Influence of Electron Beam Irradiation on Properties of Fluorine-Containing Poly(aryl ether ketone)s

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ABSTRACT: The influence of electron beam irradiation on the properties of fluorine-containing poly(aryl ketone)s (F-PEK), derived from 2,3,4,5,6-pentafluorobenzoic acid, was examined. Irradiation was performed with an electron beam at a dose of 3.63×10^3 Gy s^{-1} for which the corresponding doses were 29.0, 51.0, and 94.5 MGy. Tensile strength at break increased up to a dose of 29.0 MGy and then decreased very slightly with irradiation. Elongation at break was more susceptible to irradiation and decreased drastically to one tenth at a dose of 29.0 MGy. Young's modulus was enhanced by the irradiation. F-PEKs were changed from elastic materials to strong and brittle materials by irradiation. Relaxation of the viscoelastic property shifted toward higher temperature by irradiation. These tensile and viscoelastic property changes were attributed to the forma- tion of a bulkier and more rigid structure by crosslinking. The fluorine atoms attached to the 1,4-phenylene moiety in F-PEKs were surprisingly susceptible to the irradiation and were completely lost at a dose of 29.0 MGy. The π-electron conjugated aromatic structure was concurrently developed during irradiation. Further, polar functional groups such as carboxyl group and ester group were generated by chain scission and rearrangement. The F-PEKs retained their good transparency and the thermal stability was significantly improved after irradiation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 157–166, 2004

Key words: poly(ether ketone); fluorine; electron beam; mechanical property; crosslinking

INTRODUCTION

Aromatic polymers are often referred to as high-performance polymers because of their excellent thermal and mechanical properties, as well as chemical resistance.[1] In many cases, they exhibit neither fusibility nor solubility because of the rigid chain structures. Recently, fluorinated groups were introduced into aromatic polymers to improve their solubility in common solvents, as well as other properties such as thermal stability, high glass-transition temperature, low dielectric constant, transparency, low water absorption, and so on.[2]

We previously prepared the novel fluorinated poly(ether ketone)s (F-PEKs) derived from 2,3,4,5,6-pentafluorobenzoic acid (PFBA), which were composed of the 2,3,5,6-tetrafluoro-1,4-phenylene moiety in the

polymer chains.[3] These PEKs exhibit improved properties described above. Additionally, PFBA is widely used as a common industrial intermediate for medicines, cosmetics, and agricultural chemicals. Hence, PEKs are potential candidates for optical and microelectronic devices not only because of outstanding properties but also because of reasonable costs.

In the last few decades many aromatic polymers showing good resistance to degradation by high-energy radiation have been developed to be used as materials in high-energy radiation environments, such as those found in the nuclear and aerospace industries.[4–7] Among them, poly(ether ether ketone)s (PEEK)[4,8–11] and polyamides[6] exhibit better resistance than that of other aromatic polymers such as poly(sulfone)s (PS),[12–14] poly(ether sulfone)s (PES),[13–18] and polyesters.[14,19] However, their potential is less than that of polyimides represented by Kapton.[20–24]

Kapton is one of the best organic materials to show good resistance to degradation by high-energy radiation, although the property is not sufficient for long-term usage and besides Kapton itself has less solubility. Polymers superior to polyimides are eagerly desired with respect to resistance to degradation by
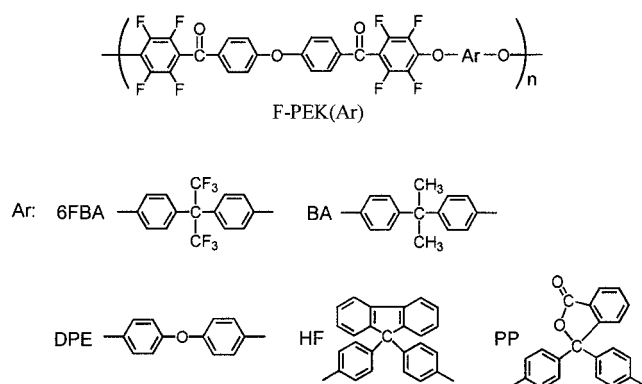
Scheme 1 Structures of F-PEKs.

high-energy radiation. The radiation chemistry of fluorine-containing aromatic polymers has been investigated, including polyimides,[25–29] poly(phosphine oxide)s,[30] and polyesters.[31–34] However, all these polymers contain fluorine atoms as a form of trifluoromethyl pendant or 1,1,1,3,3,3-hexafluoroisopropylidene group. Aromatic polymers consisting of a fluorinated aromatic moiety like 2,3,5,6-tetrafluoro-1,4-phenylene group have not yet been reported concerning their potential for resistance to degradation by high-energy radiation. In this study, the resistance to degradation of F-PEKs was examined by electron beam irradiation to evaluate the potential of F-PEKs as high-performance materials in high-energy radiation environments.

EXPERIMENTAL

Materials

Five different F-PEKs shown in Scheme 1 were synthesized according to a previously reported procedure.[3] The films of F-PEK(6FBA), F-PEK(BA), F-PEK-(HF), and F-PEK(PP) were prepared by cast method of 20 wt % toluene solution and that of F-PEK(DPE) was prepared from 20 wt % *N,N*-dimethyl acetamide

(DMAc) solution. The thickness of the obtained films was in the range of 20–50 μm.

Electron beam irradiation

Irradiation was performed with an electron beam at a dose of 3.63×10^3 Gy s^{-1} on a stainless-steel plate with a cooling water jacket to prevent an increase in the temperature of the specimen during irradiation under a slow stream of argon gas. The films were irradiated for different periods, 8.0×10^3, 14.0×10^3, and 26.0×10^3 s, for which the corresponding doses were 29.0, 51.0, and 94.5 MGy, respectively.

Measurements

Tensile tests were performed at 25°C with a crosshead speed of 200 mm min^{-1}. The specimens (size $100 \times 10 \times 0.02$–0.05 mm) for tensile testing were cut from the as-irradiated films. The tensile strength was obtained from the stress at break point, and elongation was determined by simply dividing over all displacements by the initial length of the dumbbell neck (30 mm). These tensile parameters were the average of five specimens. The viscoelastic properties were measured on a Reovibron DDV-II-EP (Orientec Co., Japan) at a frequency of 110 Hz in the temperature range of -100 to 400°C at a heating rate of 2°C min^{-1}. The water contact angle was measured on a contact angle meter CA-D (Kyowa Kaimen Co., Japan) on both surfaces of the irradiated films. Thermal properties were measured on a Perkin–Elmer TGA-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10°C min^{-1} in nitrogen atmosphere. Glass-transition temperature (T_g) and melting temperature (T_m) were measured on a DSC-7 apparatus (Perkin Elmer Cetus Instruments) at a scanning rate of 10°C min^{-1} in nitrogen atmosphere. Absorption spectra of the films, which were about 40 μm in thickness, were recorded on a V-750 spectrometer (Jasco Co., Tokyo, Japan). FTIR spectra of the films were measured on an FT/

TABLE I
Reduced Viscosity and Properties of F-PEKs

Polymer code[a]	F-PEK				
	6FBA	BA	HF	DPE	PP
Reduced viscosity (dL g^{-1})[b]	0.75	0.54	0.46	0.82	0.97
T_g[c] (°C)	174	170	239	171	235
T_m[c] (°C)	ND[d]	ND	ND	ND	ND
10% wt loss in N$_2$ (°C)[e]	524	499	553	607	523

[a] Polymer codes are shown in Scheme 1.
[b] Measured in DMAc at a concentration of 0.5 g dL^{-1} and 25°C.
[c] DSC was performed at a scanning rate of 20°C min^{-1} in nitrogen.
[d] Not detected.
[e] TGA was performed at a scanning rate of 20°C min^{-1} in nitrogen.
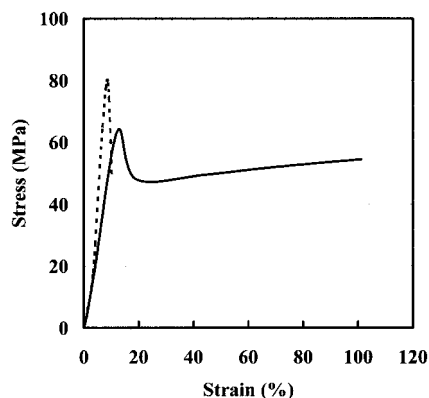
Figure 1 Stress–strain curves of unirradiated and irradiated F-PEK(6FBA) at a dose of 94.5 MGy.

IR-410 spectrometer (Jasco Co.). Wide-angle X-ray scattering (WAXS) patterns of the films were measured on a Gaiger flex 2013 diffractometer (Rigaku Co., Japan) with Cu–K_α (30 kV, 20 mA). Elemental analysis was performed by X-ray photoelectron spectroscopy (XPS; JPS-9000MX, JPS Co., Japan) with Mg–K_α (10 kV, 10 mA).

Solubility test

The irradiated films were extracted in DMAc under reflux for 6 h with a Soxhlet extractor. The residual films were dried under reduced pressure at 70°C for 24 h and then the weight losses by extraction were determined.

RESULTS AND DISCUSSION

Characterization of F-PEKs

Five F-PEKs were synthesized and characterized as summarized in Table I. Molecular weights of these F-PEKs were high enough to prepare tough films, of which the reduced viscosities were in the range of 0.46–0.97 dL g^{-1}. As previously reported,[3] they exhibited outstanding solubility in polar aprotic solvents such as N-methyl-2-pyrrolidinone and DMAc. In particular, F-PEK(6FBA), F-PEK(BA), and F-PEK(HF) exhibited greater solubility in chloroform and toluene. T_g's of the obtained F-PEKs ranged from 170 to 239°C depending on their chemical structures; F-PEK(HF) had the highest T_g (239°C) among them because of the bulky structure. They exhibited no T_m and were noncrystalline polymers, confirmed by WAXS, as discussed later. The temperature of 10% weight loss in nitrogen atmosphere of these F-PEKs ranged from 499 to 607°C and they showed excellent thermal stability.

Mechanical properties of irradiated F-PEK films

The tensile properties of the unirradiated and irradiated films were examined and the stress–strain curves
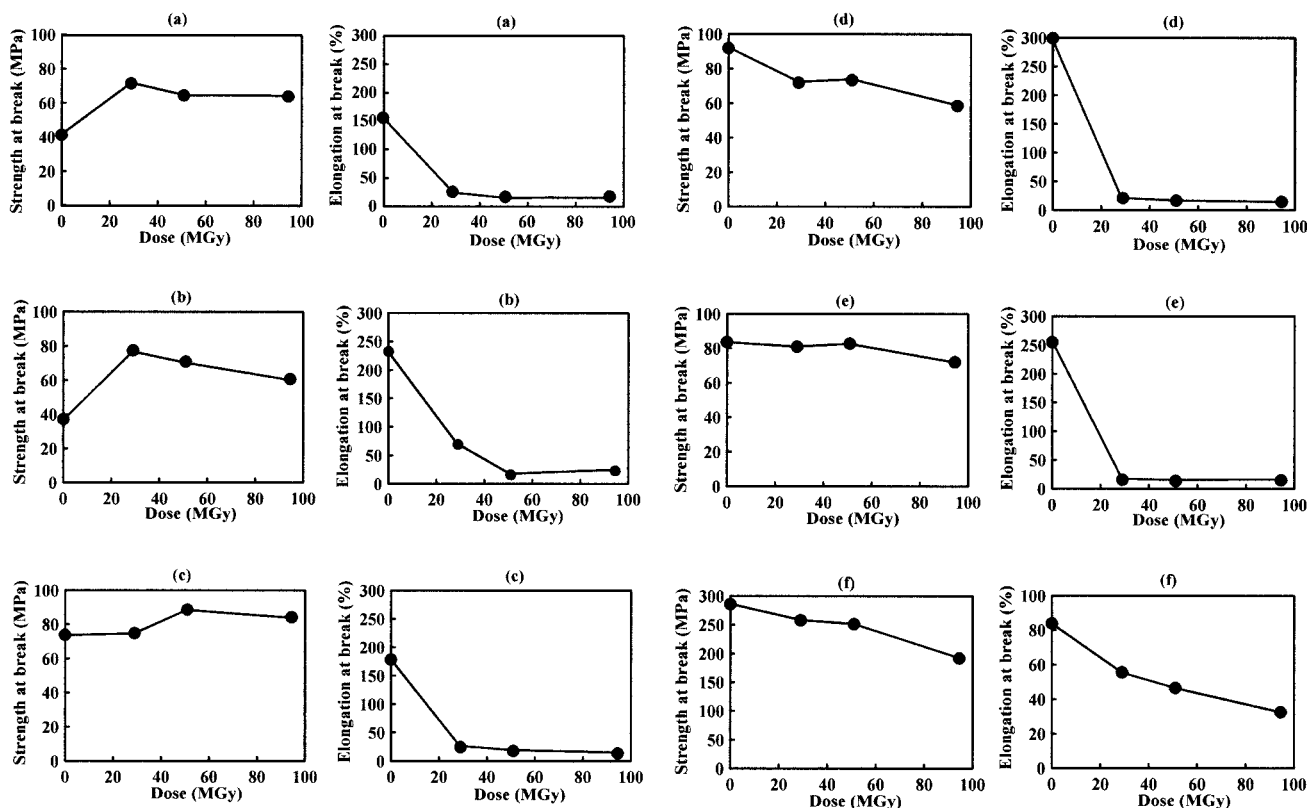

Figure 2 Plots of tensile strength and elongation at break of (a) F-PEK(6FBA), (b) F-PEK(BA), (c) F-PEK(HF), (d) F-PEK(DPE), (e) F-PEK(PP), and (f) Kapton as a function of irradiation dose.
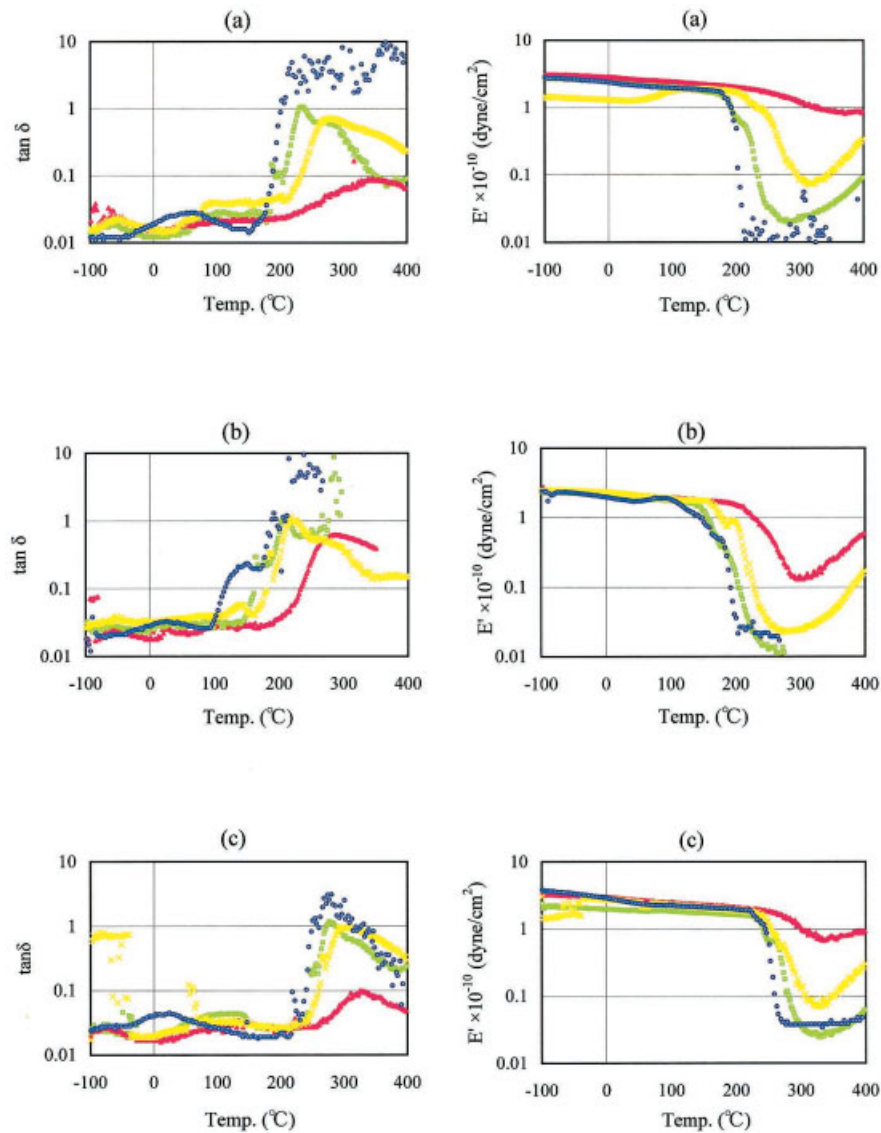
Figure 3 Plots of tan δ and dynamic modulus of (a) F-PEK(6FBA), (b) F-PEK(BA), (c) F-PEK(HF), (d) F-PEK(DPE), (e) F-PEK(PP), and (f) Kapton as a function of irradiation dose of (○) 0 MGy, (□) 29.0 MGy, (×) 51.0 MGy, and (△) 94.5 MGy.

of F-PEK(6FBA) are shown in Figure 1 as a typical example. The stress–strain curve of the unirradiated film at 25°C is characterized by necking and cold drawing, appearing like that of soft and tough plastics. On the other hand, the curve of the irradiated film shows an increase of tensile strength at yield and break, but the necking and cold-drawing process disappeared. Appearance of the yield phenomenon on that of irradiated film indicates that the irradiated film still retains a slight elasticity. Young's modulus increased significantly after irradiation. The most susceptible parameters to structural change by irradiation are tensile strength and elongation at break as previously reported.[6,23] Changes in the tensile strength and elongation at break are plotted as a function of irradiation dose in Figure 2. F-PEKs are very sensitive to irradiation. The tensile strength at break of

F-PEK(6FBA), F-PEK(BA), and F-PEK(HF) films increases up to a dose of 29.0 MGy and then decreases slightly with irradiation. An initial increase was not observed on F-PEK(PP) and F-PEK(DPE) films, and their tensile strength gradually decreased with dose. Concerning elongation at break, it is noteworthy that the elongation decreased drastically from 150–250 to 20% at a dose of 29.0 MGy after which they remained unchanged during irradiation. The tensile properties of F-PEKs were significantly degraded by irradiation and they changed from being elastic films to being strong and brittle films. Kapton film, which is very strong and tough, was also irradiated under the same conditions and the tensile properties were measured as a reference. Kapton is much more inert than F-PEKs to irradiation. Whereas the tensile strength at break of Kapton decreases continuously by irradiation, that of
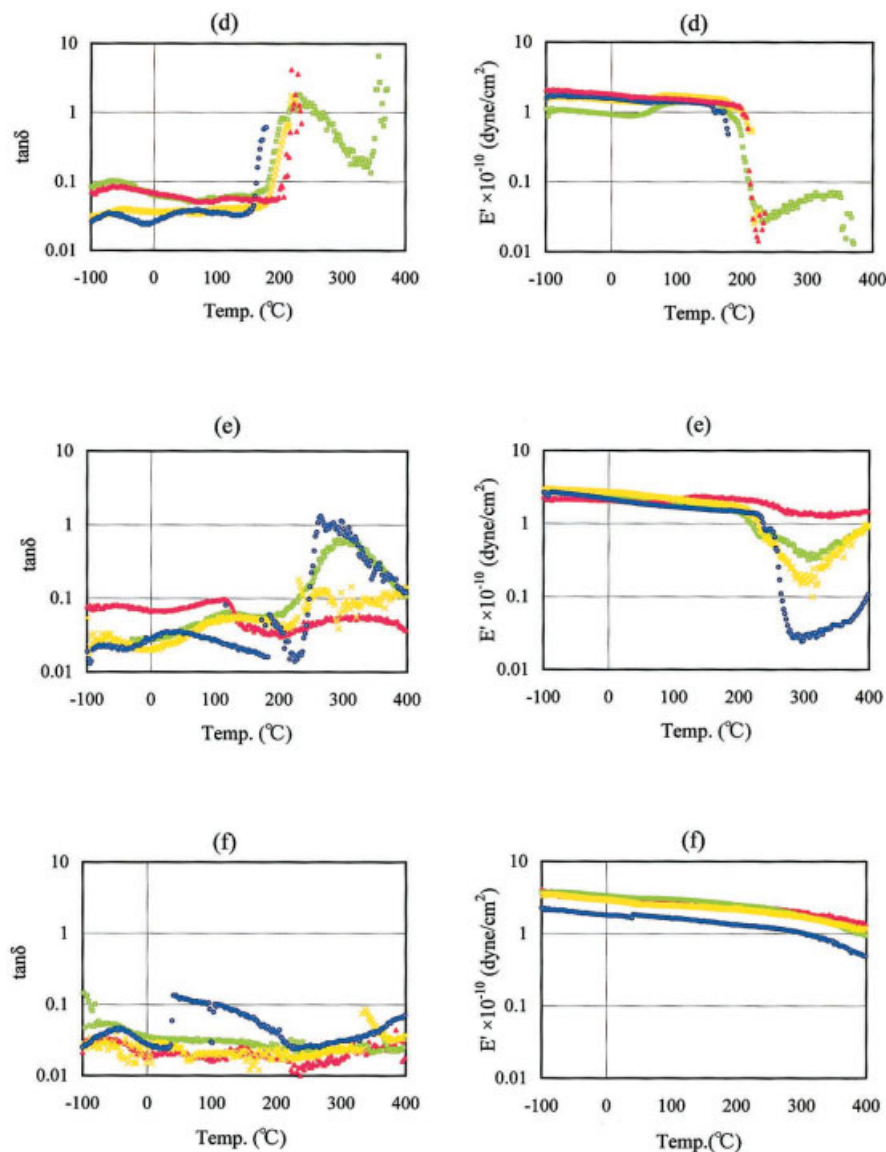
Figure 3 (*Continued from the previous page*)

F-PEKs increases with irradiation as described. This increase is an important characteristic of F-PEKs.

The dynamic viscoelasticity was measured on the irradiated films at different doses to determine the change in the relaxation behavior by irradiation. The spectra of tan δ and dynamic modulus are shown in Figure 3. The spectra of the unirradiated films are characterized by major two peaks designated as β- and α-relaxation from low to high temperature. The α-relaxation appearing over 200°C is attributable to the molecular motion reflecting the transition from glassy to elastic state because the dynamic modulus decreases significantly. This relaxation is dependent on the structure, which is in good agreement with T_g. The magnitude of tan δ of this α-relaxation is the largest among the relaxations. The β-relaxation peaks are observed at 0–100°C. This relaxation temperature and the magnitude of tan δ are not remarkably changed on the dried film. Therefore, this relaxation is not influenced by water uptake as reported.[9,15–17] This kind of relaxation has not been reported on the spectra of PEEK and noncrystalline PEEK, but the relaxation at −80°C was observed as the relaxation arising from the aryl ether group, called mechanical secondary relaxation or low-temperature mechanical relaxation.[17,35] This relaxation is often observed in rigid aromatic polymers such as poly(aryl ether), poly(aryk sulfone), and polyarylate.[36] The β-relaxation of F-PEKs appears at 100°C higher than this relaxation of PEEK but the β-relaxation of F-PEKs might be attributed to a local motion of the 1,4-phenyl moiety or 4,4'-biphenylether moiety in the polymer chain. The bulkiness of fluorine atoms substituted on 1,4-phenylene moiety results in the higher relaxation temperature.
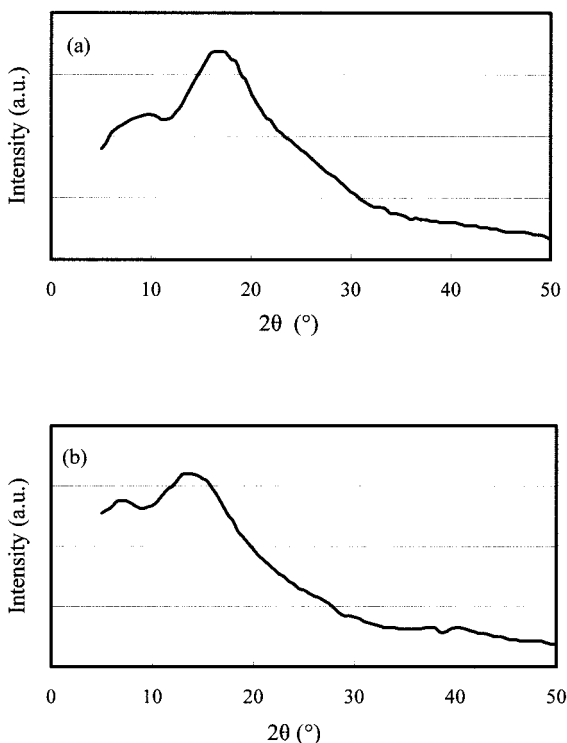
Figure 4 WAXS profiles of (a) unirradiated and (b) irradiated F-PEK(6FBA) film at a dose of 94.5 MGy.

Additionally, F-PEK(DPE) and F-PEK(PP) exhibit γ-relaxation peak at lower temperature than the β-relaxation and only F-PEK(BA) exhibits an α'-relaxation peak at 150°C. The α-relaxation shifts to higher temperature and its magnitude of tan δ decreases with dose. The peak becomes sharper at a dose of 29.0 MGy and then becomes broader with dose. The dynamic modulus of irradiated F-PEKs is almost constant up to the temperature of the α-relaxation. The decrement of the dynamic modulus becomes smaller with dose and the irradiation maintains a constant modulus to higher temperature. If the crystallization is induced by irradiation, the α-relaxation moves toward higher temperature. WAXS measurement was performed to determine the induced crystallization. The profiles of unirradiated and irradiated F-PEK(6FBA) are shown in Figure 4. The broad peak is observed in both profiles, attributed to the amorphous part, and there are no sharp diffraction peaks of the crystal. The broad peak shifts slightly toward a smaller angle of 2θ. This result indicates that crystallization is not induced by irradiation in the case of F-PEKs and they are amorphous after irradiation.

These results suggest that movement of polymer chains in the glassy state is restricted by the irradiation because of the structural change of F-PEK to a more rigid structure. This kind of phenomenon was also characterized on the irradiated PEEK film and was never observed on PS and PES.[15–17] The lowering of
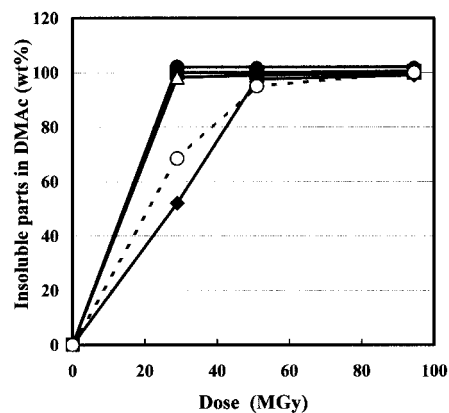

Figure 5 Plots of the insoluble part in DMAc of (a) F-PEK(6FBA) (●), (b) F-PEK(BA) (■), (c) F-PEK(HF) (△), (d) F-PEK(DPE) (◆), and (e) F-PEK(PP) (○) films as a function of irradiation dose.

the glass transition of PS and PES was accounted for by lowering of the cohesive energy density attributed to polymer chain scission. The differences of α-relaxation behavior by irradiation between PEEK and PS were attributed to the difference of structural changes of polymer chains, that is, PEEK forms bulkier structures because of the complicated crosslinking by phe-
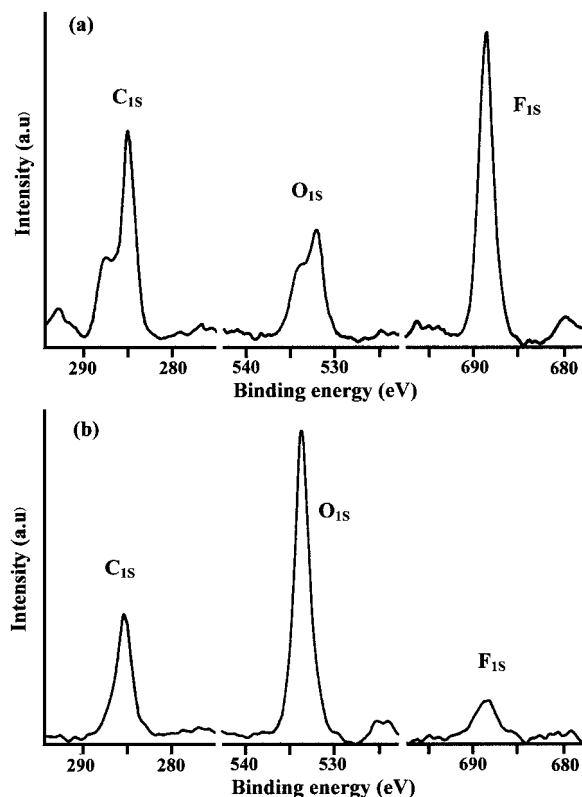

Figure 6 C_{1S}, O_{1S}, and F_{1S} photoelectron spectral profiles of (a) unirradiated and (b) irradiated F-PEK(6FBA) film at a dose of 94.5 MGy.

nyl and phenoxy radical. In the case of F-PEKs, it can be interpreted from the analogy of PEEK that the crosslinked structure should be developed by irradiation. The β-relaxation at lower temperature also shifts toward higher temperature with dose. This relaxation, which results from the local motion of the 1,4-phenylene moiety, is also restricted by the crosslinking.

The solubility test of irradiated films was carried out in DMAc to confirm the results discussed above, which are shown in Figure 5. The weight percentage of the insoluble part in DMAc increases with dose in all films. In particular, F-PEK(6FBA), F-PEK(BA), and F-PEK(HF) are completely changed to insoluble polymers at a dose of 29.0 MGy. F-PEK(DPE) and F-PEK(PP) contain insoluble parts of 50–70 wt % at a dose of 29.0 MGy and they become almost insoluble at a dose of 51.0 MGy. The outstanding solubility of F-PEKs was seriously degraded by the irradiation. These results reveal the occurrence of crosslinking reaction by irradiation and strongly support the above discussion concerning mechanical behavior.

Elemental analyses of the F-PEK(6FBA) and F-PEK(HF) films were carried out by XPS to determine the structural change by irradiation. The contents of carbon, oxygen, and fluorine elements were estimated as the corresponding peak area percentage to total peak
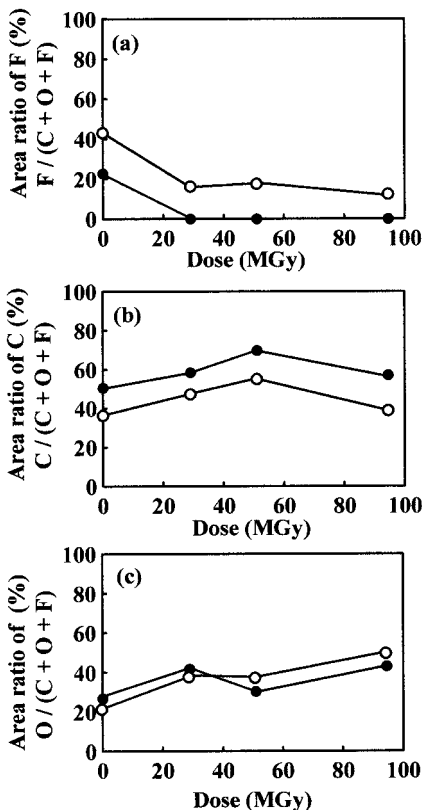

Figure 8 Absorption spectra of (a) unirradiated and irradiated F-PEK(6FBA) films at a dose of (b) 29.0 MGy, (c) 51.0 MGy, and (d) 94.5 MGy.

area. The content was calculated by the average of the data measured on the front surface and the reverse surface of the film toward the irradiation. The photoelectron spectra of the front surface of F-PEK(6FBA) film are illustrated in Figure 6. The peaks corresponding to C_{1S}, O_{1S}, and F_{1S} may be observed on both spectra. The peaks of C_{1S} and O_{1S} of unirradiated film consist of at least two peaks, which indicates the presence of at least two different types of bonding.[37–39] The largest peak at 284.7 eV in the C_{1S} spectrum corresponds to C—C bonding, whereas the peak at 287.2 eV corresponds to C—O, C—F, and C=O bonding. The largest peak at 532.0 eV in the O_{1S} spectrum corresponds to C=O, whereas the shoulder peak at 534.0 eV corresponds to C—O bonding. After irradiation of 94.5 MGy, the peak of C_{1S} is changed to a single peak at 284.7 eV and the peak of C_{1S} at 287.2 eV is significantly diminished. The peak of O_{1S} is also changed by irradiation to a single peak at 534.0 eV.

Figure 7 Plots of content of (a) fluorine, (b) carbon, and (c) oxygen atoms in F-PEK(6FBA) (○) and F-PEK(HF) (●) film as a function of irradiation dose.
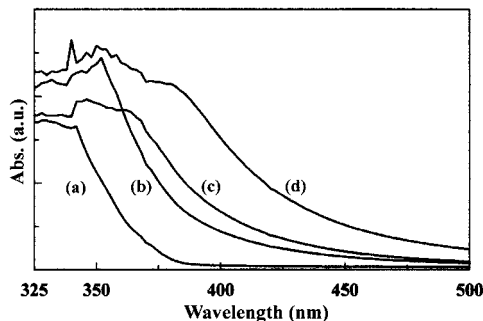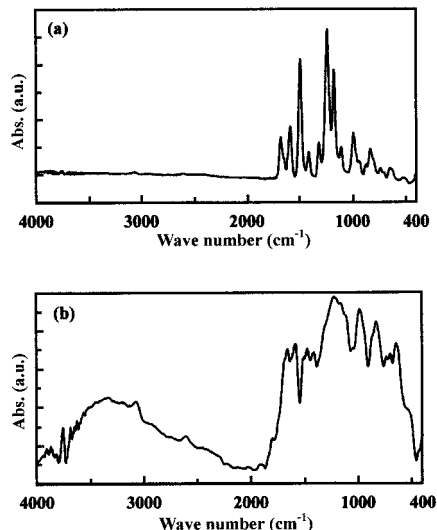

Figure 9 FTIR spectra of (a) unirradiated and (b) irradiated F-PEK(6FBA) film at a dose of 94.5 MGy.
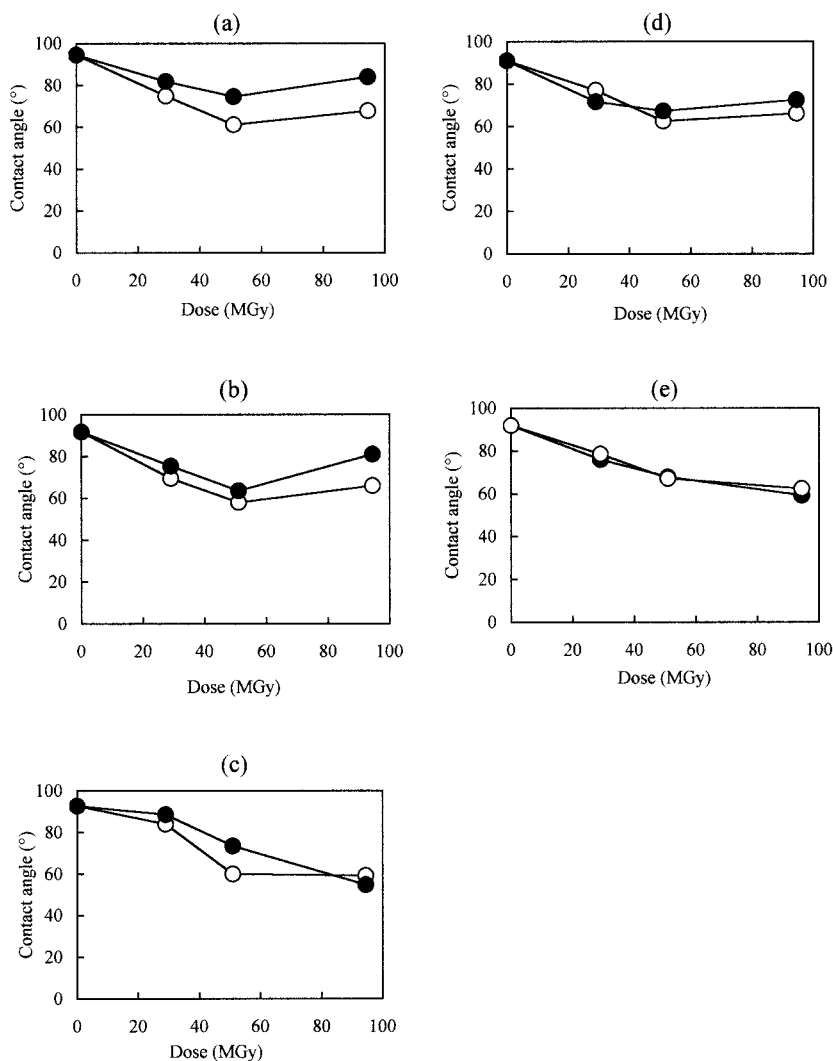
Figure 10 Plots of water contact angle of (a) F-PEK(6FBA), (b) F-PEK(BA), (c) F-PEK(HF), (d) F-PEK(DPE), and (e) F-PEK(PP) films on the front surface (○) and the reverse surface (●) as a function of irradiation dose.

These results indicate that C—F and C=O bonds are damaged by irradiation. Surprisingly, the relative intensity of the O_{1S} peak increases and that of F_{1S} peak decreases by irradiation. F-PEK(HF) becomes devoid of fluorine atoms at a dose of 29.0 MGy. The results are plotted in Figure 7 as a function of dose. The content of fluorine atom obviously decreases with dose in both films. F-PEK(6FBA) contains 12.3% of fluorine atoms after a dose of 29.0 MGy, which corresponds to the calculated fluorine content of 13.6%, assuming that fluorine atoms in the 1,1,1,3,3,3-hexafluoroisopropylidene group are retained and those in the 2,3,5,6-tetrafluoro-1,4-phenylene group are completely lost. The bond dissociation energy of C—F is 530.5 kJ mol^{-1}, which is much higher that that of C—H of 429.7 kJ mol^{-1} and C—F bond is more stable against irradiation as reported in numerous studies of radiation chemistry for aliphatic fluorine-containing polymers.[41] Fluorine atoms attached to the 1,4-phenylene group seem to be very susceptible to irradiation.

The radiation chemistry of F-PEKs has not yet been elucidated but it can be speculated that the crosslinking primarily occurs between the 2,3,5,6-tetrafluoro-1,4-phenylene groups with disappearing fluorine atoms, resulting in development of the π-electron conjugated aromatic structure. The content of oxygen atoms increases with dose and the increment is larger than the value calculated assuming the complete lack of fluorine atoms. This suggests that oxygen participates in the structural change, which might come from the atmosphere or uptake in the films despite the fact that irradiation was carried out under a slow stream of argon, or carbon atoms are lost as volatile by-products. The former reason is more appropriate because of the occurrence of the crosslinking. Absorption spectra of the films were measured to confirm the formation of π-electron conjugated aromatic structure by irradiation. The absorption spectra of F-PEK(6FBA) film are illustrated in Figure 8 as typical spectra. Absorbance was corrected by the thickness of the films. It

TABLE II
Thermal Stability of Irradiated F-PEK(6FBA)[a]

Dose (MGy)	10% weight loss (°C)	Char yield at 700°C (wt %)
0.0	465	18
29.0	514	53
51.0	538	62
94.5	504	58

[a] Thermal stability was evaluated by TGA performed at a scanning rate of 20°C min^{-1} in nitrogen atmosphere.

is very clear that the band edge of π– π^* absorption extends definitely toward the longer wavelength with dose. This indicates that the π-electron conjugated aromatic structure is developed by irradiation. The films are colored from colorless to brown by irradiation, but the irradiated films retained their transparency after irradiation.

FTIR spectra were measured to obtain information about the structural change during irradiation. All peaks were broader after irradiation and the structural change was more complicated, as shown in Figure 9. A broad peak newly appears at 2500–3500 cm^{-1} after irradiation, which can be assigned to the carboxyl and hydroxyl groups. Moreover, the peak of the carbonyl group at 1680 cm^{-1} becomes split and broader to 1760 cm^{-1}. This suggests that the carbonyl group is converted into other functional groups such as ester and carboxylic acid. The ester and carboxylic groups can be generated by oxidation and direct scission as well as rearrangements such as retro-Fries rearrangement, Cleisen rearrangement, and pinacolization reaction, for example, by radical formation as reported in the photolysis of PEEK.[41–44] If these polar functional groups are generated, the water contact angle on the film surface is reflected. The water contact angle was measured on both surfaces of the films. The F-PEK films are very hydrophobic because of the existence of fluorine atoms of which the contact angle is more than 90°. The contact angles on both surfaces decrease gradually with dose and they are about 60° at 94.5 MGy, as shown in Figure 10. The F-PEKs are changed to hydrophilic character by irradiation. The decrement up to 29.0 MGy is brought about by the disappearance of fluorine atoms as well as the formation of polar groups. However, the continuous decrease after 29.0 MGy, at which the content of fluorine atoms becomes constant, can apparently be attributed to the formation of polar groups.

The thermal stability of unirradiated and irradiated F-PEK(6FBA) was examined. The temperature of 10% weight loss and char yield at 700°C are tabulated in Table II. The temperature of 10% weight loss increases by 90°C and the char yield increases from 18 to 62%. The irradiation leads to thermally stable structure of F-PEKs as a result of crosslinking.

CONCLUSIONS

The tensile strength at break of F-PEK(6FBA), F-PEK(BA), and F-PEK(HF) increased up to a dose of 29.0 MGy and then decreased slightly with irradiation. Initial increases were not observed on F-PEK(PP) and F-PEK(DPE), and they gradually decreased with irradiation. Elongation at break decreased drastically to one tenth at a dose of 29.0 MGy after which they were unchanged by irradiation. Young's modulus of F-PEKs significantly increased by irradiation. F-PEKs became strong and brittle by irradiation. The α- and β-relaxation of viscoelastic property shifted toward higher temperature by irradiation. These tensile and viscoelastic property changes were attributed to the formation of a bulkier and more rigid structure by crosslinking. The fluorine atoms attached to the 1,4-phenylene moiety in F-PEKs were surprisingly susceptible to irradiation and were completely lost at a dose of 29.0 MGy. The π-electron conjugated aromatic structure was concurrently developed during irradiation. Further, polar functional groups such as carboxyl group and ester group were generated by chain scission and rearrangement. F-PEKs retained their good transparency and the thermal stability was significantly improved after irradiation.

References

1. (a) Cassidy, P. E. Thermally Stable Polymers: Syntheses and Properties; Marcel Dekker: New York, 1980; (b) Blumstain, A. Liquid Crystalline Order in Polymers; Academic Press: London, 1978.
2. (a) Hougham, G.; Cassidy, P. E.; Johns. K.; Davidson, T. Fluoropolymers, Vol. 1., Synthesis; Kluwer Academic Plenum Publishers: New York, 1999; (b) Hougham, G.; Cassidy, P. E.; Johns. K.; Davidson, T. Fluoropolymers, Vol. 2, Properties; Kluwer Academic Plenum Publishers: New York, 1999.
3. Kimura, K.; Tabuchi, Y.; Yamashita, Y.; Cassidy, P. E.; Fitch J. F.; Okumura, Y. Polym Adv Technol 2000, 11, 757.
4. Sasuga, T.; Hagiwara, M. Polymer 1987, 28, 1915.
5. Sasuga, T.; Kawanishi, S.; Seguchi, T.; Kohno, I. Polymer 1989, 30, 2054.
6. Sasuga, T.; Hayakawa, N.; Yoshida, K.; Hagiwara, M. Polymer 1985, 26, 1039.
7. Sasuga, T. Polymer 1988, 29, 1562.
8. Sasuga, T.; Kudoh, H. Polymer 2000, 41, 185.
9. Sasuga, T.; Hagiwara, M. Polymer 1986, 27, 821.
10. Sasuga, T.; Hagiwara, M. Polymer 1985, 26, 501.
11. Heiland, K.; Hill, D. J. T.; Hopewell, J. L.; Lewis, D. A.; O'Donnell, J. H.; Pomery, P. J. Whittaker, A. K. Adv Chem Ser 1996, 5, 637.
12. Sasuga, T.; Hayakawa, N.; Yoshida, K. Polymer 1987, 28, 236.
13. Sasuga, T.; Kudoh, H.; Seguchi, T. Polymer 1999, 40, 5095.
14. Hill, D. J. T.; Kudoh, H.; Seguchi, T. Radiat Phys Chem 1996, 48, 569.
15. Baccaredda, M.; Butta, E.; Forosini, V.; de Petris, S. J Polym Sci A-2 1967, 5, 1296.
16. Kurz, J. E.; Woodbrey, J. C.; Ohta, M. J Polym Sci A-2 1970, 8, 1169.

17. Robeson, L. M.; Farnham, A. G.; McGrath, J. E. J Appl Polym Sci 1975, 26, 373.
18. Brown, J. R.; O'Donnell, J. J Appl Polym Sci 1975, 19, 405.
19. Forsythe, J. S.; Hill, D. J. T. Prog Polym Sci 2000, 25, 101.
20. Janks, C. L.; Hamman, D. L. Radiation Effects Design Handbook, Section 3; NASA-CR: 1971; p 1787.
21. Mckannan, E. C.; Gause, R. L. J Spacecraft 1965, 2, 558.
22. Long, A. A. T.; Long, E. R., Jr. IEEE Trans Nucl Sci 1984, NS-31, 1293.
23. Sasuga, T.; Hagiwara, M. Polymer 1985, 26, 1039.
24. Hill, D. J. T.; Hopewell, J. L. Radiat Phys Chem 1996, 48, 533.
25. Hill, D. J. T.; Rasoul, F. A.; Forsynthe, J. S.; O'Donnell, J. H.; George, G. A.; Pomery, P. J., Young, R. P.; Connell, J. W. J Appl Polym Sci 1995, 58, 1857.
26. Rasoul, F. A.; Hill, D. J. T.; Forsythe, J. S.; O'Donnell, J. H.; George, G. A.; Pomery. P. J.; Young, P. R.; Connell, J. W. J Appl Polym Sci 1995, 58, 1857.
27. Hoyl, C. E.; Anzures, E. T. J Appl Polym Sci 1991, 43, 1.
28. Hoyl, C. E.; Anzures, E. T. J Polym Sci Part A: Polym Chem 1992, 30, 1237.
29. Sun, J.; Zhong, X. Makromol Chem Macromol Symp 1999, 143, 149.
30. Hill, D. J. T.; Hopewell J. L. Polym Degrad Stab 1994, 45, 293.
31. Jin, J.-I.; Choi, E.-J.; Jo, B.-W. Macromolecules 1987, 20, 934.
32. Choi, E.-J.; Hill, D. J. T.; Kim, Y.-K.; O'Donnell, J. H.; Pomery, P. J. Polymer 1997, 38, 3669.
33. Hill, D. J. T.; Choi, B.-K.; Ahn, H. K.; Choi, E.-J. Polym Int 1999, 48, 956.
34. Choi, E.-J.; Hill, D. J. T.; Kim, K.-Y., O'Donnell, J. H.; Pomery, P. J. Polym Adv Technol 1998, 9, 52.
35. David, L.; Etienne, S. Macromolecules 1992, 25, 4302.
36. Sasuga, T.; Hayakawa, N.; Yoshida, K. J Polym Sci Polym Phys Ed 1984, 22, 529.
37. Stuart, B. Polymer Analysis; Wiley: Chichester, UK, 2002; pp 178–182.
38. Briggs, D. Application of XPS in Polymer Technology in Practical Surface Analysis; Wiley: Chichester, UK, 1990; pp 437–484.
39. Beamson, G.; Briggs, D. High Energy XPS of Organic Polymers: The Scienta ESCA 300 Database; Wiley: Chichester, UK, 1992.
40. Logothetis, A. L. Fluoroelastomers. Organofluorine Chemistry: Principles and Commercial Applications; Plenum Press: New York, 1994; pp 373–396.
41. Giancaterina, S.; Rossi, A.; Rivaton, A.; Gardette, J. L. Polym Degrad Stab 2000, 68, 133.
42. Kharasch, M. S.; Stampa, G.; Nudenberg, W. Science 1952, 116, 309.
43. Hageman, H. J.; Louwerse, H. L.; Mijs, W. T. Tetrahedron 1970, 26, 2045.
44. Rivaton, A.; Gardette, J. L. Polym Degrad Stab 1999, 66, 385.