Electrical properties of polymers modified by electron beam irradiation

D. Vesely, D. S. Finch and G. E. Cooley
Department of Materials Technology, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

(Received 11 November 1987; revised 4 January 1988; accepted 22 February 1988)

The formation of electrically conductive polyene structures in electron-beam-irradiated poly(vinyl chloride) is investigated. Thin specimens are irradiated to a progressively increasing exposure and the chemical structure is characterized by Fourier-transform infra-red spectroscopy. The direct-current electrical conductivity is also measured. It is shown that short polyenes are formed, the structure being less ordered and containing more defects than polyacetylene. The conductivity changes with exposure follow initially an exponential function, related to the loss of chlorine, but at high exposures a decrease in conductivity is observed. At the peak, which for a 200 keV electron beam is at an exposure of 800 C m^{-2}, the electrical conductivity will reach the level of undoped polyacetylene, i.e. 10^{-5} S cm^{-1}. The use of zinc chloride as an activator is investigated. It is shown that it not only accelerates the dehydrochlorination, but it also increases the ultimate conductivity to the level of 10^{-2} S cm^{-1} at an exposure of 200 C m^{-2}.

(Keywords: electrical properties; conductivity; PVC; electron beam damage)

INTRODUCTION

The search for conductive polymers with a small semiconductor band gap was triggered by the discovery of doped polyacetylene 10 years ago[1]. Many new conductive systems have since been discovered and the doping improved to such an extent that conductivity comparable to that of metals has recently been achieved[2]. A new class of materials, which have some very interesting electrical, magnetic and electro-optical properties, is thus emerging. These materials may be used in many electrical applications, such as battery electrodes, heating elements, solar cells and electrical sensors. Since the conductivity of these materials can be altered by doping, they might provide a cheap alternative to conventional inorganic semiconductors. Unfortunately, our understanding of the mechanisms of conductivity and doping is still very limited, and it is therefore not possible to evaluate fully the potential of these materials. Also, the long-term stability and the development of suitable preparation techniques are needed.

The main purpose of this work is to investigate a new technique for the preparation of polymers with polyene structures from poly(vinyl chloride) (PVC) as a precursor by electron beam irradiation. Polymers are very sensitive to ionizing radiation and rapidly change their chemical structure. An attempt to study the chemical changes in the irradiated chlorinated polymers by Fourier-transform infra-red (*F*Ti.r.) spectroscopy was made recently[3]. It was found that the major changes are the loss of chlorine and hydrogen from isotactic and syndiotactic sequences and the formation of polyenes of various lengths. The rate of formation of these conjugated structures is related to the loss of chlorine, which has been well established[4–6]. It follows a double-exponential relationship:

$$I/I_0 = (1-A)\exp(-k_1 D) + A\exp(-k_2 D) \qquad (1)$$

where I and I_0 are the chlorine X-ray count rates at exposures D and zero, respectively, and k_1, k_2 and A are constants for a given material and energy of the incident electrons. For PVC, most of the chlorine is lost after an exposure of about 1000 C m^{-2} for 200 keV electrons. The resulting structure contains a high density of polyenes and is therefore very similar to polyacetylene. It is likely that some properties will also be similar, which justifies further study. The major attraction of the preparation of conductive polymers by electron beam irradiation is that the polymer can be modified selectively in very small volumes, forming channels or patterns. This new electron beam microchemistry technique can thus be utilized in conjunction with electron beam lithography, already used in the electronics industry. However, the potential and possible ways of further improvement of this technique must first be evaluated.

EXPERIMENTAL

Specimens were prepared from pure (no additives or stabilizers used) suspension PVC with molecular weight about 140 000. A solution of 7% PVC in tetrahydrofuran (THF) was prepared and thin films about 20 μm thick were cast on a glass slide. After the solvent had evaporated, the films were removed, cut to discs of 3 mm in diameter and mounted on a copper substrate of the same diameter, with a 1 mm circular hole. The films were secured in position by using a very small amount of epoxy at the edge of the film, away from the irradiated area. The specimens were irradiated in the electron microscope at 200 keV using a current density of about 0.5 A m^{-2}. The beam current was measured before and after each exposure using a Faraday cage and a picoammeter (Keithley 417). The high-energy electrons (200 keV) were used to obtain a homogeneous irradiation throughout the specimen thickness. Electrons with lower energy would significantly reduce the exposure needed for the

0032-3861/88/081402-05$03.00

dehydrochlorination, but the electrons would not penetrate the specimen thickness. The homogeneity of irradiation was evaluated by Monte Carlo calculation of the beam spreading, which showed only 3% difference in the absorbed energy between the top and bottom layers. It also indicated that 100 C m^{-2} corresponds to about 0.2 Mrad (or 2 kGy) absorbed energy for the conditions used. The accuracy of the dosimetry and the parameters influencing the measurements have been discussed previously[6]. All specimens (except those for i.r. analysis) were coated on both sides with about 5 nm of carbon, using a special technique with minimum heat damage[7]. The irradiated area, 1 mm in diameter, was sufficiently large to obtain high-quality i.r. spectra. A Nicolet 60 SXB *FT*i.r. spectrometer with a microbeam attachment was used and the spectra were averaged over 200 scans. Dry, carbon-dioxide-free air was used for purging.

The electrical conductivity of samples was measured using the two-electrode method, which is a standard measuring technique for samples of low conductivity[8]. The I–V characteristics were measured at voltages up to 40 V μm^{-1}, using a stabilized power supply and a picoammeter. The electrical contact was improved with a layer of silver electrodag, which was applied on top of the carbon coating to the centre area only. Measurements before and after addition of silver dag onto the carbon coating showed no effect. This verifies good contact and absence of diffusion of coating material or its solvent. The conductivity deviated slightly from ohmic behaviour up to 25 V μm^{-1} (300 V for a typical sample), after which a strong non-ohmic behaviour was observed. Further work is required to characterize this effect. In order to achieve comparative results, all conductivities were measured at a fixed voltage of 30 V. A small reduction in current over a period of a few minutes was observed in some cases. For this reason the reading was taken after full stabilization of the current, typically 30 min. The changes in specimen thickness due to mass loss were taken into account. The polyene length was determined by ultra-violet/visible (u.v.-vis.) spectroscopy, using the difference spectra and well established calculation procedures[9], with molar absorptivity according to ref. 10.

RESULTS AND DISCUSSION

Molecular structure of irradiated PVC

The visual evidence for chemical changes in irradiated PVC is the discolouration. The clear, transparent specimen becomes yellow, brown-red and dark brown or black with progressive exposure to the electron beam. These changes are usually interpreted as a result of the formation of double bonds and polyenes. For a better understanding of the electrical properties, it is important to know the following: how long are the polyene sequences; how many defects are present and of which type; what is the development of the structure with irradiation and how does it differ from polyacetylene?

In the case of the thermal dehydrochlorination of PVC, it is generally accepted that the reaction proceeds via an unzipping mechanism due to the sequential loss of HCl along the polymer backbone, initiated at weak sites. This results in the formation of conjugated polyenes that will absorb in the u.v.-vis. spectrum from 190 to 600 nm. Upon the conjugation reaching a certain length (typically 20 units)[11], crosslinking occurs. For electron beam degradation, the unzipping mechanism is also proposed[3]; however, the initiation appears to be totally random and the polyene length is determined by the conformation and tacticity of the PVC. Long syndiotactic and isotactic sequences lose chlorine more quickly than short or defected structures. A direct comparison of the *FT*i.r. spectra of thermally dehydrochlorinated PVC with irradiated PVC is not possible as the results will be dependent upon the temperature at which the PVC is degraded[12]. However, a general observation is that, in contrast to irradiated PVC[3], the chemical changes observed in the C–Cl stretching region of the thermally degraded polymer appear independent of the tacticity of the chain[13].

During the electron beam irradiation, unzipping is initiated by ionization. This is a highly probable event and most energy is lost in this way. The positive charge formed will destabilize the hydrogen or chlorine atoms. The formation of HCl molecules is energetically favourable, and the charge can thus propagate along the chain until stopped or neutralized. We can visualize that a molecular chain is divided into segments by the neutralization sites. When the chain is ionized by an electron, a polyene will be formed between the ionization site and the neutralization site. The total amount of chlorine left on the chain will correspond to the measured chlorine decay curve. It is apparent that the length of the polyenes formed is dependent on the relative positions of the neutralization sites and the ionization sites. Shorter polyenes are therefore formed at later stages of irradiation, but the polyenes can also join to form longer conjugated sequences.

It follows that the formation of long polyenes by irradiation is critically dependent on the density and properties of the neutralization sites. It is, however, difficult to identify their nature, but it can be suggested that the unzipping can slow down or stop at defects, thus increasing the probability of neutralization by the capture of a free electron. Some defects represent the transition between *trans* and *cis* configurations. The unzipping of the *trans* configuration might be easier than the unzipping of the *cis* configuration. This is confirmed by the fact that *trans*-polyacetylene has a lower energy than *cis*-polyacetylene, as evidence of the transformation of *cis*- to *trans*-polyacetylene upon annealing[14]. Not only conformational but also configurational defects (such as head-to-head, tail-to-tail or branching) can slow down or stop the unzipping process. Some examples of possible defects are shown in *Figure 1*. It is likely that a single-hit mechanism will remove chlorine from the sites that are difficult to dehydrochlorinate by the unzipping process. The low level of the total chlorine content (below a few per cent) at high levels of irradiation can only be explained by this mechanism.

The *FT*i.r. spectrum of heavily irradiated PVC (*Figure 2*) shows substantial differences when compared with the spectrum of polyacetylene[15]. The peak at 740 cm^{-1}, which corresponds to the C–H out-of-plane deformation band, is prominent in *cis*-polyacetylene but not visible in *trans*-polyacetylene. In irradiated PVC this peak is weak and indicates a small proportion of *cis* conjugated structures, most likely on defects.

The second peak that is strong in polyacetylenes is the C–H out-of-plane bending peak at 1015 cm^{-1}. This peak is at 990 cm^{-1} for irradiated PVC, which is closer to the

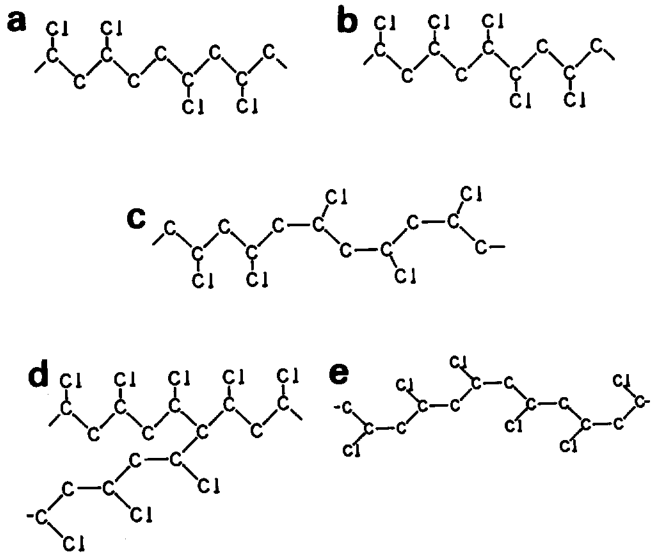

Figure 1 Some defects on a PVC chain are illustrated: (a) tail-to-tail; (b) head-to-head; (c) *trans*-to-*cis*; (d) branching; and (e) bent *trans* structures. Hydrogen atoms on the remaining carbon bonds are not shown

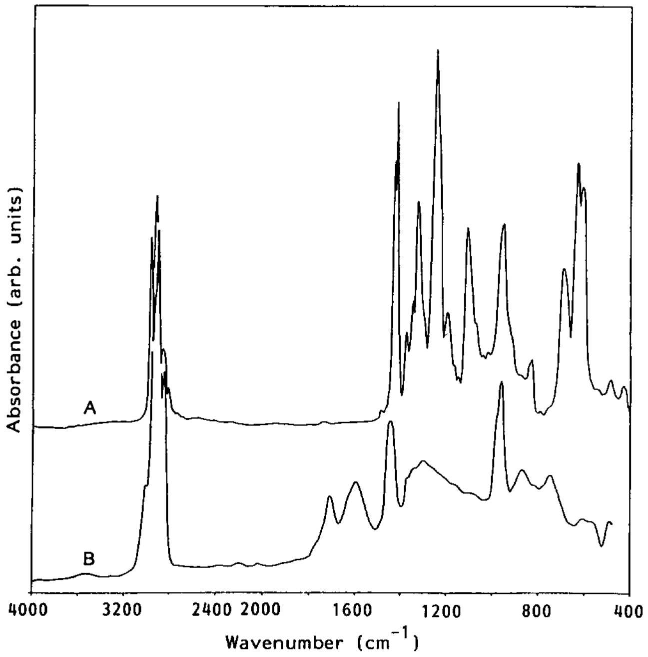

Figure 2 *FT*i.r. spectrum of PVC (A) and of PVC irradiated to 1000 C m^{-2} (B) are shown. The growth of CH_2 stretching peaks at 2927 and 2857 cm^{-1} as well as C=C peaks at 1600 and 1650 cm^{-1} and C–H out-of-plane deformation band at 990 cm^{-1} are indicative of polyene formation at the expense of C–Cl stretching peaks at 600–800 cm^{-1} and C–H_2 deformation peaks at 1200–1400 cm^{-1}. The peak at 1750 cm^{-1} indicates oxidation

polybutadiene (which contains only isolated double bonds) peak at 988 cm^{-1}. This might suggest that irradiated PVC has a lower level of delocalization of conjugated structures than polyacetylene. The irradiated PVC is less ordered than polyacetylene, i.e. molecules are more randomly arranged than in an oriented or crystalline polymer. This can result in a peak shift towards lower wavenumbers, but the observed difference of 25 cm^{-1} is probably too large for this explanation. There are two growing peaks at the C=C stretching region of PVC at 1600 and 1650 cm^{-1}, corresponding to symmetrical and asymmetrical stretching bands on conjugated carbon–carbon bonds. These peaks are much stronger than the peak at 1652 cm^{-1}, corresponding to isolated double bonds, which can only be detected at low levels of irradiation. The oxidation peak at 1700 cm^{-1} usually has a very high absorption coefficient and the results thus indicate a very low level of oxidation of the irradiated PVC. These peaks are also very small in the spectrum of polyacetylene, which might be explained by the suppression of stretching vibrations due to bond delocalization. This would indicate a lower level of delocalization in irradiated PVC, compared with polyacetylene.

The third most prominent band of peaks in polyacetylenes is in the C–H stretching region, i.e. peaks at 2989, 3013, 3044 and 3059 cm^{-1}, depending on the conformational state. The peaks that grow rapidly with irradiation of PVC are at 2857 and 2927 cm^{-1} corresponding to symmetrical and asymmetrical vibrations of C–H_2 defects on the conjugated sequences. These defects are not common in polyacetylene and are likely to affect the charge mobility in irradiated PVC. The peak at 3013 cm^{-1} corresponds to the C–H stretching mode of *trans* conjugation and is also observed on *trans*-polyacetylene.

The molecular structure of irradiated PVC is therefore different from the structure of polyacetylene. The polyene sequences are shorter, with more defects and a lower degree of molecular chain ordering. This is not unexpected, as the starting material, commercial PVC, is amorphous, with many intrinsic irregularities and defects. It cannot therefore be expected that after irradiation the structure and the resulting properties will be the same as that of oriented polyacetylene.

Electrical conductivity

Electrical conductivity measurements of pure irradiated PVC (*Figure 3*) show a maximum of 2.5×10^{-5} S cm^{-1} at about 800 C m^{-2}. The total increase in conductivity represents about seven orders and reaches the same level as undoped *trans*-polyacetylene. This had not been expected, as the molecular structure of

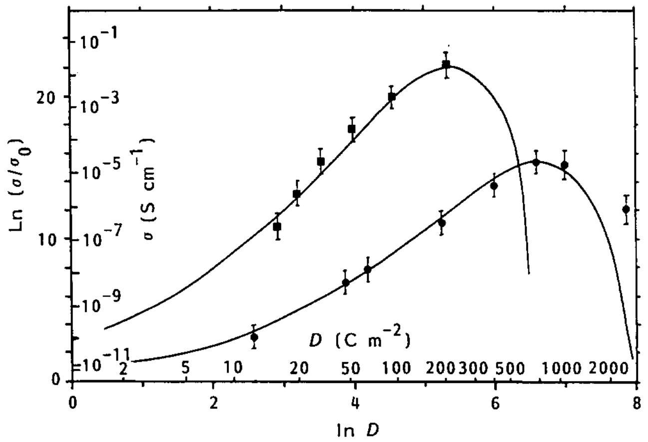

Figure 3 The measured changes of conductivity with exposure D using 200 keV electrons: (●) measured values for PVC; and (■) for PVC with 0.3% $ZnCl_2$. The curves represent the values calculated from equation (2). The values at very low and very high exposures cannot be measured accurately, but the decrease in conductivity at high exposures is clearly shown

irradiated PVC is different and only short polyenes (about six units on average, as determined by u.v.-vis. spectroscopy) are present. The comparable level of conductivity thus suggests that either the polyene length is not an essential requirement, or that the polyacetylene also contains many defects.

In order to obtain some quantitative information on the effect of irradiation on conductivity, the measured curves were analysed. It has been found that a good correlation with the experimental data can be obtained from the equation:

$$\sigma=\sigma_0 \exp(aD^{0.5}) \exp(-bD) \qquad (2)$$

where σ is conductivity, σ_0 is conductivity of unirradiated PVC and D is exposure. The first term is related to the rate of formation of a conductive structure and the second term describes the destruction of conductivity, probably by crosslinking. This equation also predicts the observed peak in conductivity at 737 C m^{-2}. The best fit to the experimental data was obtained with the constants $a=1.14$ and $b=0.021$. The physical meaning of these constants has not yet been established, as more experimental data are needed. The factors contributing to their value are, for example, the dehydrochlorination rate (described by equation (1)), the accelerating voltage of the electrons, temperature and the rate of crosslinking. The correlation of the experimental and theoretical values is not very good at low and high exposures. This is due to the accuracy in the dose measurements, which have at least 10% error[4]. At high exposures, the shrinkage of the irradiated polymer due to loss of mass can cause cracking of the specimen. Although all of the specimens were investigated on a light microscope, small fissures could not be detected. The conductivity measured at 2000 C m^{-2} is therefore likely to be higher than the true bulk conductivity.

The effect of additives

An obvious conclusion from the above discussion is that, if crosslinking can be minimized or eliminated, a much higher conductivity will be achieved. This is difficult, as the structure of PVC cannot be easily modified, but it might be possible to alter the molecular environment by additives. Several attempts were made to modify the electron beam damage characteristics by mixing PVC with organometallic compounds (such as lead, cadmium, tin and barium carboxylates), with other polymers (such as poly(methyl methacrylate), polycaprolactone and polyoxymethylene) and with inorganic compounds (zinc chloride and iodine). Most of these compounds had a small effect on dehydrochlorination rate and therefore on formation of polyenes. Some decomposed and evaporated in the vacuum during irradiation (iodine, for example). So far only zinc chloride has proved to be of some potential benefit to the ultimate conductivity. It not only substantially increased the rate of formation of conductive structures, but also increased the peak conductivity to 2×10^{-2} S cm^{-1} at an exposure of 211 C m^{-2}. This is illustrated in *Figure 3*. The best fit to the experimental data was obtained with $a=3.05$ and $b=0.105$. The chemical reactions involved in these processes are not well understood and it is difficult to propose a simple model in which the zinc chloride particle would accelerate the unzipping of the PVC chain and reduce crosslinking. It is most likely that some intermediate compounds are formed, but these are difficult to detect as they are probably in very small concentrations, and short-lived. The effect of 0.3% zinc chloride addition to PVC on the dehydrochlorination rate is illustrated in *Figure 4*. It is also difficult at present to understand the role of zinc chloride as a dopant and it is more likely that the observed increase in conductivity is mainly due to the reduction of crosslinking.

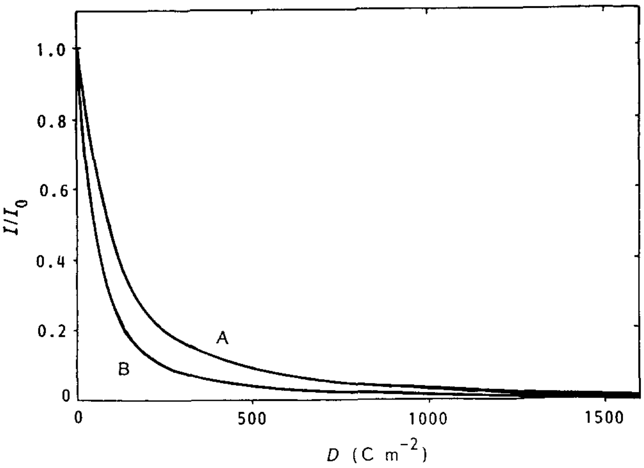

Figure 4 The changes in chlorine content of PVC (A) and PVC with 0.3% $ZnCl_2$ (B) with exposure D are measured by X-ray analysis. The substantially increased rate of dehydrochlorination with the addition of a small amount of $ZnCl_2$ is apparent

The PVC films are solvent-cast and it is not possible to remove the remaining solvent entirely. THF, the casting solvent, also has a high conductivity (of the order of 10^{-3} S cm^{-1}) and may contribute to the overall conductivity observed. However, the concentration of this solvent is below 1% and has not been detected by *FT*i.r. spectroscopy. As its contribution to the conductivity of unirradiated PVC has not been observed, it can probably be ignored. More significant could be the contribution of HCl, which is the major degradation product of PVC. However, the chlorine decay curves, measured by X-ray analysis (*Figure 4*), indicate that chlorine is rapidly lost from the specimen upon irradiation. The total content is reduced to only 3% of the original content at the optimum exposure for the peak conductivity. The *FT*i.r. analysis has shown[3] that the changes in the area under the C–Cl stretching peak follow closely the changes in the total chlorine content measured by X-ray analysis. Most of the remaining chlorine is thus bonded to carbon and the liberated HCl evaporates rapidly into the vacuum.

It is not possible at present to establish the mechanism of conductivity, but it is likely that mechanisms similar to those in polyacetylene are also applicable to irradiated PVC.

CONCLUSIONS

It has been shown in this work that PVC can be converted by electron beam irradiation to a material that has an electrical conductivity comparable to that of *trans*-polyacetylene. The *FT*i.r. spectroscopy revealed that the chemical structure, although similar to polyacetylene, contains a higher density of defects and has a lower level of delocalization. Only short polyenes, about 6 to 10 units long, were detected by u.v.-vis. spectroscopy. This shows that volume density of conjugation rather than polyene length is important for producing conductivity. Although the electron-beam-irradiated PVC material has not yet been successfully doped to achieve high electrical conductivities, this may be due to the choice of dopant and doping methods. Small amounts of zinc chloride were added to increase the rate of polyene formation substantially and thus the resulting conductivity. It is, however, not considered that the zinc chloride contributes significantly to the doping mechanism, leaving this effect still to be exploited. The major attraction of this technique is that it can be combined with electron beam lithography; an insulating polymer can be converted into a conductive material in selected regions, thus forming suitable channels, interfaces and layers as building blocks of a microelectronic device. Not all variables have so far been explored, but work is in progress to investigate the doping mechanisms and the effect of elevated temperature on the conductivity, as well as on some other properties.

REFERENCES

1 Shirakawa, H., Luis, E. J., MacDiarmid, A. G., Chiang, C. K. and Heeger, A. J. *J. Chem. Soc. Chem. Commun.* 1977, 578
2 Basescu, N., Liu, Z. X., Moses, D., Heeger, A. J., Naarman, N. and Theophilou, N. *Nature* 1987, **327**, 403
3 Vesely, D. and Finch, D. S. *Ultramicroscopy* 1987, **23**, 329
4 Vesely, D. *Ultramicroscopy* 1984, **14**, 279
5 Lindberg, K. A. H., Vesely, D. and Bertilsson, H. E. *J. Mater. Sci.* 1985, **20**, 2225
6 Vesely, D. and Finch, D. S. *Inst. Phys. Conf. Ser.* 1985, **78**, 7
7 Finch, D. S. and Vesely, D. *ibid.* p. 151
8 Blythe, A. R. *Polym. Test.* 1984, **4**, 195
9 Hauser, K. W. and Kuhn, R. *Z. Phys. Chem. (B)* 1935, **29**, 363
10 Daniels, V. D. and Rees, N. H. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **12**, 2115
11 Martinez, G., Mijangos, C., Millan, J. L., Gerrard, D. L. and Maddams, W. F. *Macromol. Chem.* 1979, **180**, 2937
12 Koenig, J. L. and Antoon, M. K. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1379
13 Millan, J., Martinez, G. and Mijangos, C. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 505
14 Ito, T., Shirakawa, H. and Ikeda, S. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 1943
15 Gussoni, M., Castiglioni, C., Miragoli, M., Lugli, G. and Zerbi, G. *Spectrochim. Acta (A)* 1985, **41**, 371