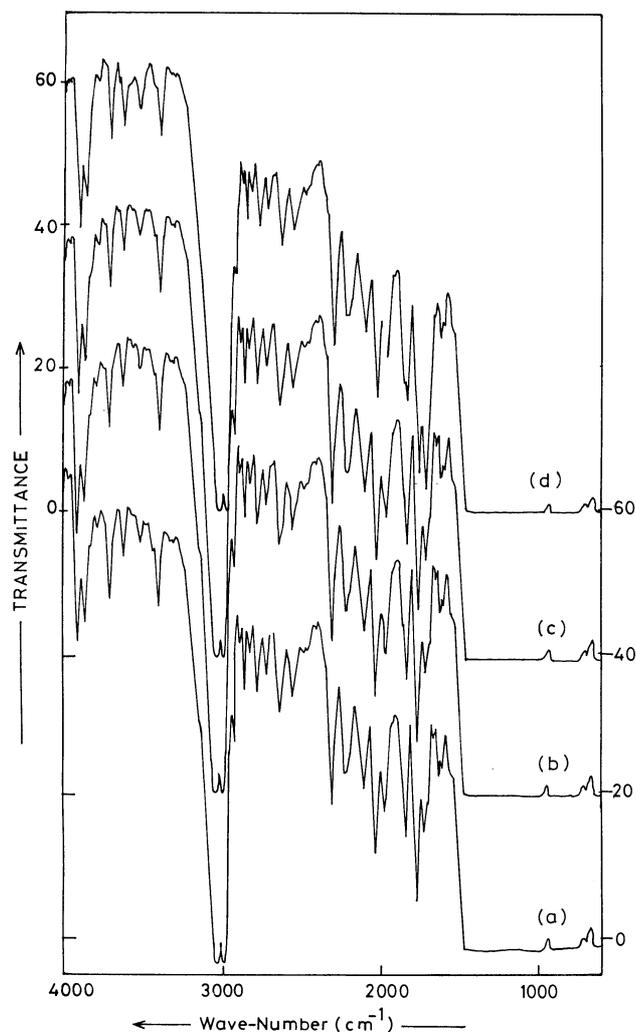


Figure 2. FTIR spectra of (a) virgin sample, and (b–d) of the sample irradiated with a 50 MeV ${}^7\text{Li}^{+3}$ ion beam at the fluences of 1.27×10^{11} , 1.45×10^{12} and 2.15×10^{13} ions cm^{-2} .

respectively and a shoulder at 3100 cm^{-1} . The constant absorption region (band absorption) from 1450–1000 cm^{-1} corresponds to fluorocarbon absorption (C–F). Figures 2b–d show the FT-IR spectra of the irradiated PVDF at three different fluences of 1.27×10^{11} , 1.45×10^{12} and 2.15×10^{13} ions cm^{-2} , respectively. No appreciable change has been observed at lower fluences, however, an appreciable change has been observed corresponding to 2.15×10^{13} ions cm^{-2} . At this dose the shoulder at 3100 cm^{-1} disappears and the broadening of the bands shows the broadening of the CH_2 stretching vibrations. The increase in the absorption and broadening of 1710 cm^{-1} band indicates the possibility of the evolution of HF during irradiation.

3.3 Electrical frequency response

Figures 3a, b show the electrical frequency response of virgin and irradiated PVDF samples. A sharp increase in admittance at 100 KHz has been observed in both the cases, with lower magnitude for the irradiated sample. This decrease in admittance on irradiation may be attributed to V-centres (charge-centres) created due to scissioning of polymeric chains. V-centres oscillate giving rise to circulatory currents under the influence of an externally applied voltage of nearly 20 mV across the electrodes between which the polymer was kept for the

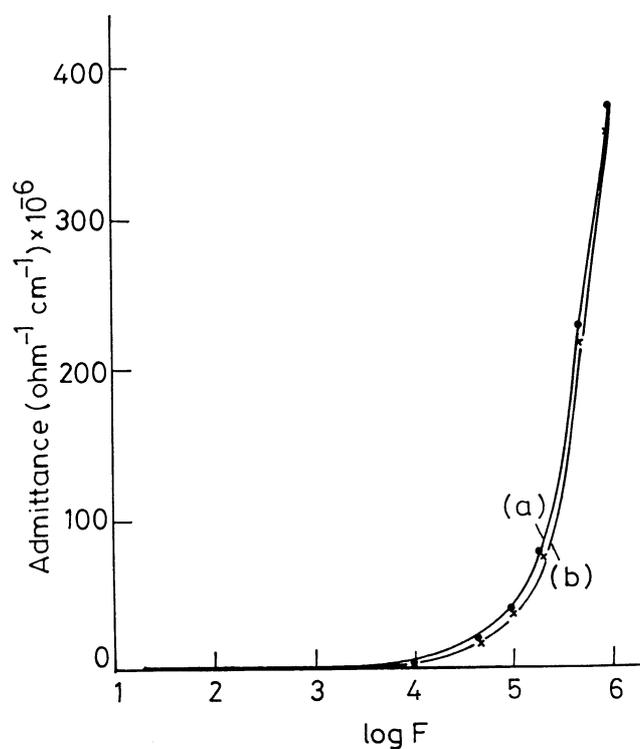


Figure 3. Variation in admittance with log (frequency) of (a) virgin sample, and (b) of the sample irradiated with a 50 MeV ${}^7\text{Li}^{+3}$ ion beam at the fluence of 2.15×10^{13} ions cm^{-2} .

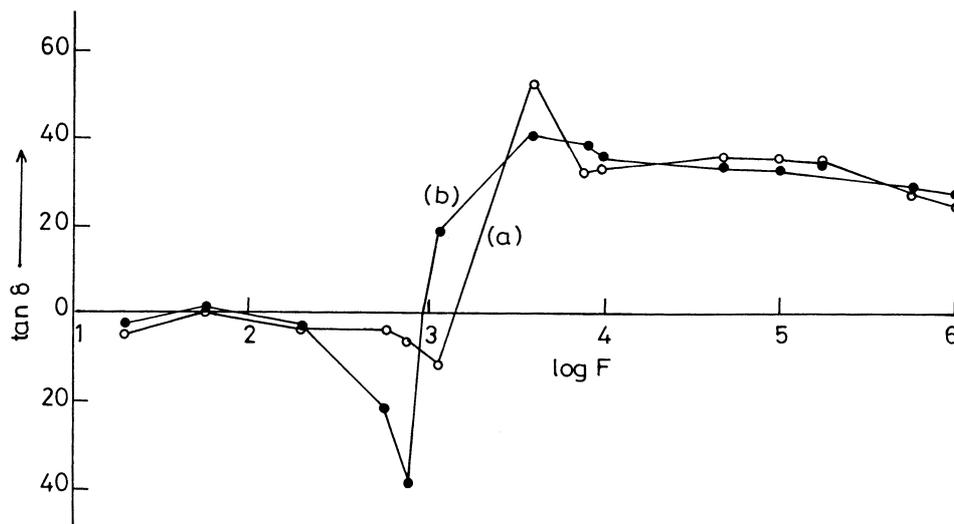


Figure 4. Variation in $\tan \delta$ with \log_{10} (frequency) of (a) virgin sample, and (b) of the irradiated sample with a 50 MeV ${}^7\text{Li}^{+3}$ ion beam at the fluence of 2.15×10^{13} ions cm^{-2} .

measurement of the frequency response. With the effective mass of the positive charge carriers being large, only slow vibrations arise, whereas the free electrons generate circulatory currents. These circulatory currents develop an inductive behaviour in the polymeric dielectric, which may be responsible for the small decrease in the admittance.

Figures 4a, b represent the loss factors ($\tan \delta$) of the virgin and of one of the irradiated samples in the frequency range 20 Hz–1 MHz. It is observed that the variation of $\tan \delta$ with frequency in log scale for both the virgin and the irradiated samples is similar. In the case of virgin sample at frequencies lower than 1600 Hz, $\tan \delta$ has negative values indicating that capacitive element is dominant whereas between 1600 Hz–1 MHz, $\tan \delta$ has positive values indicating dominance of inductive behaviour. However, in the case of irradiated one the capacitive behaviour is dominant below 944 Hz; above this frequency the behaviour is inductive. Between 30–100 Hz, the behaviour is almost resistive as values of $\tan \delta$ are very small in both the cases. It is also observed that in the case of virgin sample the value of relaxation frequency is around 1584 Hz. However, in the case of the irradiated sample relaxation frequency is observed at around 944 Hz, and the signal can be communicated with minimum energy loss.

3.4 Structural properties

Figures 5a, b represent the diffraction pattern of the virgin and irradiated PVDF polymer, at the dose level of 2.15×10^{13} ions cm^{-2} . The diffraction pattern of virgin polymer clearly indicates that this polymer is semi-crystalline in nature. The X-ray diffraction data of virgin and irradiated PVDF polymer (table 1) clearly shows a

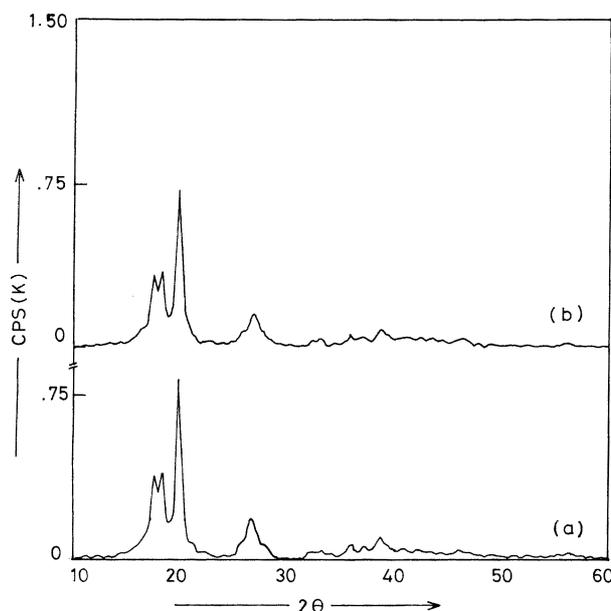


Figure 5. X-ray diffraction pattern of (a) virgin sample, and (b) of the sample irradiated with a 50 MeV ${}^7\text{Li}^{+3}$ ion beam at the fluence of 2.15×10^{13} ions cm^{-2} .

most sharp peak at $2q = 20.02^\circ$ with $d = 4.432 \text{ \AA}$, and full width at half maxima (FWHM) of 0.96. The diffraction pattern shows two closely spaced peaks at $2q = 17.80$ and 18.50 \AA with $d = 4.979 \text{ \AA}$ and 4.792 \AA , respectively, with equal FWHM. However, the diffused pattern is observed at higher angles. The diffraction pattern of virgin and irradiated one are more or less identical but with slightly changed values. Due to irradiation, a decrease in the peak intensities of about 16.4%, 12.75%, 11.8% and an increase in the FWHM by 3.84%, 0%, and 3.12% has been observed, respectively, for the first three peaks. The

Table 1. X-ray diffraction data of virgin and irradiated PVDF polymer.

Virgin PVDF				Irradiated PVDF			
2q	Intensity	Width	d	2q	Intensity	Width	d
17.80	385	0.780	4.979	17.78	322	0.810	4.985
18.50	400	0.780	4.792	18.46	349	0.780	4.802
20.02	872	0.960	4.432	19.98	729	0.990	4.440
25.66	75	0.600	3.469	25.82	72	0.600	3.448
26.66	187	1.380	3.341	26.66	155	1.200	3.341
28.00	66	0.720	3.184	32.28	37	0.780	2.771
32.20	37	1.140	2.778	35.90	60	0.804	2.499
33.26	40	0.660	2.692	37.44	43	1.260	2.440
36.04	71	0.900	2.490	38.88	83	1.170	2.314
37.36	64	0.810	2.405	41.24	46	0.720	2.187
38.82	104	1.080	2.318	43.74	40	0.630	2.068
41.38	48	0.720	2.180	44.52	35	0.630	2.033
42.46	40	0.720	2.127	46.08	43	0.870	1.968
46.64	34	1.020	1.946	55.96	25	0.930	1.642
56.38	27	0.990	1.631	—	—	—	—

broadening of diffraction maxima on X-ray diagrams is usually associated with a decrease in the crystallite size. However, the decrease in intensity and rounding of the peaks suggest an evolution of the polymer toward a more disordered state and also a change in crystallite size. Due to irradiation the observed shift of the peak angular positions towards smaller angles can be explained by an increase in lattice spacing (Guzman *et al* 1985). Particularly in case of solid polymeric materials the exact nature of the interrelation between spacing, crystallite size and degree of disorder is yet to be understood completely.

4. Conclusion

The general behaviour of the UV-vis and FT-IR spectra of this polymer before and after irradiation up to the dose of 1.45×10^{12} ions cm^{-2} being almost the same, indicates that this particular polymer, PVDF is optically and chemically stable towards high energy ${}^7\text{Li}^{+3}$ ion beam irradiation up to the above fluence level. At higher doses, the stability decreases at a faster pace. The decrease in a.c. admittance along the frequency range due to irradiation may be due to the inductive behaviour of the polymer. Due to irradiation, a shift in the relaxation frequency from around 1584 to 944 Hz has been observed. The X-ray diffraction analyses of virgin and irradiated PVDF polymer have demonstrated that the size of crystallites is decreased while the lattice spacing and amorphization or disorder is increased.

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References

- Balanzat E, Bouffard S, Mole A Le and Betz N 1994 *Nucl. Instrum. & Meth. Phys. Res.* **B91** 140
- Betz N, Mole A Le, Balanzat E, Ramillon J M, Lamotte J, Gallas J P and Jaskierowicz G 1994 *J. Polym. Sci.* **32** 1493
- Calcagno L, Musumeci P, Percolla R and Foti G 1994 *Proc. of 7th int. conf. rad. effe. in insula., Nagoya, Japan* (Amsterdam: North-Holland) p. 461
- Chailley V, Balanzat E and Dooryhee E 1995 *Nucl. Instrum. & Meth. Phys. Res.* **B105** 110
- Davenas J, Xu X L, Boiteux G and Sage D 1989 *Nucl. Instrum. & Meth. Phys. Res.* **B39** 754
- Galperin Ye L and Kosmynin B P 1973 *Vysokomol. Soyed.* **A15** 2556
- Guzman A M, Carlson J D, Baras J E and Pronko P P 1985 *Nucl. Instrum. & Meth. Phys. Res.* **B7/8** 468
- Komaki Y 1986 *Radiat. Phys. Chem.* **27** 399
- Lee E H, Lee Y, Oliver W C and Mansur L K 1993 *J. Mater. Res.* **8** 377
- Lessard R A and Manivannan G 1995 *Nucl. Instrum. & Meth. Phys. Res.* **B105** 229
- Lovinger A J 1984 *Bull. Am. Phys. Soc.* **29** 325
- Makuuchi K, Asano M and Abe T 1976 *J. Polym. Sci.* **14** 617
- Mole A Le *et al* 1989 *Nucl. Instrum. & Meth. Phys. Res.* **B32** 115
- Ochsner R *et al* 1993 *Nucl. Instrum. & Meth. Phys. Res.* **B1** 1050
- Pae K D, Bhateja S K and Gilbert J R 1987 *J. Polym. Sci.* **B25** 717
- Pivin J C 1995 *Thin Solid Films* **263** 185
- Ramillon J M and Darnez C 1989 *Nucl. Instrum. & Meth. Phys. Res.* **B42** 69
- Rao G R, Monar K, Lee E H and Treglio J R 1994 *Surf. Coat. Technol.* **64** 69

- Said M A and Balik C M 1988 *J. Polym. Sci.* **B26** 1457
- Schiestel S, Ensinger W and Wolf G K 1994 *Nucl. Instrum. & Meth. Phys. Res.* **B91** 473
- Seguchi T, Makuuchi K, Suwa T, Tamura N, Abe T and Takehisa M 1972 *Rep. Prog. Polym. Phys.* **15** 503
- Swain M V, Perry A J, Treglio J R and Demaree E D 1997 *J. Mater. Res.* **12** 1917
- Vorcik V, Rybka V, Endrst R, Hnatowicz V, Kvitek J and Seidl P 1993 *J. Appl. Polym. Sci.* **49** 1939
- Wang C Z and Ho K M 1993 *Phys. Rev. Lett.* **71** 1184
- Ziegler J F 1997 *SRIM-97, The stopping range of ions in matter* (New York, USA: IBM Research) pp 1–28
- Zhen Z X 1990 *Radiat. Phys. Chem.* **35** 194