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VINYLIDENE FLUORIDE - HEXAFLUOROPROPYLENE COPOLYMER HAVING TERMINAL IODINES

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INTRODUCTION

The vinylidene fluoride(VDF)-hexafluoropropylene(HFP) copolymers are well-known fluorocarbon elastomers which have excellent thermal, oil and chemical stability. Due to their inert structure, curing is more difficult compared with the hydrocarbon elastomers such as styrene-butadiene copolymer, acrylonitrile-butadiene copolymer etc. It is known that two curing recipes described below are practically usable for these fluorocarbon elastomers.

a) a combination of a blocked diamine and an acid acceptor such as magnesium oxide or basic lead phosphite.[1]
b) a combination of an aromatic polyhydroxy compound, an appropriate accelerator and an acid acceptor.[2,3]

Recently, we found that when the copolymerization is carried out in the presence of organic iodide compounds as chain transfer agents, the copolymers obtained can be easily cured by using an organic peroxide and a coagent to give excellent physical properties.[4] In this paper, we discuss the characteristics of the copolymers prepared in the presence of the organic mono-iodide compound, $(CF_3)_2CFI$, or the di-iodide compounds, $I(CF_2)_4I$, $I(CF_2)_6I$, as chain transfer agents.

EXPERIMENTAL

Polymerization

VDF and HFP monomers were 99.9% pure. Emulsifier used

was ammonium perfluorooctanoate obtained from Rimar Co. Organic iodide compounds were prepared and purified in our laboratory and their purities were confirmed to be greater than 99.8% by gas chromatography. Other chemicals used were reagent grade.

The copolymerization reaction was carried out in a 30-liter volume stainless steel reactor with a magnetically coupled agitater. The reactor was charged with 15-liter of demineralized and deoxygenated water. Then 30g. of ammonium perfluorooctanoate was added as an emulsifier. After replacing air with pure nitrogen gas, a VDF/HFP monomer mixture consisting of 50/50 (mol/mol) was added to the reactor until the pressure went up to 13kg/cm^2. Reaction temperature was 80°C. In order to initiate the polymerization, 0.2g. of ammonium persulfate dissolved in water was injected into the reactor using micro-pump. Since the pressure dropped with the progress of the polymerization, a VDF/HFP monomer mixture consisting of 78/22 (mol/mol) was added to the reactor to maintain the pressure at 13kg/cm^2 during the polymerization. After about one hundred grams of the copolymer was produced (about two hours after reaction started), chain transfer agent was added to control the molecular weight of the final copolymer. In order to continue the reaction, 0.1 or 0.2g. of ammonium persulfate was added every three hours during polymerization. After a definite time of the polymerization, heating and agitation were stopped and the monomers remaining in the reactor were removed. Polymers produced were isolated from the emulsion by coagulation and dried in an oven at 100°C.

Characterization

Intrinsic viscosities of the copolymers were determined in THF at 35°C with an Ubbelode capillary viscometer. Number average molecular weights were obtained from osmotic pressure measurements in THF at 35°C using a Hewlett Packard osmometer Model 502. Molecular weight distributions of the copolymers were determined in THF at room temperature using Waters Associates gel permeation chromatography having six Styragel columns of the following pore size: 10^7, 10^6, 10^5, 10^4, 10^3 and 10^2 Å. The concentrations of the samples were 1.0g./dl. and the flow rate was 1 ml./min. Mooney viscosities were measured at 100°C and 140°C in the usual way with Shimadzu Seisakusho Mooney viscometer.

Vulcanization

Peroxide used was 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane. Coagents containing inhibitor were used after washing with 5wt% sodium hydroxide aqueous solution and drying with anhydrous sodium carbonate. Copolymer, peroxide and coagent were milled by 200 mm mixing roll at room temperature. After milling thoroughly, the compounds were put into the mold and cured at 160°C for 30 min. to form sheets. Gel fractions of the vulcanizates were measured to estimate the degree of vulcanization. About 0.2g. of vulcanizates was weighed accurately and immersed in a large excess of THF at 35°C to extract the soluble fraction. THF was renewed twice during extraction. After three days, the swollen vulcanizates were removed and dried under vacuum at room temperature until constant weight. The gel fraction was calculated by the following equation:

$$G = W_2 / W_1$$

where G, W_1 and W_2 are the gel fraction, the weight before and after extraction, respectively.

RESULTS AND DISCUSSIONS

The results of the copolymerization reactions carried out in the presence of organic iodide compounds are summarized in Table I. The copolymerization reaction reqired a long time because the reaction was carried out at extremely low ammonium persulfate concentrations to avoid the production of polymer endgroups derived from ammonium persulfate.

Figure 1 shows the relationship between number average molecular weight and polymer yield in the presence of various amounts of perfluoroisopropyl iodide. The number average molecular weight increases linearly with the increase in the polymer yield and these slopes depend on the amount of perfluoroisopropyl iodide.

The relationship between number average molecular weight and the yield of polymer formed in the presence of three kinds of fluorocarbon iodides, perfluoroisopropyl iodide, 1,4-di-iodo-perfluorobutane and 1,6-di-iodo-perfluorohexane is shown in Figure 2. The first fluorocarbon iodide is a mono-iodide type chain transfer agent; the latter two are di-iodide type chain transfer agents. The relationship between number average

TABLE I

Copolymerization of VDF and HFP in the Presence of Chain Transfer Agents [a]

Run no.	Chain transfer agent	g.	Reaction time hr.	Polymer yield g.	Intrinsic viscosity dl./g.	Molecular weight x 10^{-4}	Mooney viscosity 100°C	Mooney viscosity 140°C
1	$(CF_3)_2CFI$	3.70	26.8	2395	0.90	19.5	131	65
2			40.8	3892	1.19	30.8	—	—
3			47.3	4956	1.39	37.6	—	136
4	$(CF_3)_2CFI$	5.28 [c]	19.5	2387	0.72	14.0	103	39
5			29.0	3812	0.93	21.7	—	—
6			36.3	4920	1.16	29.3	—	103
7	$(CF_3)_2CFI$	10.56	18.5	1655	0.39	5.14	—	—
8			22.7	2329	0.47	6.98	23	4
9			33.5	3947	0.64	11.5	—	—
10			37.0	4794	0.69	13.6	89	37
11	$(CF_3)_2CFI$	14.80	31.6	3105	0.45	6.40 [b]	17	3
12			51.0	6545	0.66	11.7 [b]	78	28
13	$I(CF_2)_4I$	8.13 [c]	19.2	2231	0.70	14.3	85	30
14			25.9	3258	0.82	19.9	—	—
15			33.6	5103	1.05	30.1	—	93
16	$I(CF_2)_6I$	9.92 [c]	17.9	2202	0.61	12.7	63	17
17			32.9	4888	0.98	27.9	—	84

a) Reaction conditions: reactor volume: 30-liter, water: 15-liter, $C_7F_{15}COONH_4$: 30g. $(NH_4)_2S_2O_8$: 1.1-2.2g., VDF/HFP feed ratio: 78/22 mol%, pressure: 13kg/cm^2, temperature: 80°C

b) Calculated by the equation: $[\eta] = 3.99 \times 10^{-4}\ Mn^{0.635}$ (see Fig. 6)

c) These are the same mol amounts

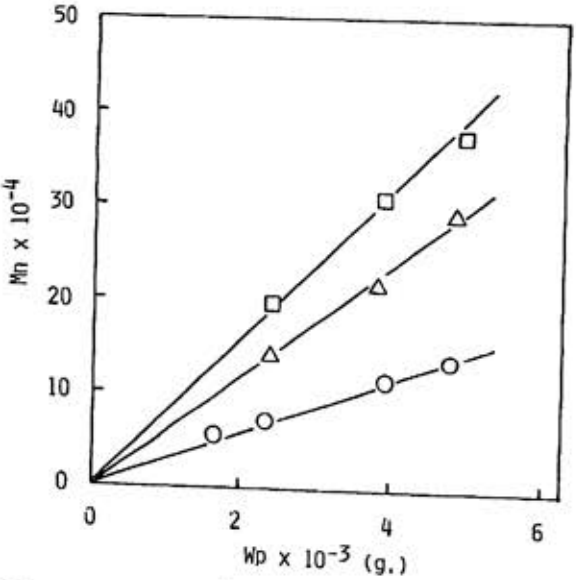

Fig. 1. Number average molecular weight Nn vs. polymer yield Wp at various amounts of chain transfer agents: $(CF_3)_2CFI$: (□) 3.70g.; (△) 5.28g.; (○) 10.56g.

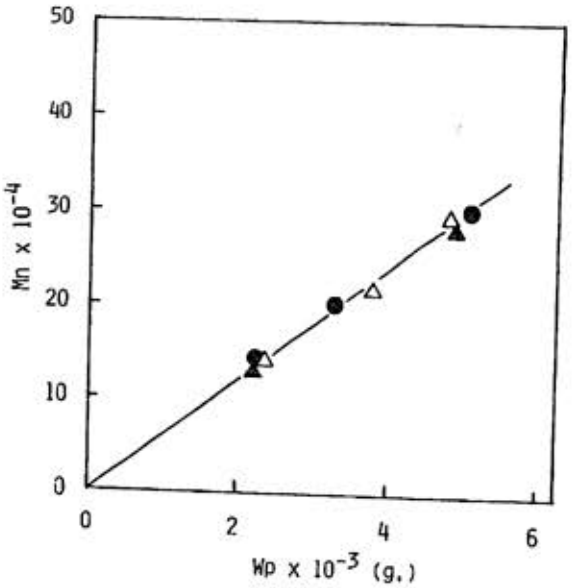

Fig. 2. Number average molecular weight Mn vs. polymer yield Wp at three kinds of chain transfer agents: (△): $(CF_3)_2CFI$ 5.28g.; (●): $I(CF_2)I$ 8.13g.; (▲): $I(CF_2)_6I$ 9.92g.

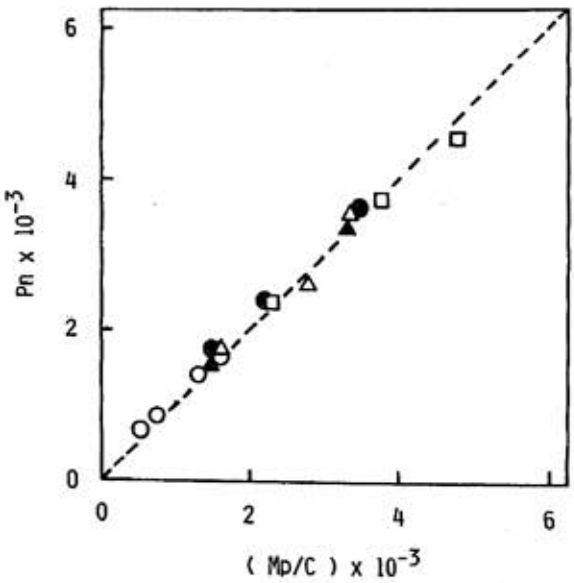

Fig. 3. Degree of polymerization Pn vs. the ratio of polymer yield (Mp, mol) to the total amount of chain transfer agents (C, mol):
(□): $(CF_3)_2CFI$ 3.70g.; (△): $(CF_3)_2CFI$ 5.28g.;
(○): $(CF_3)_2CFI$ 10.56g.; (●): $I(CF_2)_4I$ 8.13g.;
(▲): $I(CF_2)_6I$ 9.92g.

molecular weight and polymer yield is not influenced by the kind of fluorocarbon iodide.

Figure 3 shows the relationship between degree of polymerization and the ratio of polymer yield to the amount of chain transfer agent, Mp/C. The broken line shows the relationship if the degree of polymerization is directly proportional to the ratio Mp/C. The experimental results are in good agreement with the theoretical values. Thus the degree of polymerization is found to be determined by the ratio Mp/C in this copolymerization, regardless of the kind of fluorocarbon iodide.

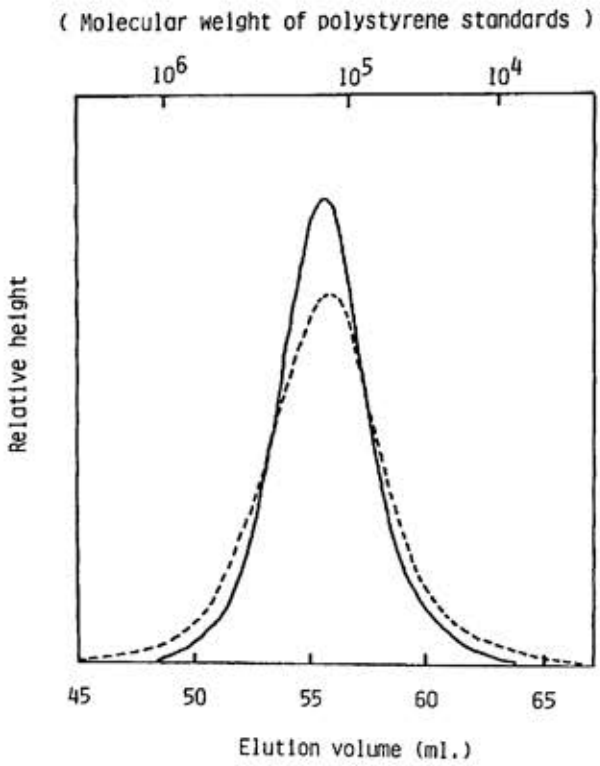

Fig. 4. Molecular weight distribution of the copolymer prepared in the presence of chain transfer agents:
(----): $(CF_3)_2CFI$, Mn = 140000, Mw/Mn = 2.71
(——): $I(CF_2)_4I$, Mn = 143000, Mw/Mn - 1.73.

The molecular weight distribution curves of two copolymers are shown in Figure 4. One is the copolymer prepared in the presence of 1,4-di-iodo-perfluorobutane, a di-iodide type chain transfer agent, and the other is that prepared using perfluoroisopropyl iodide, a mono-iodide type chain transfer agent. As reported previously[4], the molecular weight distributions of these two copolymers are very narrow compared with those prepared using other chain transfer agents such as carbon tetrachloride and isopentane. On the other hand,

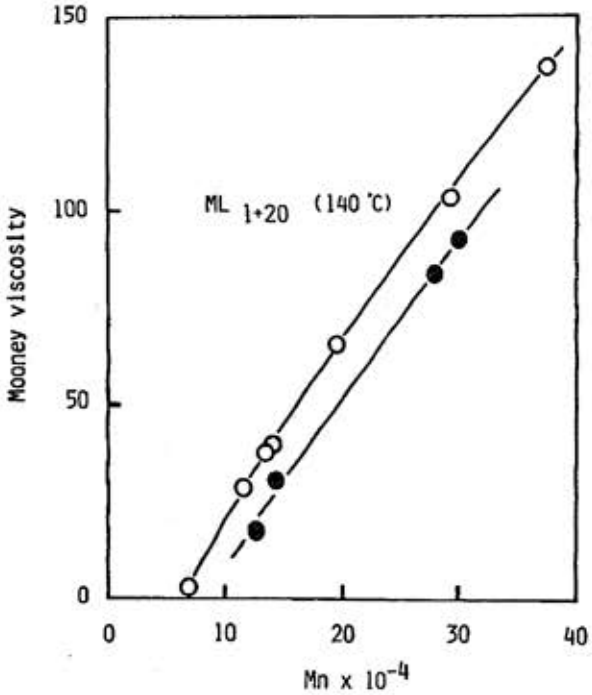

Fig. 5. Mooney viscosity ML vs. Number average molecular weight Mn:
(○): $(CF_3)_2CFI$; (●): $I(CF_2)_4I$ and $I(CF_2)_6I$.

it is evident that the copolymer prepared with di-iodide gives a narrower distribution of molecular weight compared with that prepared with mono-iodide; in other words, its Mw/Mn value is smaller than that of the copolymer prepared with mono-iodide. Such a distributional difference of two copolymers seems to affect the bulk and solution properties of the copolymer. The Mooney viscosity (Figure 5) and intrinsic viscosity (Figure 6) of the copolymer prepared with di-iodide are smaller than those of the copolymer prepared with mono-iodide at the same number average molecular weight.

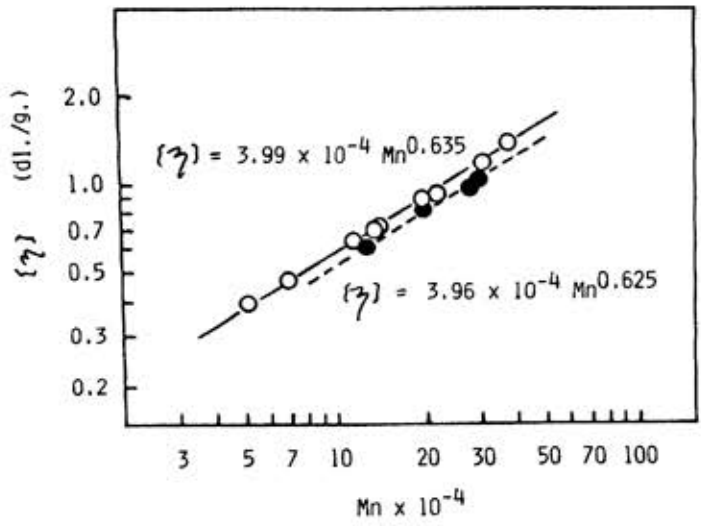

Fig. 6. Intrinsic viscosity (η) vs. number agerage molecular weight Mn:
(○): $(CF_3)_2CFI$; (●): $I(CF_2)_4I$ and $I(CF_2)_6I$.

In the case of mono-iodide

(1) $R_f\text{-}I \xrightarrow[\text{initiator}]{\text{monomer}} R_f\sim\sim I$

(2) $R_f\sim\sim I \xrightarrow[\text{initiator}]{\text{monomer}} R_f\sim\sim\sim\sim I$

(3) $R_f\sim\sim\bullet \quad \bullet\sim\sim R_f \longrightarrow R_f\sim\sim\sim\sim R_f$
(dead polymer)

In the case of di-iodide

(3') $I\sim R_f\sim\sim\bullet \quad \bullet\sim\sim R_f\sim I \longrightarrow I\sim R_f\sim\sim\sim\sim R_f\sim I$
(not dead polymer)

Fig. 7. Mechanism of copolymerization in the presence of organic iodide compounds as chain transfer agents.

Now, we suppose such a distributional difference comes from a difference in the copolymerization mechanism, as described in Figure 7. In this copolymerization, the fluorocarbon iodide is very reactive; it is easily attacked by a radical and forms the copolymer (shown in Figure 7-1). As the terminal iodine of the copolymer formed in this way remains reactive, this copolymer successively becomes a higher molecular weight copolymer by repeating the propagation reaction and the chain transfer reaction (7-2). On the other hand, this copolymerization reaction was carried out at extremely low ammonium persulfate concentration, as mentioned above. Therefore, in the case of mono-iodide, the iodine-free-copolymer(dead polymer) is generated by the recombination reaction (7-3). But in the case of di-iodide, iodine-terminated copolymer is generated by the recombination reaction (7-3'). It seems that such a difference in the recombination reactions affects the mode of molecular weight distributions of two copolymers formed.

Now, the gel fractions of peroxide-cured-vulcanizates were measured to estimate the degree of vulcanization. Table II shows the effect of coagent on peroxide vulcanization. Polymer A is the copolymer prepared in the absence of organic iodide compound. Therefore, it has no terminal iodine. Polymer B is that prepared with perfluoroisopropyl iodide; it can be considered to have terminal iodine on one side (mono-iodide-copolymer). Polymer C is that prepared with 1,4-di-iodo-perfluorobutane; it can be considered to have terminal iodines on both sides (di-iodide-copolymer). In the cases of polymer B and C, it is found that the gel fractions of thier vulcanizates are increased using various kinds of multifunctional vinyl compounds, and that triallyl isocyanurate(TAIC) is the most effective coagent. On the other hand, no gel is found in the case of vulcanizates prepared from polymer A even it was cured using TAIC. These experimental results suggest the terminal iodines react with TAIC and form gel.

Figure 8 shows the effect of TAIC on gel fractions of peroxide-cured-vulcanizates prepared from polymer B and C. No gel is found in the absence of TAIC on both vulcanizates. But the gel fractions increase with the increase in TAIC and become constant at high level. The gel fractions of vulcanizates prepared from mono-iodide-copolymer are smaller than those from di-iodide-copolymer.

TABLE II

Effect of Coagents on Peroxide Cured Vulcanizates [a]

Coagent		Gel fraction (%)		
	g.[b]	Polymer A[c]	Polymer B[c]	Polymer C[c]
None		—	0	0
Ethyleneglycol dimethacrylate	2.4	—	17	18
Diallyl phthalate	3.0	—	33	35
N,N-Methylenediacrylamide	1.7	—	37	41
Trimethylolpropane trimethacrylate	2.8	—	37	39
Triallyl trimellitate	2.7	0	63	73
Triallyl isocyanurate	2.0	0	84	97

a) Curing recipe (phr): copolymer 100, peroxide 0.5 Conditions: press cure at 160°C for 30min.

b) Double bond concentration of coagents are the same

c) Polymer A has no terminal iodine
Polymer B has terminal iodine on one side
Polymer C has terminal iodines on both sides

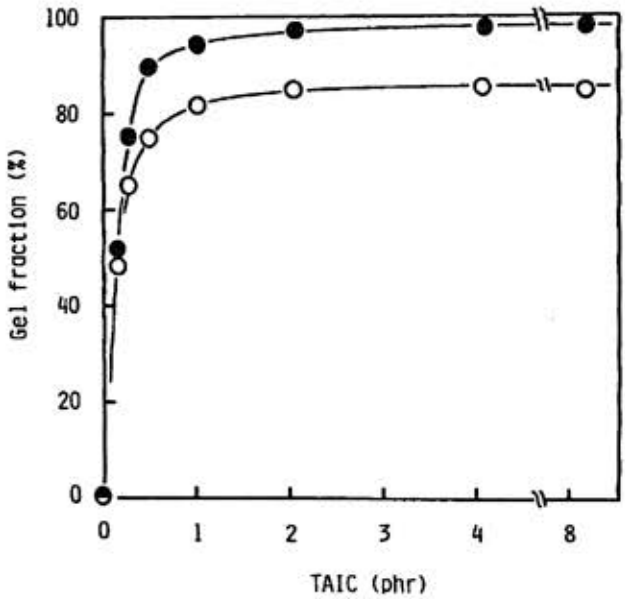

Fig. 8. Effect of TAIC on gel fraction of peroxide cured vulcanizates.
Recipe (phr): copolymer 100, peroxide 0.5
Conditions: press cure at 160°C for 30 min.
(○); copolymer with terminal iodine on one side
(●); copolymer with terminal iodines on both sides.

Figure 9 shows the effect of peroxide on gel fractions of peroxide-cured-vulcanizates prepared from polymers B and C. The gel fractions of vulcanizates prepared from mono-iodide-copolymer are smaller than those from di-iodide-copolymer even it was cured using a great quantity of peroxide. Analyses of extracts were done to investigate the cause of difference of gel fractions. Consequently, it was found that the extracts were low molecular weight copolymers which have no iodine. Thus it seems the mono-iodide-copolymer contains about 10-15% iodine-free-copolymer by weight.

Now the reaction mechanism of iodine-terminated-copolymer with TAIC in the presence of peroxide was proposed, as shown in Figure 10. An initial radical formed by the decomposition of peroxide attacks the double bond of TAIC to form radical (II)[step(1), step(2)]. The radical (II) subtracts iodine from iodine-terminated-copolymer to form polymer radical [step(3)]. And then the polymer radical attacks the double

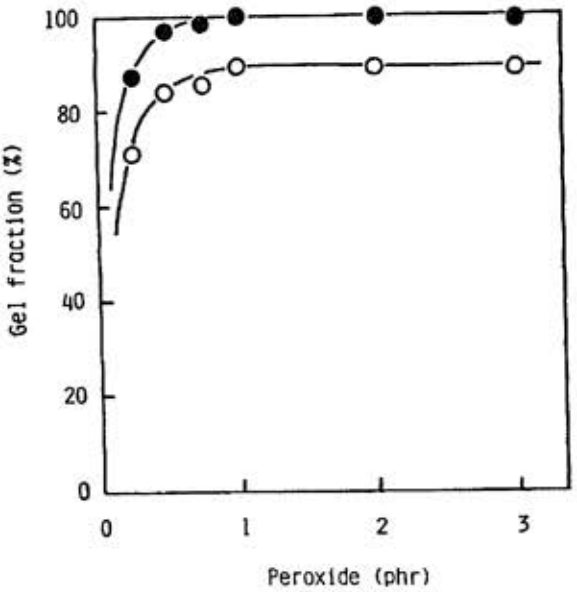

Fig. 9. Effect of peroxide on gel fraction of peroxide cured vulcanizates.
Recipe (phr): copolymer 100, TAIC 2
Conditions: press cure at 160°C for 30 min.
(○); copolymer with terminal iodine on one side
(●); copolymer with terminal iodines on both sides.

bond of TAIC to form radical (IV) [step(4)], which subtracts iodine from another iodine-terminated copolymer [step(5)]. Crosslinking network seems to be formed by repeating such reactions of iodine-terminated copolymer with the double bond of TAIC.

SUMMARY

The copolymerization reactions of vinylidene fluoride and hexafluoropropylene were carried out in the presence of an organic mono-iodide compound, $(CF_3)_2CFI$, or di-iodide-compounds, $I(CF_2)_4I$, $I(CF_2)_6I$, as chain transfer agents and the following results were obtained.

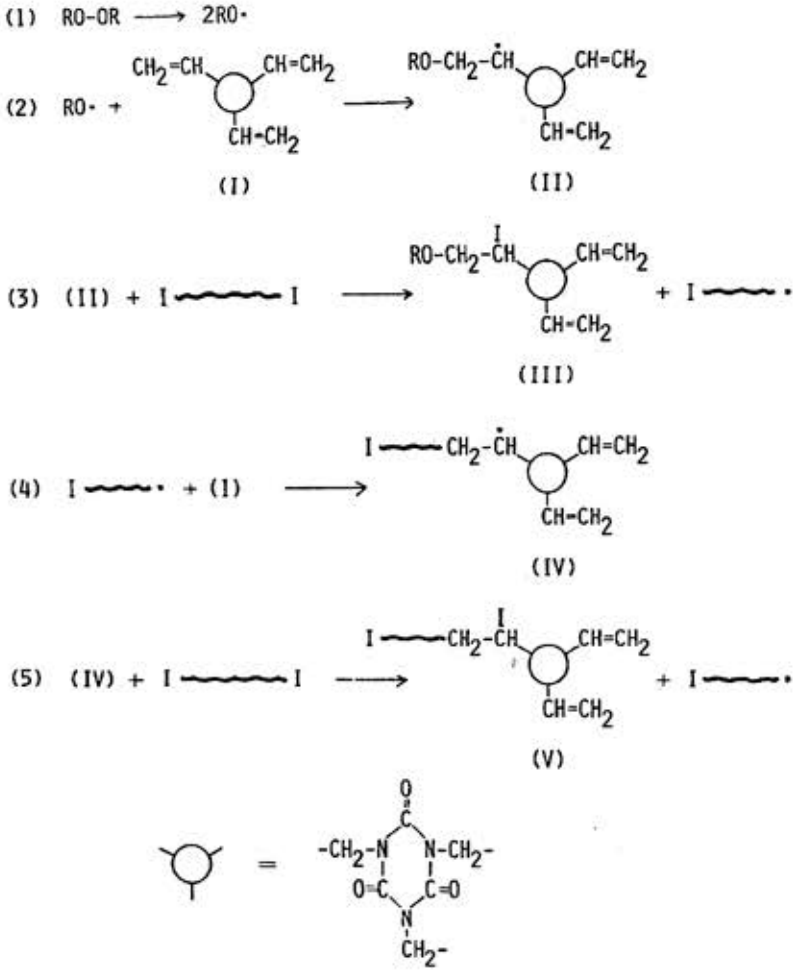

Fig. 10. Proposed reaction mechanism of iodine-terminated-copolymer with triallyl isocyanurate.

(1) The number average molecular weight of the copolymer is determined by the ratio of polymer yield to the amount of chain transfer agent.

(2) The molecular weight distribution of the copolymer prepared with di-iodide is narrower than that prepared with mono-iodide.

(3) Such a distributional difference seems to come from a difference in the recombination reaction of the copolymerization.

(4) The terminal iodines of the copolymer seem to react with multifunctional vinyl compounds to form gel in the presence of peroxide.

(5) The gel fractions of the vulcanizates prepared from mono-iodide-copolymer are smaller than those from di-iodide-copolymer.

(6) The difference of gel fractions seem to arise from that mono-iodide-copolymer contains iodine-free-copolymer.

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