Chemistry of Radiation Crosslinking of Branched Fluorocarbon Resins

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Synopsis

A number of commercial and experimental fluoropolymers were subjected to ionizing radiation at elevated temperatures and the changes in melt viscosity were measured as an indication of the degree of crosslinking or degradation which occurred.   Polytetrafluoroethylene, polychlorotrifluoroethylene, polyhexafluoropropylene, and a copolymer of hexafluoropropylene with perfluoroheptene-1 decrease in melt viscosity when irradiated at 200–250°C., while copolymers of tetrafluoroethylene with hexafluoropropylene, octafluorobutylene, or perfluoroheptene-1 increase in melt viscosity, indicating crosslinking.   The results suggest that the reaction of species of the type $\sim\!\!\!\sim(\sim\!\!\!\sim CF_2 \!\!\;)_2 CX\!\!-\!\!(CF_2)_n \cdot$ (where X is F or CF_3) with $\sim\!\!\!\sim CF_2\!\!-\!\!CF_2 \cdot$ is the important one leading to crosslinking.

INTRODUCTION

The effects of ionizing radiation on polytetrafluoroethylene have been extensively studied for several years.   Recently, the discovery was made that a copolymer of tetrafluoroethylene and hexafluoropropylene crosslinks when subjected to high energy radiation at temperatures above the glass I transition of the resin.[1]   This paper reports radiation studies carried out on a number of branched fluorocarbon resins at several temperatures and in various atmospheres in an effort to gain an understanding of the nature of this crosslinking reaction.

EXPERIMENTAL

Irradiation Equipment and Dose

All electron irradiations were carried out with the use of 2 M.e.v. electrons from a 3 M.e.v. Van de Graaff accelerator.   The samples were passed under a 250 μamp. beam at a rate such that they were exposed to a beam energy of 11 w.-sec./cm.^{2}/pass and received a dose of 1.5 Mrad/pass.   Doses less than 1.5 Mrad/pass were obtained by reducing the beam current proportionately.

The samples to be irradiated, compression-molded sheets 10–120 mils thick, were placed in an oven reactor which was maintained at the de-

sired temperature.   Nitrogen, preheated to the reactor temperature, was continuously fed into the oven, thereby minimizing possible effects of oxidation.   The top of the oven was aluminum foil (1 mil thick) covered with Fiberglas insulation ($^1/_2$ in. thick).   The test specimens were irradiated through the oven cover and insulation after a 15-min. warm-up period.   A control sample was given a similar thermal treatment as the specimen exposed to radiation, except that a lead shield was placed over the sample to prevent exposure to the radiation source.

Preparation of Polymers

The polymers and copolymers irradiated in this study were either commercial materials or were prepared by procedures described in the published literature.   These materials consisted of the following: polytetrafluoroethylene as Teflon TFE-fluorocarbon resin (E. I. du Pont de Nemours and Co.);   tetrafluoroethylene–hexafluoropropylene   copolymer   as   Teflon FEP-fluorocarbon resin (E. I. du Pont de Nemours and Co.); polyhexafluoropropylene and a copolymer of hexafluoropropylene and perfluoroheptene-1 synthesized by procedures described in a patent by Eleuterio;[2] copolymers of perfluoroheptene and perfluoroisobutylene with tetrafluoroethylene as described in a patent by Bro;[3] and Kel-F polychlorotrifluoroethylene resin (Minnesota Mining and Manufacturing Company).

DISCUSSION

Recent work by Bowers and Lovejoy[1] has shown that Teflon 100 FEP-fluorocarbon resin increases in melt viscosity when irradiated in a nitrogen atmosphere at temperatures above the glass I transition (internal friction).   The glass I transition in polycrystalline high polymers has been attributed to the onset of molecular motion resulting from the relaxation of large chain segments, 10 to 20 carbon atoms in length, in the amorphous regions of the material.[4]   As the temperature is raised, chain mobility increases to the melting temperature where movement is restricted only by the viscosity of the melt.   The glass I transition temperature of tetrafluoroethylene copolymers decreases with increasing comonomer content, decreasing, for example, from 127°C. in the homopolymer to 80°C. for a copolymer containing 14% hexafluoropropylene when measured at frequencies of 2 cycles/sec.

The effect of temperature of irradiation at constant dose rate is shown in Figure 1, in which the apparent melt viscosity of tetrafluoroethylene/hexafluoropropylene copolymer containing 14% hexafluoropropylene is plotted against the temperature of irradiation.   Of significance is the observation that a decrease in melt viscosity occurs when irradiation is conducted below 80°C.   Above this temperature (the glass I transition) the viscosity increases with increasing temperature to a maximum at 300–320°C., above which lower melt viscosities are again observed.   At temperatures above 320°C., thermal degradation becomes a factor.   The
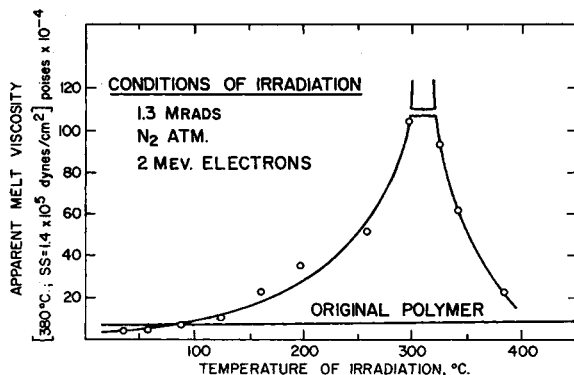
Fig. 1. Effect of temperature of irradiation on apparent melt viscosity of FEP resin.

change in physical and mechanical properties indicates clearly that chemical crosslinking has occurred during this treatment.

The observation that polytetrafluoroethylene shows molecular degradation during a similar treatment suggested that the mechanism of crosslinking must somehow involve the branched chain structure as well as the increased mobility obtainable in the amorphous regions of the copolymer above the glass I transition. To test the plausibility of this generalization, a series of fluorocarbon polymers was irradiated under similar conditions. The results are presented in Table I. The polymers can be clearly separated into two groups. The three homopolymers, polytetrafluoroethylene, polychlorotrifluoroethylene, and polyhexafluoropropylene, as well as the copolymer of hexafluoropropylene and perfluoroheptene-1 show overall molecular degradation when irradiated at elevated temperatures in inert atmospheres (Resins 1–4). The second group (5–7) consisting of copolymers of tetrafluoroethylene and other fluorinated olefins showed increases in melt viscosity and, hence, crosslinking when irradiated under similar conditions. The experiments were carried out at temperatures well above the glass I amorphous transitions of the resins involved so as to provide sufficient chain mobility to remove this variable from our comparisons. The glass I amorphous transitions for the three homopolymers and the fluorinated ethylene–propylene copolymer are known.[4-6] While this transition has not been determined for all of the various copolymers tested, experience has shown that the glass I transition of tetrafluoroethylene copolymers lies below that of the homopolymer and therefore below the irradiation temperatures used.

In the cases of polytetrafluoroethylene (sample 1) and polychlorotrifluoroethylene (sample 2), the irradiation results in net degradation as has previously been observed at ambient temperatures. The degradation observed on irradiation of polyhexafluoropropylene (sample 3) and the copolymer of hexafluoropropylene with perfluoroheptene-1 (sample 4) shows conclusively that the relationship between crosslinking and branching is not a direct one. Net crosslinking is observed only when a branched

TABLE I
Melt Viscosity of Fluorine-Containing Polymers
Irradiated at Elevated Temperatures in Nitrogen

No.	Resin structure	Radiation temp., °C.	Radiation dose, Mrads	Melt viscosity, poises $\times 10^{-4}$
1	$-(CF_2-CF_2)_n$	RT	0 (control)	No flow
		250	0 (lead shielded)	No flow
		RT	10	508
		350	5	530
2	$-(CFCl-CF_2)_n$	RT	0 (control)	102 (270°C.)
		250	0 (shielded control)	114 (270°C.)
		250	1	72 (270°C.)
		250	3	7 (270°C.)
3	$\left(\begin{array}{c} CF_3 \\ \| \\ -C-CF_2- \\ \| \\ F \end{array}\right)_n$	RT	0 (control)	0.39 (280°C.)
		200	0 (shielded control)	0.40 (280°C.)
		200	1	0.24 (280°C.)
		200	3	0.16 (280°C.)
4[b]	$\left[\left(\begin{array}{c} CF_3 \\ \| \\ -C-CF_2- \\ \| \\ F \end{array}\right)_x \begin{array}{c} C_5F_{11} \\ \| \\ C---CF_2- \\ \| \\ F \end{array}\right]_n$	RT	0 (control)	Tough sample at RT
		200	0 (shielded control)	"
		140	5	Friable and weak at RT
		200	5	"
5[c]	$\left[\begin{array}{c} CF_3 \\ \| \\ -C-CF_2-(CF_2-CF_2-)_x- \\ \| \\ F \end{array}\right]_n$	RT	0 (control)	6
		250	0 (shielded control)	14
		250	1	68
		250	3	93
6[d]	$\left[\begin{array}{c} CF_3 \\ \| \\ -C-CF_2-(CF_2-CF_2-)_x- \\ \| \\ CF_3 \end{array}\right]_n$	RT	0 (control)	101
		250	0 (shielded control)	193
		250	5	286
7[e]	$\left[\begin{array}{c} C_5F_{11} \\ \| \\ -C-CF_2-(CF_2-CF_2-)_x- \\ \| \\ F \end{array}\right]_n$	RT	0 (control)	13
		240	0 (shielded control)	25
		240	1	66
		240	10	106
8[f]	$\left[\begin{array}{c} CF_3 \\ \| \\ -C-CF_2-(CF_2-CF_2-)_x- \\ \| \\ F \end{array}\right]_n$	RT	0 (control)	7
		250	1 (in 1 pass)	69
		250	1 (in 10 passes)	151
9[g]	As above	RT	0 (control)	7
		250	1 (in 10 passes)	4.3

TABLE II
Effect of Comonomer Ratio on Crosslinking Behavior
of Hexafluoropropylene/Tetrafluoroethylene Resins as a
Function of Hexafluoropropylene (N_2 Atmosphere, 250°C.)

Hexafluoro-propylene content, wt.-%	Radiation dose, Mrads	Melt viscosity (380°C.), poises $\times$ 10^{-4a}	Increase in viscosity
4.7	0	28	
	1	96	3.5-fold
	10	172	6.2-fold
8.7	0	39	
	1	392	10-fold
	10	NF^b	—
15.8	0	7.2	
	1	63	9-fold
	10	NF^b	—
21.0	0	1.5	
	1	20	13.5-fold
	10	111	74-fold
29.8	0	0.05^c	
	1	4.05^c	81-fold
	10	$NF^{b,a}$	—

^{a} At shear stress of 1.4×10^5 dynes/cm.^{2}.
^{b} No flow at shear stress used.
^{c} Viscosity at 230°C.

comonomer is copolymerized with the highly reactive tetrafluoroethylene (samples 4–6). The ratios of the branched comonomer to tetrafluoroethylene in the resultant copolymer also influence radiation resistance. Qualitative evidence of this is found in Table II, where copolymers containing 5–30 wt.-% of hexafluoropropylene have been irradiated at varying dosages and the melt viscosities of the resulting products determined.

The experiments described indicate that the irradiation of branched copolymers of tetrafluoroethylene produces combinations of reactive species that are not found in the irradiated homopolymers or the very highly branched hexafluoropropylene/perfluoroheptene copolymer. Bombardment with high energy radiation such as electrons from an accelerator leads to a complex series of primary reactions involving excitation and ionization of the target material. Secondary reactions involve energy transformations and chemical rearrangement of the reactive species. In

^{a} Flow determined in a melt rheometer at a shear stress of 1.4×10^6 dynes/cm.^{2} and at 380°C. unless otherwise noted.
^{b} Contains about 98 wt.-% hexafluoropropylene.
^{c} Contains about 10–20 wt.-% hexafluoropropylene.
^{d} Contains about 5 wt.-% perfluoroisobutylene.
^{e} Contains about 5 wt.-% perfluoroheptene-1. Perfluoroheptene-1 is a mixture of branched and straight chain isomers.
^{f} In $CF_2{=}CF_2$ atmosphere.
^{g} In $CF_3{-}CF{=}CF_2$ atmosphere.

TABLE III

Radicals Produced by Random Scission in Fluorocarbon Resins
By Ionizing Radiation and Their Possible Recombination Reactions

No.	Radical	End-coupling combinations	Branching combinations	"Forbidden" combinations
1	$\text{\sim}CF_2\text{—}CF_2\cdot$	1-1, 1-3,	1-2, 1-5	2-2, 2-3,
2	$\text{\sim}CF_2\text{—}CF\text{—}CF_2\text{\sim}$	1-4, 3-3,	1-6, 1-7,	2-4, 2-5,
		3-4	1-8, 3-6	2-6, 2-7,
	$\begin{array}{c}CF_2\cdot\\|\end{array}$		6-6	2-8, 3-4,
				3-5, 3-7,
3	$\text{\sim}CF_2\text{—}CF\text{—}CF_3\text{\sim}$			3-8, 4-4,
	$\begin{array}{c}CF_3\\|\end{array}$			4-5, 4-6,
4	$\text{\sim}CF_2\text{—}CF\cdot$			4-7, 4-8,
	$\begin{array}{c}CF_3\\|\end{array}$			5-5, 5-6,
				5-7, 5-8,
5	$\text{\sim}CF_2\text{—}CF\text{—}CF\text{\sim}$			6-7, 6-8,
				7-7, 7-8, 8-8
	$\begin{array}{c}CF_2\cdot\\|\end{array}$			
6	$\text{\sim}CF_2\text{—}CF\text{—}CF_2\text{\sim}$			
	$\begin{array}{c}CF_3\\|\end{array}$			
7	$\text{\sim}CF_2\text{—}C\text{—}CF_2\text{\sim}$			
	$\begin{array}{cc}CF_3 & CF_3\\| & |\end{array}$			
8	$\text{\sim}CF\text{—}CF\text{—}CF\text{\sim}$			

the case of fluorocarbon resins the observed final products can be rationalized in terms of radical mechanisms involving radicals which vary in reactivity due to differences in molecular structure and degree of excitation. The concentration in the various polymers of these species and the relative reactivities determine the degree of branching or degradation which occurs. Assuming that bonds are broken at random during exposure to ionizing radiation, the relative numbers of the various possible radicals can be estimated. Based on a general knowledge of the mobility and reactivity of the radicals produced, the feasibility of recombination can also be estimated.

In Table III are summarized the structures of radicals obtainable from the homopolymers of TFE and HFP and from the copolymers of these two monomers. The probable head-to-tail nature of the HFP homopolymer and the extreme conditions needed for its polymerization make the possibility of adjacent —CF_3 groups in the copolymer unlikely and this structure was not considered further. Table III also summarizes the possible recombination reactions. Three classes of combination are indicated: end-coupling, branching, and "forbidden" combinations. The end-coupling combinations maintain the linearity of the molecule since the reactions,

TABLE IV

Relative Numbers of Randomly Produced
Radicals in Some Fluorocarbon Resins

Radical[a]	TFE resin $+(CF_2—CF_2)_n$	HFP resin $\overset{\displaystyle CF_3}{\overset{\displaystyle \mid}{+(CF_2—CF)_n}}$	FEP resin $\overset{\displaystyle CF_3}{\overset{\displaystyle \mid}{+(CF_2—CF_2)_n—(CF_2—CF)_m+}}$
1	$4n$	0	$4n$
2	$4n$	$1n$	$4n—2m + m = 4n—m$
3	0	$2n$	$2m$
4	0	$2n$	$2m$
5	0	0	$4m$
6	0	$3n$	$3m$
7	0	$1n$	$1m$
8	0	$2n$	0

[a] See Table III.

with one exception, involve primary radicals at the ends of chains. Radical 4 is, in reality, a special case of a chain-end radical since the CF_3 group is not considered to be a chain branch here. The branching reactions result from the combination of radicals to give at least three long chains with one carbon atom in common. The "forbidden" combinations are potential branching combinations which are deemed unlikely from a knowledge of radical reactivity, chain mobility, and steric factors. To form readily, adjacent long chain branches should be at least two carbons apart as CF_2 groups, as shown by molecular models and model compounds, and, therefore, any combination leading to one or less carbons between branch points is in the "forbidden" group.

In Table IV, the relative numbers of the radicals formed by random scission and shown in Table III are summarized for each resin. The linear TFE resin can form only two types of radicals, 1 and 2. For each unit, n, cleavage may be at either end or between —CF_2— groups giving a frequency of $4n$ for radical 1. Since each F atom may be cleaved, radical 2 also has a frequency of $4n$. In HFP resin, there are no adjacent —CF_2— groups and radical 1 cannot be formed. Cleavage of the —CF_3 groups gives radical 2 with frequency n, and cleavage at carbons two and one atom away from the CF_3 group gives radicals 3 and 4 in frequency $2n$. Similar analyses give the relative frequencies of the other radicals in both HFP and FEP resins. Radical 5 cannot be formed in HFP resin, while radical 8 cannot be formed in the copolymers since there are no adjacent HFP units in the latter resins.

Consideration of the types of radicals and their relative frequencies in each resin in light of the experimentally observed degradation or crosslinking permits selection of combination 1-6 as the important one leading to branching and, ultimately, crosslinking in FEP resin. Only two types of radicals, 1 and 2, can be produced in TFE resin, and the only permitted combination to form a branch is 1-2. Reasoning from the overall degrada-

tion of TFE resin, however, this combination does not occur to any great extent. Combination 1-2 at best can only slow the overall degradation. In HFP resin, which is also degraded by ionizing radiation, combinations 3-6 and 6-6 could permit branching. Again, based on the observed degradation, these combinations must only slow the degradation. A combination of steric effects and relative chain mobility is probably responsible for the inability of combinations 1-2, 3-6, and 6-6 to promote overall branching and crosslinking.

In the copolymer, however, there are additional branching combinations, 1-5, 1-6, and 1-7, one of which must be the principal branching reaction. Of these, 1-5 and 1-7 are unlikely from steric considerations, which leaves 1-6 as the probable branching/crosslinking reaction. The primary radical 1 at a chain end apparently can combine more readily with a radical of type 6 which is removed from the main polymer chain than it can with a radical of type 2 on the main chain. The formation of radical 1 occurs with main polymer chain cleavage and participation of this radical in a branching reaction "heals" part of the degradation produced by the initial ionizing radiation. This phenomenon has been discussed by Charlesby[7] and Bovey.[8] Crosslinking via the trifunctional "end-links" produced by combination 1-6 can occur provided that one-third of the polymer molecules initially present actually form links. This requirement assumes both radicals produced in the chain cleavage can react in a branching reaction. This requirement is met since cleavage forms radical 1 in pairs. As reported previously, one condition for crosslinking FEP resin is sufficient chain mobility to allow the crosslinking species to react with each other, a condition which is operable above the glass I transition in the polymer.

Other reactions occur during irradiation of fluorocarbon resins which also merit consideration. Fluorine radicals are formed which combine with the various radical species mentioned above and prevent recombination of chains. It has been previously postulated also that CF_2: and $CF_2{=}CF_2$ are formed and would be expected to recombine with the radicals present to produce species similar to type 6 increasing the concentration of this

TABLE V
Comparison of the CF_4 Content of
Gases Evolved from Fluorocarbon Resins

Resin	Total gas evolved, moles[a]	CF_4 evolved, moles
FEP Resin 1	1.2×10^{-5}	1.2×10^{-5}
TFE Resin 1[b]	1.20×10^{-3}	1.0×10^{-6}

[a] Irradiation was carried out on 1-g. samples of finely divided resins in evacuated quartz tubes cooled in an ice bath. Samples were given 100 passes at standard beam energy of 11 w.-sec./cm.^{2}/pass. Only traces of CO_2 were observed in the off-gases of the irradiated samples as measured by mass spectroscopy.
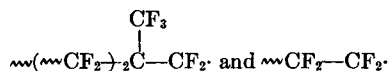
[b] Small amounts of $CF_3{-}CF_3$, $CF_3{-}CF_2{-}CF_3$, $CF_3{-}CF{=}CF_2$, $(CF_3)_2C{=}CF_2$ and COF_2 were also detected by mass spectroscopy.

important reactive species.   Large amounts of CF_4 are also formed during the irradiation of FEP.   Comparative experiments with TFE are shown in Table V.   The mechanism of the formation of CF_4 during irradiation of TFE resin has been discussed in a previous paper.[9]   The additional CF_4 observed on irradiation of FEP resin results from the cleavage of the trifluoromethyl group followed by combination of $CF_3\cdot$ with $F\cdot$.   The other product of the reaction is $-CF_2-CF-CF_2-$, species 2 in Table III.

Two additional experiments were carried out which further support the postulated crosslinking mechanism.   FEP resin was shown to crosslink when irradiated in an atmosphere of tetrafluoroethylene, but to degrade when irradiated in hexafluoropropylene.   In the first experiment polymerization of tetrafluoroethylene occurred on the various radical species generated to produce primary radicals of types similar to 1 and 6.   In the second case the much less reactive hexafluoropropylene probably reacted only with the primary radicals to produce the nonreactive species 4.   Thus only nonreactive species remained in the resin and net degradation resulted.

The ultimate fate of the nonreactive species has also been outlined in a previous paper.[9]   Secondary radicals are stable thermally at temperatures in excess of 200°C.   They react rapidly, however, with oxygen at room temperature to produce peroxides of varying stability to heat, water, and other reagents.
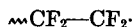
The observation that the copolymer of hexafluoropropylene and perfluoroheptene-1 degrades (example 4) on irradiation and that copolymers of tetrafluoroethylene with octafluoroisobutylene and perfluoroheptene-1 (examples 6 and 7) crosslink can be explained using the same general approach outlined for the polyhexafluoropropylene and the fluorinated ethylene propylene copolymer above.   We postulate, then, that the important cross-linking species in the octafluoroisobutylene copolymer are

$$\underset{\displaystyle \overset{|}{\underset{}{}}}{} $$

$$\text{CF}_3$$
$$|$$
$$\text{ww}(\text{ww}CF_2\!-\!)_2 C\!-\!CF_2\!\cdot \text{ and } \text{ww}CF_2\!-\!CF_2\!\cdot$$

while in the perfluoroheptene copolymer they are

$$\text{F}$$
$$|$$
$$\!+\!CF_2)_2 C\!-\!C_5F_{10})\!\cdot$$
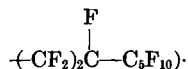
(where the radical is attached to a primary carbon) and

$$\text{ww}CF_2\!-\!CF_2\!\cdot$$

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Résumé

On a soumis plusieurs fluoropolymères commerciaux et expérimentaux à une radiation conisante à des températures élevées, et on a mesuré les changements de viscosité à la fusion comme indication du degré de pontage ou de dégradation. Les viscosités à la fusion du polytétrafluoroéthylène, du polychlorotrifluoroéthylène, du polyhexafluoropropylène et d'un copolymère de l'hexafluoropropylène avec le perfluoroheptène-1 diminuent par irradiation à 200–250°C, tandis que celles des copolymères du tétrafluoroéthylène avec de l'hexafluoropropylène, de l'octafluoroisobutylène ou du perfluoroheptène-1 augmentent, ce qui indique du pontage. Les résultats montrent l'importance de la réaction entre une espèce du type $\sim\!\!\sim(\sim\!\!\sim CF_2\!\!\rightarrow_2 CX\!\!-\!\!(CF_2)_n\cdot$ (où X est F ou CF₃) avec $\sim\!\!\sim CF_2\!\!-\!\!CF_2\cdot$ dans l'obtention du pontage.

Zusammenfassung

Eine Anzahl handelsüblicher und experimenteller Fluorpolymerer wurde bei erhöhten Temperaturen ionisierender Strahlung ausgesetzt und die Änderung der Schmelzviskosität als Mass für den auftretenden Vernetzungsoder Abbaugrad gemessen. Polytetrafluoräthylen, Polychlortrifluoräthylen, Polyhexafluorpropylen und ein Kopolymeres aus Hexafluorpropylen mit Perfluorhepten-1 zeigten bei der Bestrahlung bei 200–250°C abnehmende Schmelzviskosität, während Kopolymeres aus Tetrafluoräthylen und Hexafluorpropylen, Oktafluorisobutylen oder Perfluorhepten-1 zunehmende Schmelzviskosität zeigen, was für Vernetzung spricht. Die Ergebnisse lassen erkennen, das die Reaktion einer Spezies vom Typ $\sim\!\!\sim(\sim\!\!\sim CF_2\!\!\rightarrow_2 CX\!\!-\!\!(CF_2)_n\cdot$ (wo X gleich F oder CF₃ ist) mit $\}\ CF_2\!\!-\!\!CF_2\cdot$ für den Eintritt der Vernetzung ausschlaggebende ist.