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Synchrotron radiation ablation of polymers having double bonds in their main chains

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Abstract

Polyacetylene (PA), poly(*cis*- and *trans*-1,4-butadiene)s (*cis*- and *trans*-PBs), and poly(*p*-phenylene vinylene) (PPV) were ablated by synchrotron radiation (SR), aiming to deposit thin, uniform films of each on a substrate. When PA was irradiated by SR, gaseous phenyl compounds were produced, and a thin amorphous film was deposited on the substrate, exhibiting no characteristics of PA. In the cases of PPV and *trans*-PB, the source materials were reproduced in the form of thin film on the substrate by SR ablation. When alkali halides, e.g. NaCl and KBr, were used as deposition substrates, PPV was deposited, in an ordered way, on their cleavage surfaces. However, the deposited film of *trans*-PB by SR ablation was non-crystalline, because it was produced as a copolymer by 1,4- and 1,2-addition polymerizations of ablated butadiene-based fragments. In comparison, thin films of these polymers were also prepared by thermally evaporating them in a vacuum. When *trans*-PB and PPV were thermally evaporated, thin films with chemically and structurally identical features to the source polymers were produced, respectively. In contrast, a deposited film from *cis*-PB by SR ablation consisted of carbon compounds, showing no sign of hydrocarbon compounds in it, while *trans*-PB was produced from *cis*-PB by thermal vapor deposition.

Keywords: Synchrotron radiation ablation; Thermal vapor deposition; Polyacetylene

1. Introduction

As a nano-technology to produce new carbon compounds not through chemical synthesis, the laser ablation method has been used. It is a high-temperature process in which materials are thermally excited to a plasma state by laser irradiation, to induce their bond scission for evaporation. Evaporated substances are deposited onto a substrate to form novel compounds. When graphite is used as a target material for laser ablation, such carbon compounds as fullerens and nano-tubes, which are expected to contribute to development of nano-technology, are available [1]. Recently, as a low-temperature process for preparing new materials, the photoexcitation process by synchrotron radiation (SR) chemical reaction, so-called SR ablation [2,3], is used [4]. Soft X rays can excite inner-shell electrons [5]. The inner-shell electron excitation creates many localized holes in the valence orbital and results in a Coulomb explosion of materials. Thus, materials with excited inner-shell electrons are broken into fragments [6].

A compact synchrotron light source facility has been installed at Ritsumeikan University [7]. Using the facility, SR ablation experiments on polymers, such as polyethylene [8], polytetrafluoroethylene (PTFE) [3,9], and polyvinylidenefluoride [10,11], have been carried out. In the present work, SR ablation of polymers that have double bonds in their main chains, e.g. polyacetylene (PA), *cis*- and *trans*-1,4-polybutadienes (*cis*-and *trans*-PBs), and poly(phenylene vinylene) (PPV), was carried out. Since PA and PPV are insoluble in any solvent and infusible with thermal decomposition, it is impossible to process them in a normal procedure into a fiber and thin film. In particular, since PA and PPV exhibit practically important properties, such as high electro-conductivity and electro-luminescence, efforts are made to chemically modify their chains, to make practical processing feasible. The present work is a trial to make thin films of these high-performance polymers, not through chemical modification of polymer chains. The SR ablation experiment also sought to understand ablation

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behavior of these conjugated polymers. Further, for comparison, another non-chemical process: a thermal vapor deposition (TVD) method, was carried out. Here, ablation behavior of these polymers by SR irradiation is discussed, focusing on the products by the process.

2. Experimental section

A small-scale superconductive SR installation that was constructed at Ritsumeikan University, and which is nicknamed AURORA, was used for the present ablation experiments [7]. The entire system is outlined in Fig. 1. SR rays were guided into a beam line from an outlet of the storage ring of the SR installation. The apparatus for ablation consists of three chambers, and they are disposed along the beam line. The setup and usage are as shown in Fig. 2. Cylindrical and toroidal mirror systems, which were designed for appropriate selection according to purpose, were installed in the first chamber, so that SR radiation beams were converged onto the target. When the cylindrical mirror was used, the photon density at a target position was 10 times higher than that of the inlet beam. When the toroidal mirror was selected, the beam was converged with a photon density as high as 50 times the density of the as-inlet beam. A buffer chamber was intermediately disposed to adjust the vacuum of the whole system. Various devices for ablation experiments were set up in the chamber at the end of the beam line. Polymer samples were set on an aluminum plate at a target position. Substances ablated by beam irradiation were deposited on a substrate. To attach various equipments, there is an outlet in the sample chamber: a quadrupole mass spectrometer (QMS) was connected, in the present case. The vacuum of the whole ablation apparatus reached $2–3 \times 10^{-8}$ Torr in a non-irradiated condition, and it was kept at a level not exceeding the order of 10^{-8} Torr while a sample was being irradiated. In comparison, thin films of these polymers were also prepared by TVD in a vacuum, using a conventional vapor deposition apparatus.

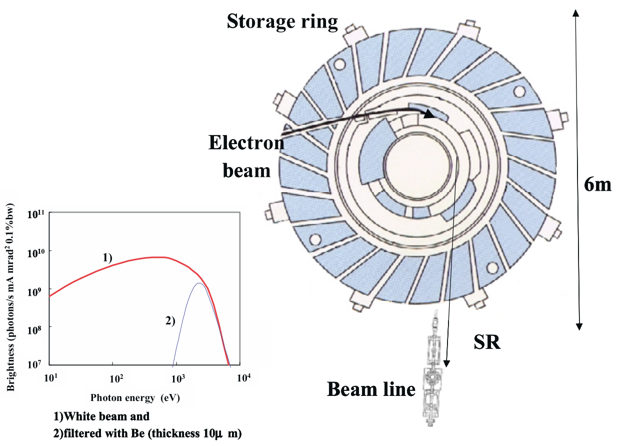

Fig. 1. (a) Schematic drawing of the synchrotron radiation installation, and (b) distribution spectra of photon energy of as-emitted and filtered rays.

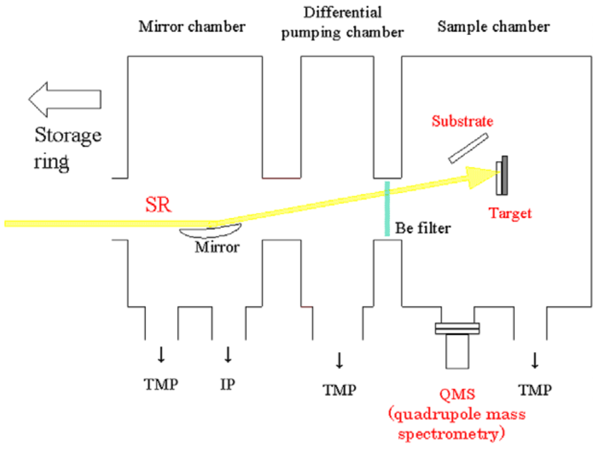

Fig. 2. Schematic diagram of the ablation apparatus: TMP, IP, and QMS denote a turbo-molecular pump, ion pump, and quadrupole mass spectrometer, respectively.

In SR ablation and TVD, Si wafers were mainly used as deposition substrate.

In Fig. 1, photon energy spectra of an as-emitted (as-inlet) beam and a beam filtered by beryllium are compared. By filtration by beryllium, photons with energy less than 10^3 keV were cut off.

The molecular structure and texture of thin deposited films were examined by IR spectroscopy, mass spectroscopy, transmission electron microscopy, and atomic force microscopy (AFM). From practical and academic viewpoints, it is very important whether or not the molecular orientation in the films can be controlled. For the purpose, such alkali halides as NaCl, KCl, and KBr, on which a variety of polymers can epitaxially crystallize [12], were also used as substrates.

PA was synthesized according to the Shirakawa and Akagi method [13], and poly(*p*-phenylene vinylene) (PPV) was synthesized according to the procedure by Zhang et al. [14]. *cis*- and *trans*-1,4-Polybutadienes (*cis*- and *trans*-PBs) were provided by Asahi Chemicals Co. Ltd and Japan Synthetic Rubber Co. Ltd, respectively.

3. Results

To gain beam intensity, all of the experiments were carried out using the toroidal mirror system. By using the system, samples were irradiated with an as-emitted beam and a beryllium-filtered beam. Since the distribution of photon energy differs between as-emitted beams and filtered beams, as seen in Fig. 1, the scission behavior of chemical bonds can be expected to differ between with and without a filter. Comparison of the ablation results obtained using both beams found no significant difference in ablation products. This implies that photons with cut-off, low energy do not selectively affect the scission behavior of polymer chains. However, to understand the mechanism and application of ablation by SR, it is very important to know the dependence of scission behavior of bonds on photon energy. It is necessary to carry out ablation experiments using spectroscopically well-separated beams in a narrow energy range. When the filtered beam was used, the total beam intensity became low, and hence the ablation rate of mass decreased. Therefore, the ablation was carried out using the as-emitted beam, to gain deposition efficiency of mass on the substrate. Here, the ablation behaviors of individual polymers by as-emitted beams are described.

3.1. Polyacetylene

When PA was irradiated by SR rays, it was fragmented. As a result, the released substances were deposited onto a Si wafer substrate, in the form of a thin film. In comparison, thin films were also prepared on a Si wafer substrate by thermally evaporating PA in a vacuum. Fig. 3 shows infrared spectra of an as-synthesized PA film and of ablation-deposited and thermally deposited films. The thickness of these films was estimated at less than 1 μm, judging from interference color of light of films. C–H out-of plane motions characteristic of *cis*- and *trans*-isomers are observed at 740 and 1015 cm^{-1}, respectively, in the spectrum of as-prepared film. The original PA comprised *cis*- and *trans*-PAs. However, there are no such characteristic peaks in the IR spectra (b) and (c) in Fig. 3. Neither *cis*- nor *trans*-PA was produced in both ablation-deposited and thermally deposited films.

Fig. 4 shows a mass distribution spectrum of gaseous substances that were produced in the ablation process of PA. It was measured by a QMS. The intense peaks present at $m/z = 77$ and 91 are to be noted. The mass numbers: 77 and 91 just correspond to those of a phenyl cation fragment: $C_6H_5^+$, and a benzyl cation fragment: $C_6H_5CH_2^+$, respectively. Phenyl and substituted phenyl rings were formed by ablation of PA. It is considered that fragments containing the phenyl rings were directly deposited onto the substrate to form a thin film. It is evident, thus, that the deposited films were not composed of PA. Our aim was to produce a thin film of PA by SR ablation, but unfortunately, it was unsuccessful. It is known that in the early stage of PA synthesis using Ziegler–Natta catalyst, benzene was produced as a by-product [15], and that trimers were produced by thermal decomposition of PA [16]. Here, it was found that aromatic compounds are also produced by means of the cold process of SR ablation.

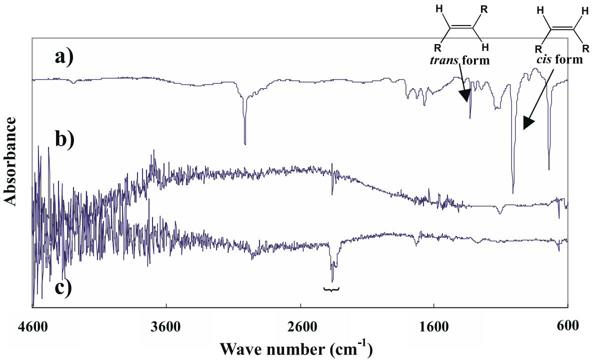

Fig. 3. IR spectra of (a) as-synthesized polyacetylene, and of thin films that were deposited on an Si wafer substrate by (b) SR ablation and (c) TVD. Peaks with a mark are assigned to the C–H stretching motion of $-CH_2-$ and $-CH_3$.

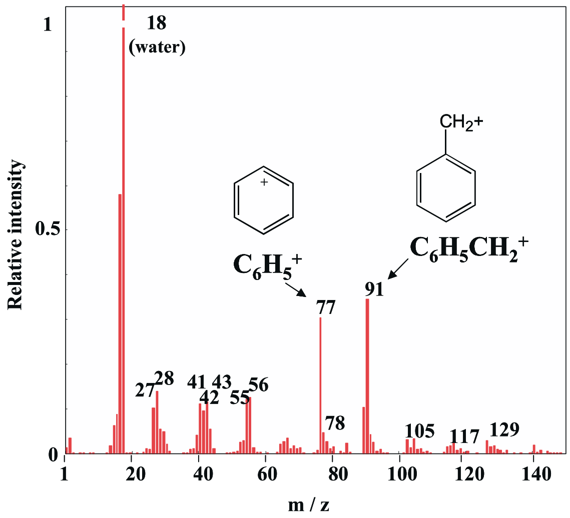

Fig. 4. Mass distribution spectrum of gaseous substances released from polyacetylene by SR ablation. Numbers for peaks denote mass number.

3.2. Polybutadiene

The skeleton of PA consists of conjugated double bonds. As a counterpart, polybutadiene was studied to compare its ablation behavior with that of PA, because its main chains comprise double bonds as well, but they are linked in a non-conjugated way. Further, it is interesting that there are two isomers of polybutadiene: *cis*- and *trans*-PBs. It would be interesting to determine if the ablation behaviors differ between the two isomeric PBs.

Four kinds of thin films were prepared from *cis*- and *trans*-PBs in the following ways: films (a) and (b) were deposited on a silicon wafer by SR ablation of *cis*- and *trans*-PBs, respectively, and films (c) and (d) were deposited by TVD of *cis*- and *trans*-PBs, respectively. Fig. 5 compares the whole IR spectra of these films, and the enlarged ones of the parts enclosed by boxes in Fig. 5 are represented in Fig. 6. *cis*-PB is characterized by C–H out-of plane motion at 735 cm^{-1}, and *trans*-PB by C–H out-of plane motion at 970 cm^{-1}. The films deposited in these various ways were investigated by taking these IR bands as an index for characterization.

- There are no observed absorption peaks characteristic of *cis*- and *trans*-PBs in Figs. 5(a) and 6(a). Instead, a strong peak appears at about 1100 cm^{-1}. The absorption should be assigned to the stretching vibration of C–C in amorphous carbon (discussed later).

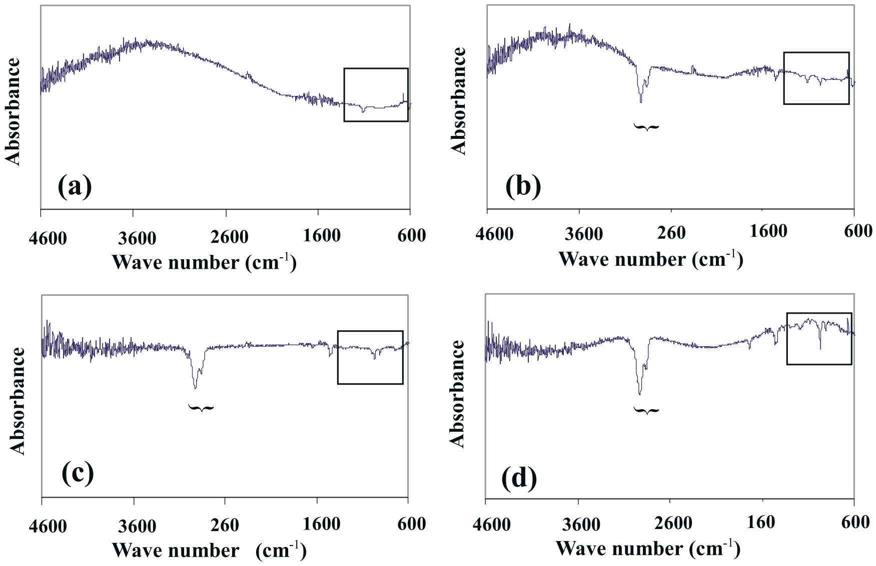

Fig. 5. IR spectra of thin films prepared in two deposition methods from *cis*- and *trans*-PBs; by SR ablation of (a) *cis*- and (b) *trans*-PBs, and by TVD of (c) *cis*- and (d) *trans*-PBs. Peaks with a mark are assigned to the C–H stretching motion of $-CH_2-$ and $-CH_3$.

- In Figs. 5(b) and 6(b), the characteristic band of *trans*-PB was identified. In addition, the above-mentioned peak at 1100 cm^{-1} is also observed. Further, an absorption peak is observed at 910 cm^{-1}. It is assigned to the C–H out-of plane motion of the pending $-CH{=}CH_2$ groups of diene compounds. The last peak suggests that 1,2-addition of ablated diene fragments took place on the substrate, and the fragments were incorporated into the resulted polymeric substances.
- In Figs. 5(c) and 6(c), absorption peaks characterizing *trans*-PB and 1,2-linkage are confirmed at 970 and 910 cm^{-1}, respectively. It is natural that *trans*-1,4-polybutadiene was mainly produced from *trans*-PB by TVD (Fig. 6(d)). It is to be pointed that when *cis*-PB was thermally evaporated, *trans*-PB was also formed. Isomerization from *cis*-form to *trans*-form occurred in the thermal process. Of course, *cis*-PB coexists. That *trans*-PB was involved in the deposited film of *cis*-PB, means that the ablated or thermally evaporated diene fragments were polymerized in the *trans*-form. No peak appears at 1100 cm^{-1}.

Fig. 7 shows the mass distribution spectra of ablated gaseous substances from *cis*- and *trans*-PBs. In both spectra, we see that various kinds of hydrocarbon fragments were produced, and that the peak intensity at *m/z* corresponding to 'cyclic compounds' in Fig. 4 is weak. The mass distributions of both spectra are almost the same independently of the difference in the chain configurations. This implies that chain scission behavior is basically identical between the two PBs: main chains were broken at random by SR irradiation.

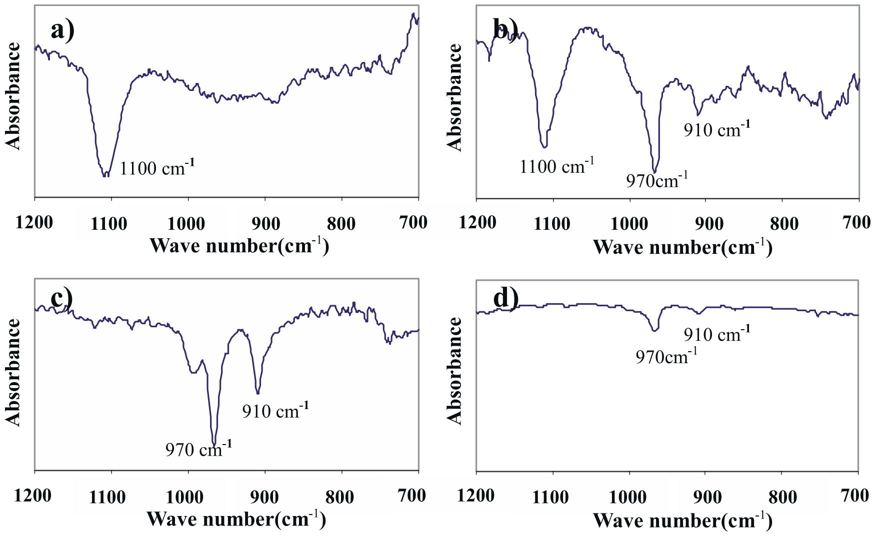

Fig. 6. Enlarged IR spectra of the part enclosed by a rectangle in Fig. 5. Figure indices (a), (b), (c), and (d) correspond to those in Fig. 5.

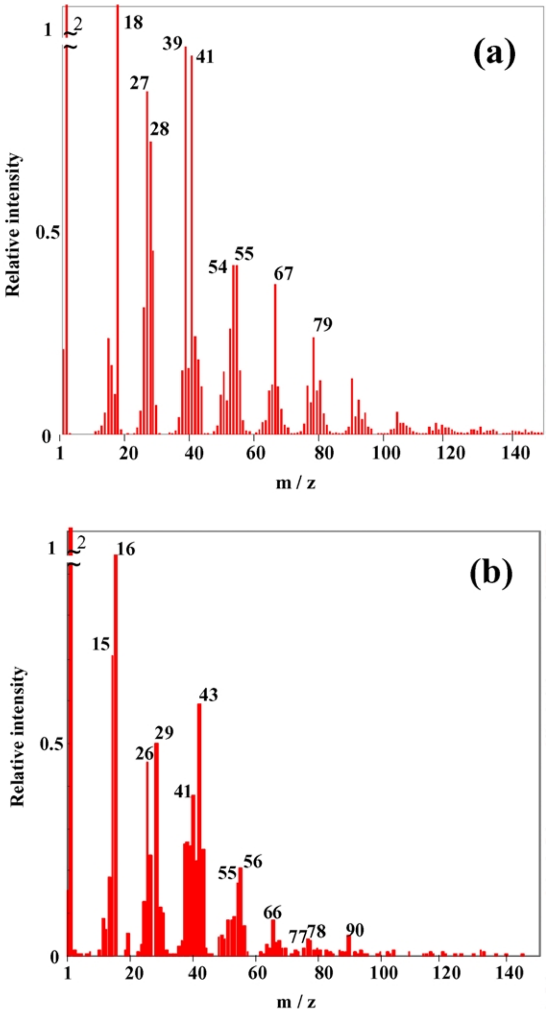

Fig. 7. Mass distribution spectra of ablated gaseous substances by SR irradiation: (a) *cis*-, and (b) *trans*-PBs. Numbers corresponding to peaks denote mass number.

3.3. Poly(*p*-phenylene vinylene)

Fig. 8 shows IR spectra of as-synthesized PPV and of PPVs deposited on a silicon wafer by SR ablation and by TVD. Fig. 9 shows an expansion of the part enclosed by a box in Fig. 8. Here, PPV is characterized by absorption peaks of C–H out-of plane vibration of the *p*-substituted benzene ring at 837 cm^{-1}, and C–H out-of plane vibration of the vinyl group at 965 cm^{-1}. These characteristic peaks are observed in both spectra (b) and (c) of Fig. 9 (the peak at 837 cm^{-1} is blurred in the spectrum). It is clear that PPV was reproduced in the films formed by SR ablation and by TVD.

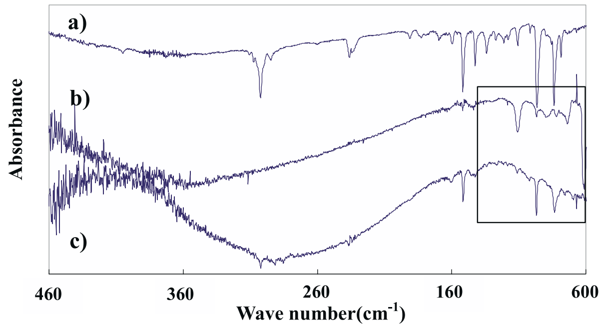

Fig. 8. IR spectra of PPVs prepared by various ways: (a) as-polymerized, and deposited on an Si wafer (b) by SR ablation and (c) by TVD.

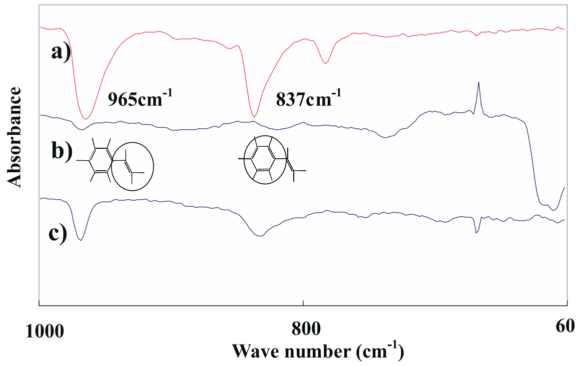

Fig. 9. Magnified spectra of the part enclosed by a box in Fig. 8. Spectra indices (a), (b), and (c) are correspond to those in Fig. 8.

The mass distribution spectrum of gaseous ablated substances of PPV was also measured in the same way as above. Fig. 10 shows the mass spectrum. Intense peaks are seen at $m/z = 90$, 91, and 105. The mass numbers of 91 and 105 correspond to those of benzyl cation: $C_6H_5CH_2^+$, and phenylvinyl cation: $C_6H_5CH_2CH_2^+$, respectively. The mass number of 90 is for benzyl radical cation: $C_6H_5CH^{\cdot +}$. A weak peak at $m/z = 77$ is assigned to the phenyl cation: $C_6H_5^+$. As the phenyl cation peak is weak, it is less probable that both single bonds at the *para* position of a phenyl group could be broken simultaneously.

3.4. Morphology and texture of deposited films

If polymer chains are arrayed in an ordered way in thin, SR-ablated film, it is valuable from the practical viewpoint.

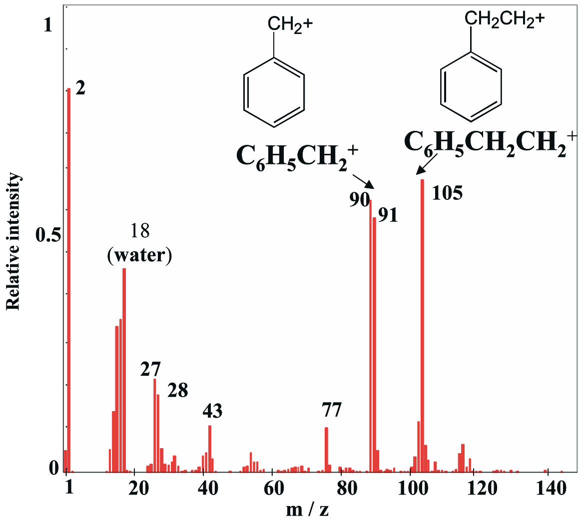

Fig. 10. Mass distribution spectrum of gaseous ablated substances by SR ablation of PPV. Numbers for peaks denote mass number.

One purpose of this work is to make such films. In all of the kinds of polymers examined here, the SR-ablated and thermally evaporated substances sheeted the substrate surface in the form of thin, 'macroscopically uniform' film. All of the film products of PA and *cis*- and *trans*-PBs were non-crystalline, and their chemical constituent is different from that of the original polymer. Only PPV was reproduced in the crystalline state.

Fig. 11(a) and (d) shows the electron diffraction (ED) pattern and AFM image of thin PPV film, respectively, that was formed on (100) cleavage surface of NaCl by SR ablation. The ED pattern and AFM image of the thermally deposited PPV film on NaCl are shown in Fig. 11(b) and (e), respectively. The substrates were at room temperature in both cases. As the reflections are more arced in Fig. 11(b) than in Fig. 11(a), PPV was arrayed in a more ordered way in the SR ablation film. As shown in both figures, the arced reflections are indexed as 110, 200, and 210. The simultaneous presence of these diffractions shows that molecular chains stand at the surface, although not always perpendicular to the substrate surface. From the AFM image of Fig. 11(d), we see that the surfaces of ablated film are not always smooth at the nano-level, and small particles are dispersed.

Fig. 11(c) shows the ED pattern of a PPV thin film that was deposited on (100) surface of KCl by the ablation method. As sharp ring reflections are seen, the film is crystalline. These reflections are indexed as shown in the figure. Debye–Scherrer rings show that the constituent crystallites are not ordered. The morphology of Fig. 11(f) is distinct from that of Fig. 11(d) in that lager particles are dispersed.

Two types of electron diffraction patterns were observed in the PPV film that was prepared on KBr surface by SR ablation. One type is the same as the ED pattern in Fig. 11(a) (Type I), and the other is shown in Fig. 12. Molecular chains stand at the substrate surface in Type I, as discussed above. The strong reflections indicated by arrows in Fig. 12 are not definitely indexed—probably indexed as 202 reflection—but could correspond to some intense reflection of the second layer line of the fiber patterns [17]. The presence of the reflections indicates that the molecular chains lie down parallel to the substrate surface (type II).

4. Discussion

When polyethylene is irradiated by SR rays, hydrogen gas and gaseous hydrocarbons, such as methane, ethane, propane, and butane, are ablated, and polyethylene is

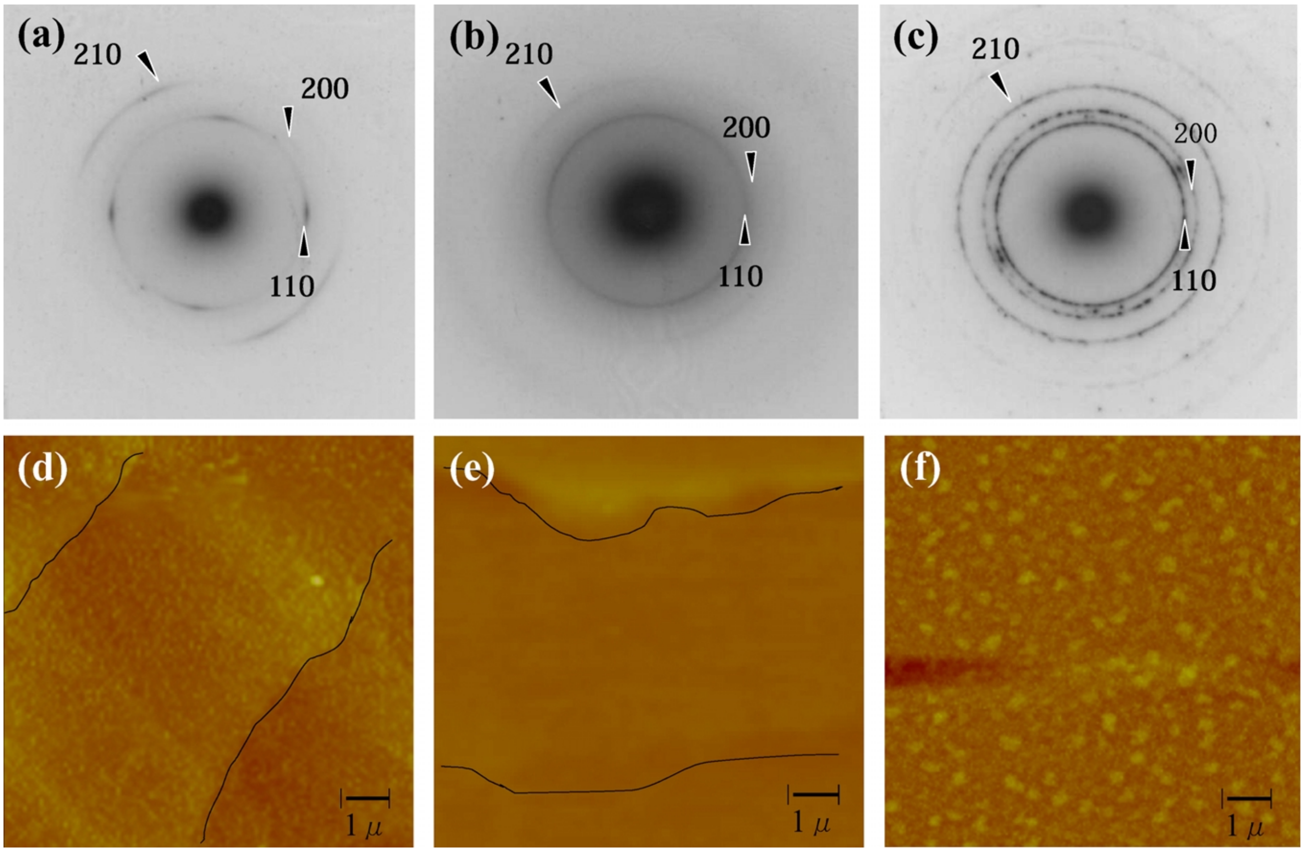

Fig. 11. Electron diffraction patterns of thin PPV films deposited in various ways: on (001) NaCl surface (a) by SR ablation, and (b) by thermal evaporation, and (c) on (001) KCl surface by SR ablation. AFM images (d), (e), and (f) correspond to the electron diffraction patterns in (a), (b), and (c), respectively. Dark lines in (d) and (e) indicate the steps on the substrate surface.

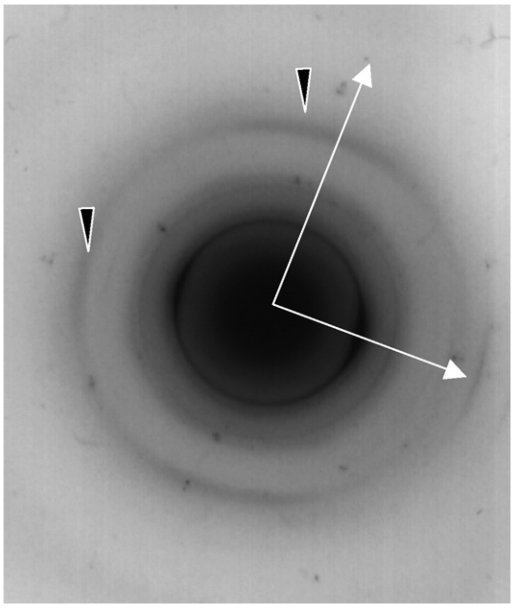

Fig. 12. Electron diffraction pattern of Type II, showing the parallel molecular orientations of PPV crystallites on KBr substrate surface. White lines denote the directions of the strong intensity of reflections of interest (see the text).

deposited on substrate [8]. By SR irradiation, C–H bonds are broken, and hydrogen atoms thus released are recombined into hydrogen molecules. Scission of C–C bonds, of course, takes place. Hydrocarbon radicals resultantly produced are recombined into polyethylene on substrate surface. The formation mechanism of polyethylene by SR ablation is supported by the following ablation experiment: when frozen *n*-octane was ablated by SR irradiation, polyethylene was also produced [18]. Various kinds of linkages other than those in the source polymers occur in the deposited films by SR ablation and by TVD, as seen from the IR spectra in Figs. 3, 5, and 8. This implies that gaseous fragments produced by these procedures, some of which could change their chemical structure and/or configuration, are recombined or polymerized onto the substrate, e.g. the production of *trans*-PB from *cis*-PB is an example. Further, the existence of pendant $-CH{=}CH_2$ groups in the deposited film from PBs proves that polymerization by 1,2-addition of ablated diene fragments takes place. When hydrogen atoms are released from a long chain, a long chain with many radical sites could be formed within the target material. The cross-linkage could be formed by inter- and intra-recombination of long chain radicals, leading to the graphitization. As a result, graphitized materials remained in the target after SR ablation. In the case of ablation of PETF, F_2 gas was not detected, and hence C–F bond scission does not preferentially occur [9,10]. Thus, PETF are not so heavily graphitized. As graphitized materials were left after ablation in the present polymers, inter- or intra-molecular cross-linkage occurred.

Hydrocarbon fragments consisting of two to five carbons were produced by the ablation of PA, as seen in Fig. 4. The QMS intensity at $m/z = 2$ (H_2) is low, and the peak heights for different carbon numbers are almost equal but not high. C–H stretching vibration of $-CH_3$ and $-CH_2-$ was observed in the deposited films from PA and PBs (see Figs. 3 and 5), showing that released hydrogen atoms were consumed to saturate double bonds of ablated fragments. Fragments with six or seven carbons, i.e. at $m/z = 70–80$, are less produced by ablation of *cis*- and *trans*-PBs (see Fig. 7). It is less probable that six or seven carbons of fragments could be directly ablated from the PB target. In other words, it is unlikely that higher-numbered hydrocarbons could be ablated and cyclized into phenyl and substituted phenyl compounds from PBs. This means, therefore, that phenyl and benzyl cations in PA ablation could not be directly produced by cyclization of higher-numbered carbon fragments. How can these compounds be formed? By trimerization of unsaturated CC or CCC fragments, phenyl and benzyl compounds could be formed: When three CC fragments are trimerized, a phenyl ring could be formed, and when a CCC fragment is incorporated in the trimerization process, a benzyl cation could be produced. This explains the characteristic profile of the MQS spectrum in Fig. 4, in which the peaks at m/z from 20 to 70, are weak, and those at $m/z = 77$ and 91 are high.

There is no significant difference between QMS spectra of ablated substances from *cis*- and *trans*-PBs (see Fig. 7). The spectrum peak decreases with increasing m/z, although peaks at $m/z = 27$ and 28, corresponding to two carbon fragments, are less intense. Since a CC single bond is energetically less stable than a CC double bond, a single bond could be broken more readily than a double bond. However, the finding of less intense peaks at $m/z = 27$ and 28 implies that two single bonds putting a double bond in between should be less readily broken at the same time. 1,2-Disubstituted diene compounds in the *trans*-form are energetically more stable than in the *cis*-form. As-ablated diene compounds from *cis*-PB are supposed to be in the *cis*-form. However, since the gaseous diene substances thermally produced are in the excited state, these compounds are isomerized to be stabilized in the *trans*-configuration. The isomerized *trans*-dienes could be recombined and polymerized into *trans*-PB on substrate. *cis*-1,4-Polybutadine was photochemically isomerized into the *trans*-form by UV irradiation [19]. Thus, it is readily understood that *trans*-PB could be reproduced by TVD of *cis*-PB.

The IR spectra of an SR ablation film of *cis*-PB in Figs. 5(a) and 6(a) show no trace of both *cis*- and *trans*-PBs. Fig. 13 shows the IR spectra of a film that was deposited from amorphous carbon by TVD in a vacuum. Since amorphous carbon is not easily ablated by SR irradiation, the thin film of carbon was prepared by TVD. Evidently, hydrocarbon-based substances are never produced in the film in the process. The spectrum of the thin film of carbon just referred to above indicates no signals of existence of hydrocarbon

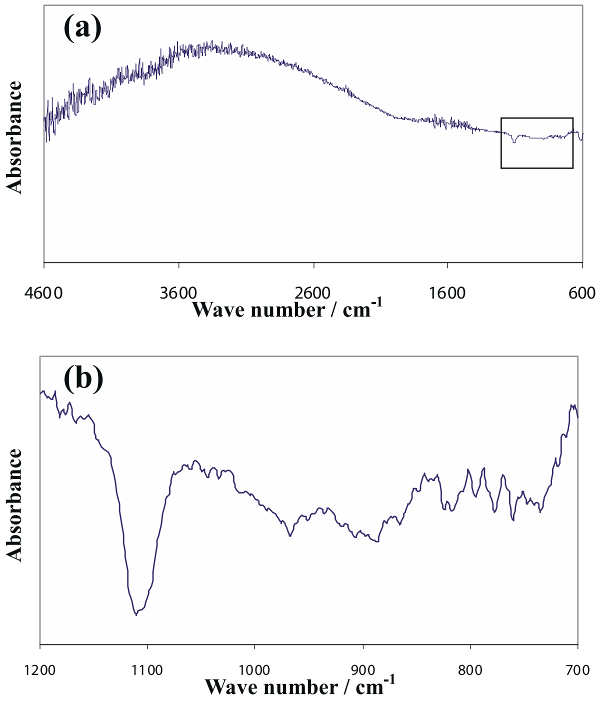

Fig. 13. (a) IR spectrum of a thin film prepared from amorphous carbon by TVD. (b) Magnification of the part enclosed by a square in (a).

compounds, and it is quite similar to those the spectra in Figs. 5(a) and 6(a). Thus, this confirms that carbon compounds are produced by SR ablation of *cis*-PB. It has been attempted to make a diamond thin film by SR ablation, using frozen acetone as a target for a carbon source [20]. Another experiment uses frozen methane, instead of frozen acetone, by SR ablation. It is required in these experiments to produce methane and hydrogen radicals. In the present ablation of *cis*-PB, such compounds as methane radicals were produced, as seen in QMS of Fig. 7. However, it is unclear why the carbon compounds could be formed exclusively from *cis*-PB and along with from *trans*-PB. It is to be expected here that *cis*-PB could be useful as a carbon source to form carbon compounds by the cold process of SR ablation.

The QMS spectra of PPV have peaks at $m/z = 77, 90, 91$, and 105, which correspond to the phenyl, two kinds of benzyl groups, and phenylvinylene cations. As seen in Fig. 5, the compounds with the same m/z values were not well produced from PB by SR ablation. Phenyl compounds are formed by SR ablation of poly(1,4-phenylene) [21]. These results suggest that the phenyl compounds in the deposited films were produced not through cyclization of linear chain fragments but by recombination–deposition of phenyl ring products from PPV. In other words, PPV undergoes, highly, chain scission at vinylene groups, so that substituted phenyl compounds are formed. The peak at $m/z = 77$, corresponding to the phenyl cation, is low in Fig. 10. Less probably, single bonds at the *para* position of a phenylene group of PPV should be broken at the same time. From the characteristics of mass distribution, the following scission mechanism of PPV chains is considered: once either of single bonds at the *para* position of a phenyl ring is broken, the second scission of the polymer chain are likely to occur at the double bond or at the single bond belonging to another phenyl group.

The electron diffraction patterns in Fig. 11(a) and (b) are not straightforwardly explained based on a simple hk0 net pattern. The orientational relationship between 210 and 110 reflections in the ED are appropriately explained by the twinning of an hk0 net pattern with respect to (110) plane, as schematized in Fig. 14. In the ED patterns, 200 reflections are only faintly observed. That is, (200) plane is inclined from the normal at the substrate surface. Basically, (110) plane is normal to the substrate surface. As a result, molecular chains incline at an angle from the normal in (110) plane. It is considered that crystallites of Type I orientation could grow, performing the following crystallographic, orientational relationship with the substrate. The 200 lattice spacing of PPV: $d(200)_{\mathrm{PPV}}(=0.398\ \mathrm{nm})$, is comparable to the 110 lattice spacing of NaCl: $d(110)_{\mathrm{NaCl}}(=0.404\ \mathrm{nm})$. The lattice misfit between the two lattice spacings is 1.5%, which is within allowance for epitaxial matching. In the alkali halides used here, the lattice misfit between $d(200)_{\mathrm{ppv}}$ and $d(110)$ of alkali halides increases in the order of NaCl, KCl, and KBr: The lattice constants (the *a*-axis dimension) of NaCl, KCl, and KBr are 0.563, 0.628, and 0.659 nm, respectively. Hence, only from the viewpoint of lattice misfit, epitaxial matching would be less favorable in the above order. However, controlled overgrowth of PPV occurred on KBr substrate, although not on KCl substrate.

The ED pattern of Type II is possibly explained based on the epitaxial mechanism. The *c*-axis dimension of the unit

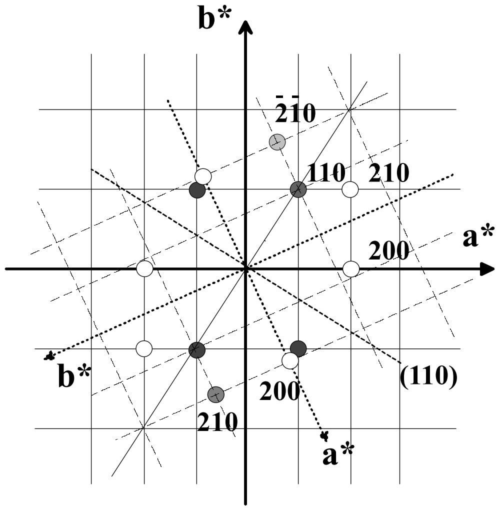

Fig. 14. Schematic representation of the ED pattern of PPV thin film with the orientation of Type I. The dotted net pattern of reciprocal lattice is the mirror pattern of the solid net plane with respect to (110) plane. In the real ED pattern, another set of ED pattern, which is produced by the mirror operation with respect to ($\bar{1}10$) plane, is overlapped. Open-circled reflections are not observed or are very weak even if they appear.

cell of PPV is 0.658 nm. The value is very close to the *a*-dimension of the unit cell of KBr. Taking into account that both values are comparable, it is considered that PPV crystallites could grow aligning their chain axes, i.e. the *c*-axis, parallel to the *a*-axis of KBr crystal lattice on its surface. The directions of intense peaks of the reflections are cross perpendicular to each other, shown with white arrow lines in Fig. 12. The orthogonal orientation of the intense peak of ED supports the above explanation of epitaxy: when PPV crystallites grow performing the above parallel alignment of their chains to the *a*- axes of KBr substrate, there occur two orientations of molecular chains crossing perpendicular to one another (it is not confirmed experimentally that the directions of white lines are parallel to the *a*-axis of KBr). The exact molecular orientational relationships of the Types of I and II with the substrate crystal lattice are open for further studies.

The ‘nano-size’ or larger size of particles or blocks could be released by SR irradiation and form a thin film by deposition on a substrate. Generally, crystalline polymers are composed of nano- or larger size of crystalline blocks with ordered chains. When a crystalline polymer, e.g. PPV, is irradiated by SR, the blocks could be released and accidentally deposited in an ordered way on substrate surface. Thus, an oriented ED pattern is given, even if there is no epitaxial relationship with the substrate. Based on the deposition of molecular fragments, we interpreted, as described above, the crystallite orientation of PPV on the alkali halide surface. In the case of PPV, however, there is a possibility that the ordered materials could be accidentally formed in this way by deposition of nano-size of crystalline particles. In comparing the AFM images of Fig. 13(a) and (c), larger size of particles were deposited in Fig. 13(c). The ED pattern is almost the Debye–Scherrer pattern in Fig. 13(c). Further, the ED in Fig. 13(b), where PPV was deposited on NaCl by TVD with a smooth surface, is slightly oriented. These results explain that the orientation of crystallites is independent of their size. Further, we observed that the intensity relationship among reflections, i.e. 110, 200 and 210, in the other ordered EDs of PPV on NaCl surface was such as in Fig. 11(a). Taking these results into account, we consider that it is less probable that the oriented thin film of PPV could be formed by deposition of crystallites that are in the form of a particle size.

5. Concluding remarks

Of PA, *cis*- and *trans*-PBs, and PPV, which have double bonds in their main chains, *trans*-PB and PPV were produced and deposited in the form of a thin film on substrate by SR ablation. It has been attempted to make PPV soluble and fusible by chemically modifying it so that it is feasible for processing, for example, in the form of thin film. It was found here that instead of the chemical process, the cold process by SR ablation could be used to make a thin film of PPV. This process could be applied to polymers that cannot be processed from a melt or solution. Moreover, there is the possibility that a PPV film in which molecular chains are arrayed in a controlled way, standing at or lying down parallel to the substrate, could be produced by using alkali halides as substrate.

When *cis*-PB was deposited by the TVD method in a vacuum, isomerization of *cis*-PB to *trans*-PB occurred, and as a result, a composite thin film of *cis*- and *trans*-PBs was formed. However, when *cis*-PB was ablated by SR irradiation, neither *cis*- nor *trans*-PB was produced on the substrate. Instead, carbon compounds were produced. Thus, the present cold process by SR ablation of *cis*-PB could be useful for producing carbon compounds.

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