Structural change in poly(hexafluoro-1,3-butadiene) during heat treatment

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The structural change in poly(hexafluoro-1,3-butadiene) that takes place during heat treatment was investigated by measuring its i.r. spectra. The polymer obtained from hexafluoro-1,3-butadiene (HFBD), produced by t-C_4H_9OCs initiation in toluene, showed excellent thermal properties, such as a high thermal decomposition temperature and a low thermal expansion coefficient. The thermal properties of poly(HFBD) were found to be similar to those of conventional thermosetting polymers, since the thermal expansion coefficient of poly(HFBD) decreased after the heating process. The absorption at $\sim 2970\,cm^{-1}$, which was assigned to traces of initiator (t-C_4H_9–), disappeared after heating at 200 or 400°C for 10 h. The absorption at $\sim 1710\,cm^{-1}$, which was assigned to the –CF=CF– bond in the main chain, and the peak at $1840\,cm^{-1}$, both increased after heating at 400°C for 10 h. It is suggested that the chemical structure of the polymer was changed during the heating process. Furthermore, the radical species which was produced by cleavage of the bonds with heating at high temperatures might react with the –CF=CF– bonds in the polymer chain to yield crosslinked species.

(Keywords: poly(hexafluoro-1,3-butadiene); heat treatment; structural changes)

INTRODUCTION

Fluorine-containing polymers are of great industrial interest because of their many excellent physical and chemical properties. Poly(tetrafluoroethylene) (PTFE), which is a typical fluoropolymer, is widely used as an insulator and lubricant. Perfluorocarbon polymers, however, show poor dimensional stability at high temperatures since they are thermoplastic in nature. A thermoplastic polymer has, in general, a low glass transition temperature and a high thermal expansion coefficient[1]. In order to improve such properties of these perfluorocarbon polymers, it is necessary to develop a polymer possessing functional groups which are able to produce crosslinks between the polymer chains.

The polymer obtained from hexafluoro-1,3-butadiene (HFBD) should have both –C=C– functional groups in the main chain or side groups which could act as crosslinking agents. Crosslinked poly(HFBD) might be expected to have good thermal properties, such as a high thermal decomposition temperature and a low thermal expansion coefficient, since the chemical structure of the polymer is similar to that of crosslinked PTFE. HFBD, however, hardly polymerized at all under radical or normal anionic conditions[2–4]. As has been previously reported, the anionic polymerization of HFBD, initiated with cesium derivatives, such as cesium fluoride[5], or cesium t-butoxide and rubidium analogs, produces high yields of the polymer, with toluene or tetrahydrofuran (THF) as solvents[6]. The structure of the poly(HFBD) obtained by anionic polymerization was investigated by measuring the solid-state ^{13}C n.m.r. spectra, the X-ray photoelectron spectra (x.p.s.) and the Raman spectra[7]. These spectral data generally agreed with those obtained for poly(hexafluoro-2-butyne) (poly(HFBY)) which was produced under similar polymerization conditions to those used for HFBD[8].

The poly(HFBD) obtained by CsF initiation showed excellent thermal stability, as demonstrated by thermogravimetric analysis. Poly(HFBD) behaved as a thermosetting polymer since its thermal expansion coefficient decreased during the heating process[9]. This present paper is concerned with a study of the change in chemical structure of the poly(HFBD) which takes place during the heating process.

EXPERIMENTAL

Preparation of poly(HFBD)

The experiments involving anionic polymerization were carried out under a purified nitrogen atmosphere in order to exclude oxygen and atmospheric moisture.

Commercially available hexafluoro-1,3-butadiene (HFBD) (PCR) was purified by passing it (in the vapour phase) through columns of calcium sulfate and molecular sieves and collecting at dry-ice temperatures under reduced pressure. Commercially available cesium fluoride

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Table 1 Anionic polymerization of HFBD using initiators containing the cesium cation[a]

Initiator[b]	Solvent[c]	Time (h)	Yield (%)
CsF	Toluene	168	54.4
	THF	168	78.8
t-C_4H_9OCs	Toluene	3	83.9
	THF	3	92.8

[a] HFBD, 25.5 mmol; polymerization temperature = 60°C
[b] Initiator, 0.5 mmol
[c] Solvent, 10 ml

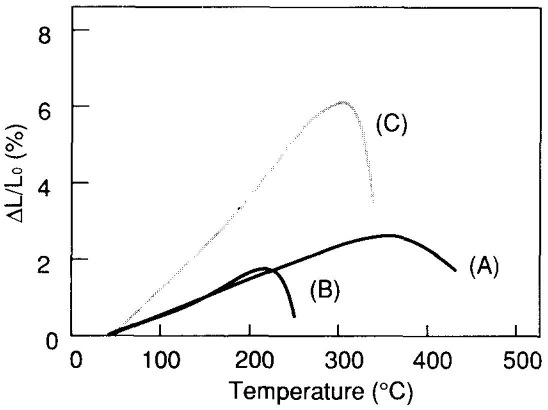

Figure 1 Thermal expansion behaviour of poly(HFBD) obtained by using t-C_4H_9OCs in toluene (A) and THF (B); the behaviour of PTFE (C) is also shown for comparison

(Aldrich) was dried under reduced pressure at high temperatures. Cesium t-butoxide was synthesized from cesium metal (Aldrich) and 2-methyl-2-propanol (Aldrich). Toluene and THF were purified by refluxing with sodium and potassium benzophenone ketyl and then distilled before use.

A glass ampoule was charged with initiator (0.5 mmol), HFBD (25.2 mmol) and solvent (10 ml) under a nitrogen atmosphere. The ampoule was then sealed and kept at a constant temperature. After an appropriate length of time the polymer was isolated by precipitation with methanol and was then dried to constant weight.

The polymerization conditions and the respective yields of poly(HFBD) are summarized in *Table 1*. The structure of the poly(HFBD) obtained in this work was determined by the same method used for poly(HFBY)[7], the study of which has been reported elsewhere[8].

Measurements

Infra-red spectra were obtained by the use of a Hitachi I-5040 Fourier transform infra-red spectrometer. Thermogravimetric analysis was carried out by using a Shinku-Riko TGD-7000RH instrument, at a heating rate of 5°C min^{-1} under a nitrogen atmosphere, with a sample of ~10 mg. The thermal expansion behaviour was investigated by the use of a Shinku-Riko thermomechanical analyser (model TM-3000) at a heating rate of 2°C min^{-1}; the sample thickness was 1.5 mm and the sample size was 7×7 mm. The thermal expansion measurements were carried out by using the compression method, with a load of 10 g cm^{-2}. Solid-state pulse saturation ^{13}C n.m.r. spectra were recorded at 67.8 MHz on a JEOL JNM-GX400 n.m.r. spectrometer at 25°C. The chemical shifts (in ppm) of each carbon were derived by using the peak of hexamethylbenzene as a reference.

RESULTS AND DISCUSSION

Thermal expansion coefficient of poly(HFBD)

The thermal expansion behaviour of the poly(HFBD) obtained by using t-C_4H_9OCs in toluene (A) and THF (B) is shown in *Figure 1*; results obtained for PTFE (C) are also shown for comparison. The softening point is defined here as the temperature where the thermal expansion coefficient becomes zero, i.e. the equilibrium point of the thermal expansion and the softening compression. The softening point of the poly(HFBD) produced in toluene using t-C_4H_9OCs is 339°C, which is higher than that of the corresponding polymer produced in THF. It is also found that the softening point of the polymer obtained in toluene is higher than that of PTFE. The thermal expansion coefficients of poly(HFBD) are much lower than that of PTFE, being similar to those of poly(HFBD) produced using CsF[9]. The samples of poly(HFBY) required for measuring the thermal expansion behaviour could not be obtained by press moulding.

The effect of heat treatment on the thermal expansion behaviour was then investigated. The results obtained for the temperature dependency of the thermal expansion coefficient of poly(HFBD) after heat treatment are shown in *Figure 2*. The softening point measured after heating the poly(HFBD) at 400°C for 10 h is 417°C, which is 78°C higher than that obtained for a sample which had not been treated. It is also ~100°C higher than that of PTFE. It is found that the differential thermal dimensional change coefficient of the same sample is about one third of that of PTFE. These coefficients scarcely change as a function of temperature. This expansion behaviour is similar to that of a crosslinked resin and different to the case of PTFE, as shown in *Figure 2*. The softening points and thermal expansion coefficients are summarized in *Table 2*.

The densities of the polymers after heat treatment are also listed in *Table 2*; an increase in density is observed after heating. Furthermore, a pronounced increase in density occurs at 400°C. It is considered that the observed improvement in thermal dimensional change properties with heating is due to enhancement in intermolecular interactions, caused by reduction in the free volume of poly(HFBD).

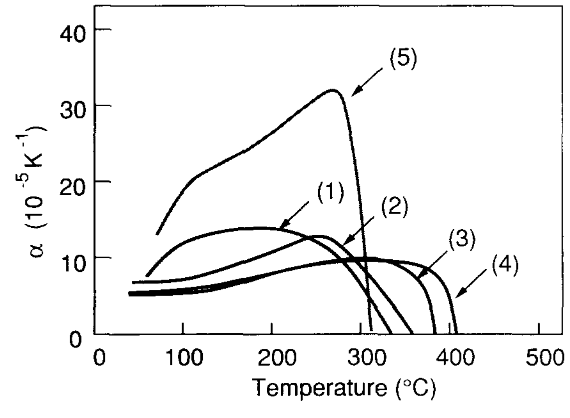

Figure 2 Dependence of thermal expansion coefficient (α) of poly(HFBD), produced by using CsF in toluene at 60°C for 168 h, on heat treatment: (1) no treatment; (2) 200°C/2 h; (3) 400°C/2 h; (4) 400°C/10 h (see *Table 2*). The behaviour of PTFE (5) is also shown for comparison

Table 2 Thermal expansion properties and densities of the poly(HFBD) produced by using CsF in toluene (see *Table 1*)

Run	Heating condition	Softening point, T_s (°C)	Thermal expansion coefficient, α (10^{-5} K^{-1})	Density, ρ (g cm^{-1})
1	None	339	12.2	2.11
2	200°C/2 h	360	8.1	2.10
3	400°C/2 h	392	6.9	2.16
4	400°C/10 h	417	7.0	2.17
PTFE		310	20.5	2.28

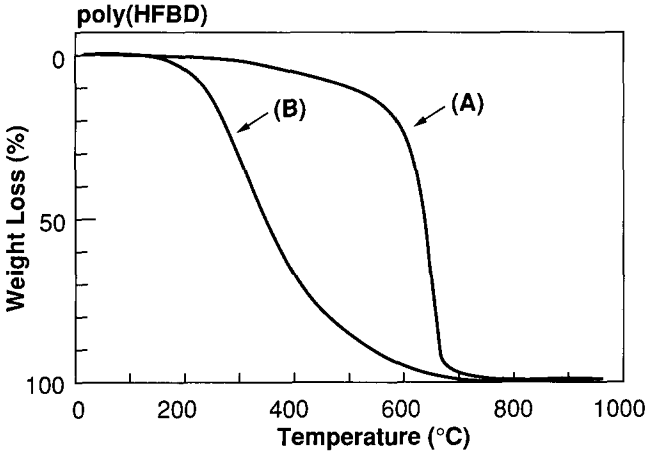

Figure 3 T.g.a. curves of poly(HFBD), obtained with t-C_4H_9OCs at 60°C for 3 h, in toluene (A) and THF (B)

Structural changes in poly(HFBD) and poly(HFBY) during heat treatment

As has been described before[9], poly(HFBD) is a thermosetting polymer. In order to clarify the thermosetting mechanism, the thermal characteristics of poly(HFBD) and poly(HFBY) were analysed by thermogravimetric analysis (t.g.a.) and differential scanning calorimetry (d.s.c.). The t.g.a. results for poly(HFBD) obtained by using t-C_4H_9OCs in toluene (A) and THF (B) are shown in *Figure 3*, a brief report of which has appeared in a previous paper[5]. The poly(HFBD) obtained in toluene has a high thermal stability, with its decomposition beginning at 360°C. In contrast, the poly(HFBD) obtained with the same initiator in THF begins to decompose at 160°C. Therefore, the decomposition temperature is influenced by the solvent used in the polymerization reaction. Virtually no effects of the other polymerization conditions, such as the nature of the initiator, the polymerization temperature or the polymerization time, are observed[9]. The observed difference appears to originate from the molecular-weight difference between these two samples. A detailed study of the thermal decomposition behaviour is discussed in detail elsewhere[10]. *Figure 4* shows the t.g.a. results for poly(HFBY) obtained by using t-C_4H_9OCs in toluene (A) and THF (B). Poly(HFBY) has a much higher thermal stability than poly(HFBD); in this case the polymer begins to decompose at 450°C, with the decomposition temperature not being influenced by the polymerization solvent.

The d.s.c. curves for poly(HFBD), obtained by using t-C_4H_9OCs in toluene (A) and in THF (B), plus the corresponding curves of poly(HFBY) obtained with the same initiator in toluene (C) and in THF (D), are shown in *Figure 5*. No obvious exothermic or endothermic peaks are observed in the curves of poly(HFBD) produced in toluene (A), nor in either of the poly(HFBY) systems (C, D). The curve obtained for poly(HFBD) when using THF as a solvent (B) clearly shows an exothermic peak at 200°C, which may be assigned to the decomposition reaction of the polymer, since its value corresponds to the thermal decomposition temperature.

In order to clarify the structural change that takes place during the heating process, changes in the i.r. spectra of poly(HFBD) during heat treatment were examined. Since the i.r. spectrum of poly(HFBD) has a very strong C–F stretching absorption, spectra were measured using thick samples (thickness = 0.1 mm), produced by press moulding. *Figure 6* shows the i.r. spectra of the

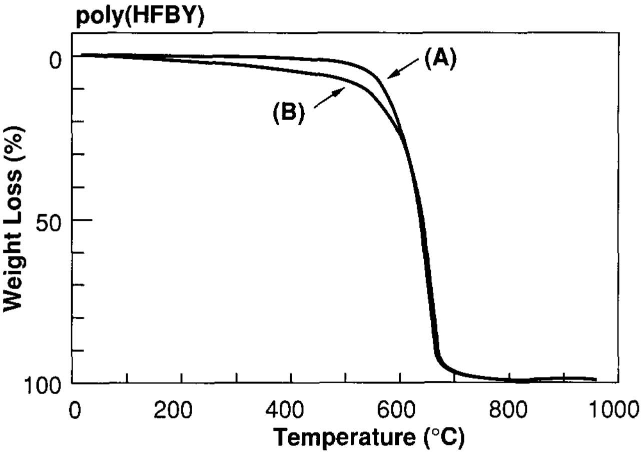

Figure 4 T.g.a. curves of poly(HFBY), obtained with t-C_4H_9OCs at 60°C for 3 h, in toluene (A) and THF (B)

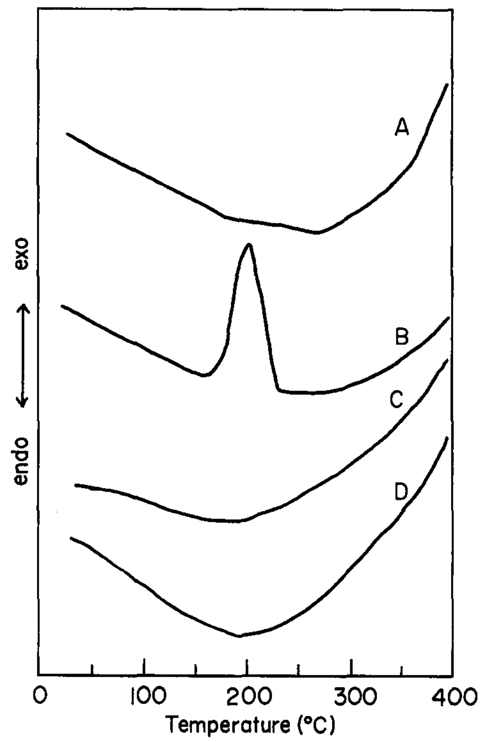

Figure 5 D.s.c. curves of poly(HFBD), obtained with t-C_4H_9OCs at 60°C for 3 h, in toluene (A) and THF (B), and poly(HFBY) obtained under the same conditions, in toluene (C) and THF (D)

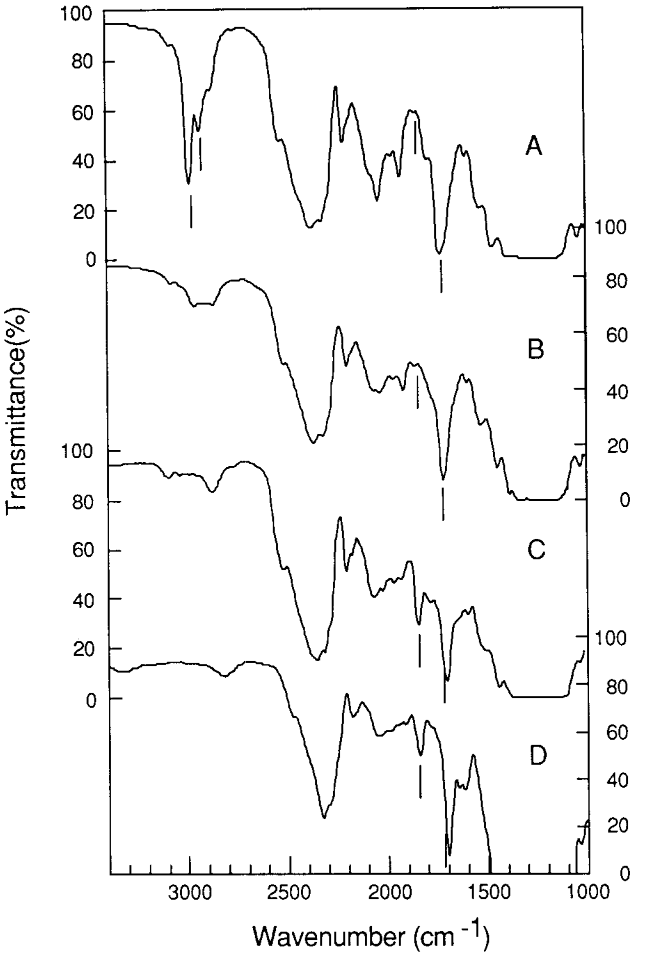

Figure 6 I.r. spectra of poly(HFBD), obtained with t-C_4H_9OCs at 60°C for 3 h in toluene, after heat treatment: (A) no treatment; (B) 200°C for 2 h; (C) 400°C for 2 h; (D) 400°C for 10 h

poly(HFBD) as obtained in toluene (A), plus the same sample which had been heated at 200°C for 2 h (B), 400°C for 2 h (C), and 400°C for 10 h (D). The spectrum (A) shows a small peak at $\sim 2970\,cm^{-1}$, which is assigned to the t-C_4H_9– group of the residual initiator bound at the end of the polymer chain. The absorption at $\sim 2400\,cm^{-1}$ is considered to be the overtone of the C–F stretching band, while the absorption at $\sim 1710\,cm^{-1}$ can be assigned to the –CF=CF– bond of the 1,4-addition segment[2]. The absorptions assigned to the t-C_4H_9– group have disappeared in spectra (B), (C), and (D). The absorption at $\sim 1710\,cm^{-1}$ is reduced, and a peak at $1840\,cm^{-1}$ has appeared in the spectra (C and D) of the samples treated at 400°C. It is likely that the absorption at $1840\,cm^{-1}$ can be assigned to a structure containing crosslinking between the main chains, produced by the heat treatment at 400°C. *Figure 7* shows the i.r. spectra of poly(HFBY) obtained with toluene as solvent (A) and the same sample which had been heated at 400°C for 10 h (B). In the case of poly(HFBY), the absorption corresponding to residual initiator has disappeared, and an absorption at $\sim 1840\,cm^{-1}$ has appeared in spectrum (B). This latter absorption may be assigned, as before, to a structure with crosslinking between the main chains, brought about by the heat treatment.

Figure 8 shows the solid-state ^{13}C n.m.r. spectra of the poly(HFBD) obtained in toluene (A) and the same sample after heat treatment at 400°C for 10 h (B), as measured by the pulse saturation method. In both spectra, the peaks at 120 and 133 ppm are assigned to the $-CF_3$ and $>C=$ groups, respectively. *Figure 9* shows the solid-state ^{13}C n.m.r. spectra of poly(HFBY) obtained in toluene (A) and the same sample after heating at 400°C for 10 h (B). These two spectra coincide completely with each other. It is difficult to identify the crosslinked structure from the n.m.r. spectra because the number of crosslinks between the polymer chains might be very small.

The i.r. spectroscopy results demonstrate clear evidence of structural changes in poly(HFBD) after heat treatment, although the ^{13}C n.m.r. results give little information on the changes, probably because the structural change is too 'small' to be detected by this method.

These i.r. and ^{13}C n.m.r. spectral changes appear to indicate the following structural changes. First, the t-C_4H_9– group attached to the end of the polymer chain is cleaved at high temperatures to produce the

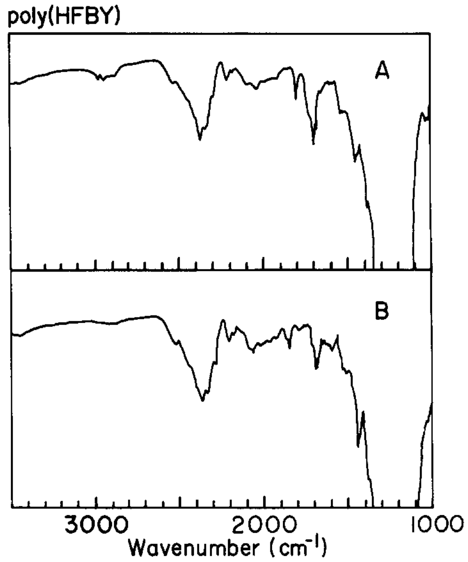

Figure 7 I.r. spectra of poly(HFBY), obtained with t-C_4H_9OCs at 60°C for 3 h in toluene, after heat treatment: (A) no treatment; (B) 400°C for 10 h

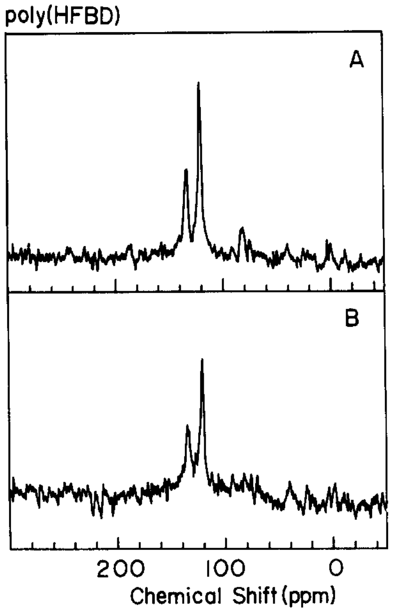

Figure 8 Solid-state pulse saturation ^{13}C n.m.r. spectra of poly(HFBD), obtained by t-C_4H_9OCs in toluene, after heat treatment: (A) no treatment; (B) 400°C for 10 h

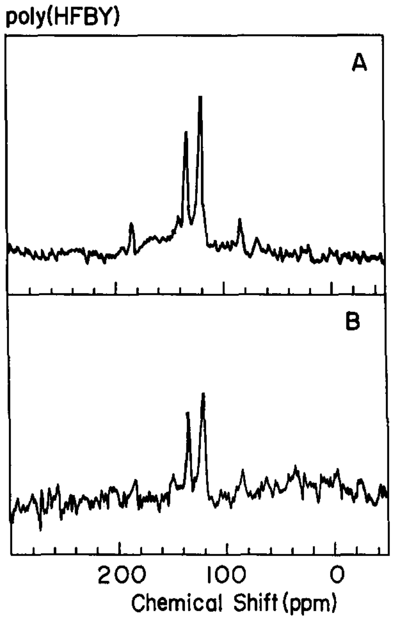

Figure 9 Solid-state pulse saturation ^{13}C n.m.r. spectra of poly(HFBY), obtained by t-C_4H_9OCs in toluene, after heat treatment: (A) no treatment; (B) 400°C for 10 h

corresponding radical. Secondly, the $-CF{=}CF-$ double bonds in the polymer chains are then attacked by this radical, thus producing crosslinks between the main chains.

CONCLUSIONS

Poly(HFBD), produced by using t-C_4H_9OCs as initiator in toluene, showed excellent thermal properties, such as thermal decomposition temperature and thermal expansion behaviour, when compared to the same polymer produced in THF. Poly(HFBD) produced with initiators containing cesium showed thermosetting behaviour. The structural changes that take place in both poly(HFBD) and poly(HFBY) during heat treatment were investigated by i.r. spectroscopy. From these results, it may be concluded that the chemical structure of both polymers changed during the heating process. The radical species which were produced by cleavage of the bonds with heating at high temperatures could react with the $-CF{=}CF-$ bonds in the main chains to yield crosslinked species.

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