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Registry No. (BPA)(PC) (copolymer), 25037-45-0; (BPA)(PC) (SRU), 24936-68-3; DBP, 84-74-2.

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^{13}C NMR Study of Radiation-Induced Cross-Linking of Linear Polyethylene

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Received March 6, 1989

ABSTRACT: Structural changes of linear polyethylene induced by ^{60}Co γ-ray irradiation have been studied by solution-state ^{13}C NMR spectroscopy. Relatively low molecular weight fractions were irradiated in the molten state in vacuo to different doses below the gel dose. As a result, sharp resonance lines assignable to the CH, α-CH$_2$, and β-CH$_2$ carbons associated with H-type cross-links have been evidently observed for each irradiated sample, in contrast to the previous reports. Concomitantly, Y-type long branches are also found to be significantly formed during the irradiation. The *G*-values of the H-links and Y-branches are estimated to be 0.74 and 0.27, respectively, indicating that H-links are more effectively produced in the molten state than Y-branches. Spin–lattice relaxation times, T_1, and nuclear Overhauser enhancement (NOE) have been also measured for the respective carbons of the H-links and Y-branches. These values suggest the less mobility of these carbons compared to the main-chain carbons and chain ends, but it does not significantly reduce the signal intensity of the H-links and Y-branches. Radiation effects of other structural units are also discussed.

Introduction

Although the effect of high-energy irradiation on polyethylene has been extensively studied, many fundamental problems still remain unsolved.[1] One of these is the chemical structure of cross-linking points of irradiated polyethylene samples. Bennett et al.[2] determined ^{13}C chemical shifts of the CH carbon and the neighboring CH$_2$ carbons for the H-type cross-link, which is connected by a C–C single bond, using a model compound in solution. According to this assignment, many H-links were found to be produced for *n*-alkanes by the irradiation in the crystalline or molten state.[3–7] Nevertheless, almost no line associated with the H-links could be observed for irradiated polyethylenes with considerably high molecular weights.[5–7] In contrast, the resonance lines assignable to long branches significantly increase in intensity with increasing irradiation dose, although such long branches, which are referred to as Y-branches, are not distinguished from the long branches usually involved in unirradiated polyethylene samples by ^{13}C NMR spectroscopy. Therefore, Randall et al. proposed that the production of the Y-branches would be a main cause of the gelation of polyethylene.[6]

The irradiation dose used in their work was suppressed to a level (10–40 kGy) less than the gel dose to obtain a soluble sample for solution-state ^{13}C NMR measurements. Therefore, the concentration of the H-links seems to be very close to the sensitivity limit of ^{13}C NMR. In this paper we report that the H-links are also produced in linear polyethylene samples by the irradiation in the molten state. In our experiments relatively lower molecular weight fractions, which were obtained by liquid–liquid fractionation, were used to increase the irradiation dose up to 100–500 kGy. The *G*-values of H-links and Y-branches are also estimated for these samples.

Experimental Section

Samples. A high-density linear polyethylene, Showadenko AZ3442, was fractionated into 10 fractions in a *p*-xylene–poly(ethylene glycol 400) system. The molecular weights and the molecular weight distributions of the fractions, which were determined by GPC using the calibration curve modified for polyethylene, are shown in Table I. For comparison, a low molecular weight polyethylene, Mitsui Hi-wax 200p (HW) ($\bar{M}_v = 5440$), and *n*-hexatriacontane (*n*-C$_{36}$H$_{74}$) purchased from Nakarai

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Table I
Molecular Weights and Molecular Weight Distributions of Linear Polyethylene Fractions[a]

fraction	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
FZ-3	20.2	33.8	1.7
FZ-4	21.8	30.5	1.4
FZ-5	17.1	24.1	1.4
FZ-6	12.9	18.8	1.5
FZ-7	10.7	14.5	1.4
FZ-8	6.2	8.1	1.3
FZ-9	2.8	3.7	1.3

[a] Determined by GPC.

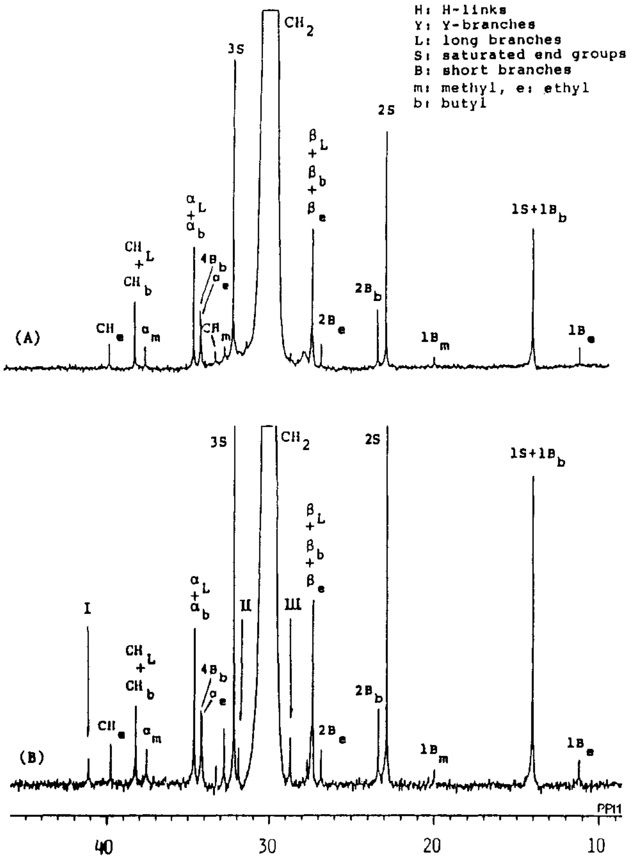

Figure 1. 100-MHz ^{13}C NMR spectra of polyethylene samples in solution: (A) unirradiated FZ-5, (B) FZ-5 irradiated to 200 kGy at 150 °C in vacuo.

Tesque, Inc., were also used. The former sample was purified by Soxhlet extraction with methanol, but the latter was used without further purification.

Irradiation. Each sample was sealed at 150 °C in a glass tube in vacuo after degassing at room temperature for 24 h and then at 150 °C for 1 h. Irradiations were performed at 150 °C using a ^{60}Co source in the Research Reactor Institute, Kyoto University. The dose rate was 9.35 kGy h^{-1}. Following irradiation, each sample was left in the tube at room temperature at least for 24 h to reduce the long-lived radical concentration.

^{13}C NMR Measurements. ^{13}C NMR measurements were made at 125 °C on a JEOL JNM-GX400 spectrometer operating at 100.4 MHz. The samples were dissolved in 1,2,4-trichlorobenzene/benzene-d_6 (80/20) at 20 wt % and sealed in NMR tubes under an argon atmosphere. Measurement conditions were as follows: flip angle, 45°; pulse delay (PD) after FID, 15 s; acquisition time, 0.819 s; data points, 32 000; FID's accumulation, 10 000–30 000.

Results and Discussion

Formation of H-Links and Y-Branches. Figure 1 shows 100-MHz ^{13}C NMR spectra of unirradiated FZ-5 and FZ-5 irradiated to 200 kGy at 150 °C in vacuo. As shown by arrows in Figure 1B, three new resonance lines appear by the irradiation. These lines are referred to as lines I–III in the order of decreasing chemical shift, and their chemical shifts are shown in Table II together with those of the carbons associated with the H-links obtained for the model compound[2] and *n*-alkanes.[3-7] Since the chemical shifts of lines I–III are in good accord with the values of the CH and α- and β-CH_2 carbons for the H-links, it is concluded that the H-links are also produced for polyethylene by the ^{60}Co γ-ray irradiation.

Table II
Chemical Shifts of Resonance Lines I–III Observed in Irradiated Polyethylene and Those of the Carbons Associated with the H-Link

	chemical shift, ppm				
sample	CH_H[a]	α_H[a]	β_H[a]	γ_H[a]	refs
$[(C_{13}H_{27})_2CH]_2$	39.45	30.70	28.22	30.19	3
n-$C_{44}H_{90}$	40.5	31.9	28.6		4
n-$C_{36}H_{74}$	41.01	30.47	28.61	30.60	5
polyethylene	41.10 (line I)	31.88 (line II)	28.66 (line III)		this work

[a] Abbreviated according to the following structure:

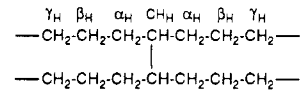

Figure 2 shows 100-MHz ^{13}C NMR spectra of the unirradiated low molecular weight polyethylene (HW) and HW irradiated to 388 kGy at 150 °C in vacuo. In this case lines I–III, which are assignable to the CH and α- and β-CH_2 carbons in the H-links, are also clearly observed for the irradiated sample. In addition, the resonance lines associated with long branches, which are referred to as CH_L, α_L, and β_L in Figure 2, are significantly increased in intensity by the irradiation, whereas these lines are very small in the unirradiated sample. This indicates that long branches are also formed by the irradiation, in good agreement with the conclusion obtained by Randall et al.[5-7] Although the long branches thus detected are indistinguishable in ^{13}C NMR from the long branches involved in the unirradiated sample, the former branches are referred to as Y-branches in this paper.

In order to estimate the yield of Y-branches, we assume that there is no change of the concentration of the original long branches by the irradiation. This assumption seems reasonable, judging from the fact that ethyl and butyl branches are hardly changed in their concentrations during the irradiation as will be shown later. Under this assumption, the yield of the Y-branches can be calculated as an increase in concentration of the long branches. However, the resonance lines of the CH carbons (CH_L) and α-CH_2 carbons (α_L) of the long branches are completely superposed on the lines of the corresponding carbons, CH_B and α_B, for the butyl branches, respectively. Therefore, we first subtract the integral intensity of the line $2B_b$ at 23.38 ppm from the integral intensities of CH_L and α_L resonances, respectively, by assuming the former intensity to be the concentration of the butyl branches. The intensities of CH_L and α_L carbons thus obtained are then divided by the total integral intensity of the spectrum to determine the concentration of the long branches as the number of units per 10 000 carbons. After such a calculation is performed for the spectra of the unirradiated and irradiated samples, the differences in concentration for the CH_L and α_L carbons between the irradiated and unirradiated samples are assumed to be the yields of the CH_Y and α_Y carbons of Y-branches produced by the irradiation, respectively. On

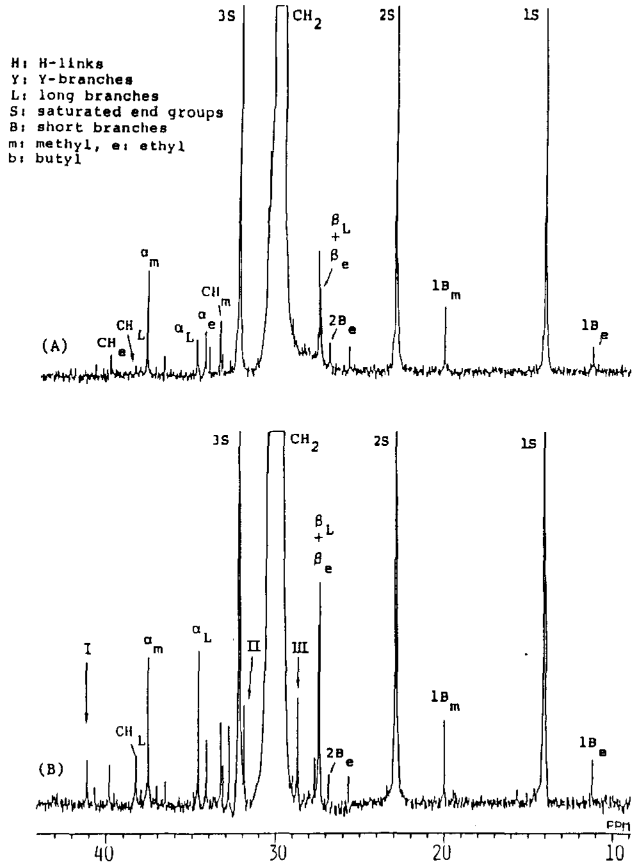

Figure 2. 100-MHz ^{13}C NMR spectra of low molecular weight polyethylene samples (HW) in solution: (A) unirradiated, (B) irradiated to 388 kGy at 150 °C in vacuo.

Table III
Radiation Yields of H-Links and Y-Branches for Different Samples

		no. of units per 10 000 carbon atoms	
sample	dose, kGy	H-links	Y-branches
HW	82	1.0	0.6
	167	1.5	0.9
	265	2.7	1.7
	388	3.4	2.2
FZ-3	100	0.8	0.5
FZ-4	100	1.0	0.5
FZ-5	200	1.8	0.8
FZ-6	200	2.4	0.9
FZ-7	300	2.8	1.7
FZ-8	500	5.7	1.8
FZ-9	500	5.1	2.3
n-$C_{36}H_{74}$	167	1.2	0
	388	3.0	1.0

the other hand, the line assignable to the β_L carbon also contains the contributions from the β_b carbon of the butyl branch and the β_e carbon of the ethyl branch. Therefore, those additional contributions should be removed from the total integral intensities using the integral intensities of the resonance lines ($2B_b$ and $2B_e$) of the CH_2 carbons connected to the terminal CH_3 groups in the butyl and ethyl branches, respectively. Then, the yield of β_Y is determined in the same manner as for the CH_Y and α_Y carbons. The ratio of the yields thus obtained for the CH_Y, α_Y, and β_Y carbons is found to be about 1:3:3 for each irradiated sample, and then their number-averaged values are assumed to be the yield of the Y-branches.

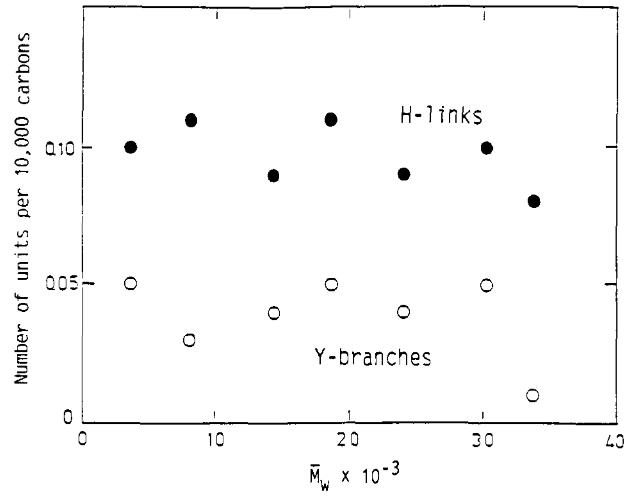

Figure 3. Concentrations of H-links and Y-branches produced per 10 kGy irradiation vs molecular weight.

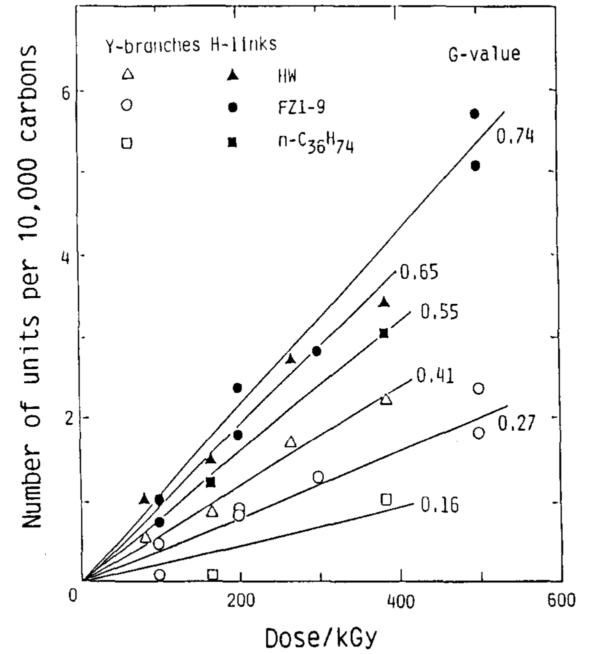

Figure 4. Radiation yields of H-links and Y-branches for different samples as a function of the dose.

Table IV
^{13}C Spin-Lattice Relaxation Times (T_1) and Nuclear Overhauser Enhancement (NOE) of the Respective Carbons of Irradiated Polyethylene Fraction (FZ-6)

carbon	T_1, s	NOE
$-(CH_2)_n-$	3.30	2.8
1S	12.4	2.8
2S	11.2	2.8
3S	7.6	2.9
CH_H	0.30	2.3
α_H	0.70	2.5
β_H	1.0	2.4
CH_Y	1.4	2.7
α_Y	1.3	2.6
β_Y	1.5	2.6

In contrast, the yield of the H-links is easily obtained by conducting the number average of the integral intensities of lines I–III, which are assignable to the CH_H, α_H, and β_H carbons in the H-links, because these lines contain no other contributions. Table III shows the yields of the H-links and Y-branches thus determined for different irradiated samples. In the irradiation with the dose of 100–500 kGy, 0.8–5.7 H-links are formed per 10 000 carbons, whereas the yield of the Y-branches is less than half of the H-links.

Table V
Radiation Yields of Different Structural Units for Molecular Weight Fractions of Polyethylene

	no. of units per 10 000 carbon atoms							
	FZ-3		FZ-5		FZ-7		FZ-9	
structural units	unirradiated	100 kGy	unirradiated	200 kGy	unirradiated	300 kGy	unirradiated	500 kGy
saturated end groups	19.8	21.0	24.7	25.6	42.5	43.0	174	173
vinyl end groups	1.0	0.0	1.0	0.0	1.0	0.0	2.3	0.0
long-chain branches[a]	6.1	6.4	5.7	6.2	5.2	8.7	4.5	7.5
ethyl branches	3.9	3.3	3.1	2.3	3.3	2.0	2.7	2.5
methyl branches	2.1	2.5	1.7	2.2	2.1	2.4	3.8	3.8
butyl branches	6.2	6.4	5.4	5.6	5.2	7.5	4.3	5.2
trans double bonds	0.0	5.1	0.0	4.6	0.0	8.0	0.0	11.6
cis double bonds	3.6	4.5	5.5	6.0	6.8	7.8	9.5	11.2
$\bar{M}_w \times 10^{-3}$ [b]	33.8	81.5	24.1	53.3	14.5	2.74	3.70	3.80
$\bar{M}_n \times 10^{-3}$ [b]	20.2	14.4	17.1	14.6	10.7	8.80	2.80	2.10
$\bar{M}_w/\bar{M}_n$	1.7	5.7	1.4	3.7	1.4	3.1	1.3	1.8

[a] Involving Y-branches for the irradiated samples. [b] Measured by GPC.

In Figure 3 the yields of the H-links and Y-branches for fractions FZ-3–9 are plotted against the molecular weight. Here, each yield is expressed as the number of units per 10 000 carbons produced by the irradiation to 10 kGy. It is found that the yields of the H-links and Y-branches are almost independent of the molecular weight, although there seems to be a tendency of the slight decreases in both yields for higher molecular weights. Hence the effect of the molecular weight is neglected here for further discussion about the formation of the H-links and Y-branches.

Figure 4 shows the radiation yields of the H-links and Y-branches for different samples as a function of the irradiation dose. For every sample both yields increase linearly with increasing dose. The G-values for the formation of the H-links and Y-branches, which were determined from the slopes of the respective lines, are also indicated in this figure. It is concluded from the evaluation of the G-values that H-links are produced 1.5–3.4 times more effectively than the Y-branches for these samples. This conclusion is not consistent with the previous result that the Y-branches are preferably formed in the irradiation of polyethylene in the solid or molten state.[5–7] The cause of this discordance is not clear at present, but we believe that the concentrations of the H-links and Y-branches are too low to be compared with each other in the previous work. Under our experimental condition we have also found that the G-values of H-links and Y-branches greatly depend on the temperature of the irradiation, which will be reported in the following paper.

The differences in the G-values of the formation of the H-links and Y-branches among the samples are prominent; for example, both G-values for the polyethylene fractions are 35–69% larger than those for n-hexatriacontane. This suggests that the heterogeneous structures involved in polyethylene may be responsible for the increase in the yields of the H-links and Y-branches.

Spin Relaxation Parameters of the Carbons Associated with the H-Links and Y-Branches. In ^{13}C NMR spectroscopy, the signal intensities of the respective carbons are not always proportional to their chemical compositions even if their equilibrium magnetizations are used for each acquisition of the free induction decay (FID). This is due to the nuclear Overhauser enhancement (NOE), which induces the increase in signal intensity by a factor of 1.2–3.0 depending on the molecular mobility of each carbon. Therefore, we have determined NOEs of the carbons associated with the H-links and Y-branches by comparing the integral intensities of the spectra obtained by complete and gated decoupling methods. The results for the polyethylene fraction (FZ-6) are compiled in Table IV together with ^{13}C spin–lattice relaxation times, T_1. Since the T_1 values of the carbons (1S, 2S, 3S) at the saturated chain ends are extremely large compared to those of other carbons, the T_1's and NOEs for the H-links and Y-branches are measured separately by using shorter pulse delay times (PD) after FID. As clearly seen in Table IV, the NOE values for the H-links are smallest, indicating that the molecular motion is most hindered in the H-links. This is also reflected on the extremely short T_1's for the carbons of the H-links. The NOEs for the Y-branches are also slightly smaller than those for the carbons of the main chains and the saturated ends. The less molecular mobility of the Y-branches is also more strongly suggested from their short T_1 values.

According to the results of the NOEs, it seems to be better to correct the G-values for the formation of the H-links and Y-branches. However, we did not correct these values, because the correcting factors are as small as 1.1 and 1.2 for the Y-branches and H-links, respectively. Moreover, these factors may be slightly changed from sample to sample. It is most important to point out here that the reduction of the signal intensity is not very serious for the H-links and Y-branches, although their molecular mobilities are considerably hindered.

Radiation Effects on Other Structural Units. Table V shows the concentrations of the different structural units of the unirradiated and irradiated polyethylene fractions, together with the number-average and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, determined by GPC. The saturated end groups are not significantly increased by the irradiation, but the decrease of the molecular weight is more evidently observed in the $\bar{M}_n$ values. This indicates that the irradiation induces the scissions of the main chains, and then a considerable amount of the fragments are stabilized without the recombination with other polymer molecules. In contrast to the decrease in $\bar{M}_n$, $\bar{M}_w$ evidently increases for each fraction by the irradiation. This results in the wider molecular weight distribution for the irradiated samples.

We have estimated the probability, f, of the stabilization of the fragments produced in the chain scissions as follows. The number, N, of irradiated polymeric molecules per an appropriate unit is given by

$$N = N_0 + fN_S - (1 - f)N_S - N_H - N_V \qquad (1)$$

where N_0, N_S, and N_H are the numbers of the unirradiated molecules, the chain scissions, and the H-links, respectively. N_V is the number of vinyl end groups in the unirradiated sample. This term should be included in eq 1, because these end groups may be associated with the formation of the Y-branches[5-7] though the amount is very small in our samples as shown in Table V. The term $(1 - f)N_S$ indicates the number of the fragments to form the Y-branches by the recombination with other polymeric molecules. Therefore, the number N_Y of the Y-branches is expressed as

$$N_Y = 2(1 - f)N_S + N_V \tag{2}$$

Then from eqs 1 and 2, f is given by

$$f = 1 - \frac{1}{2}\frac{N_Y}{N - N_0 + N_Y + N_H} \tag{3}$$

When the numbers of the respective structural units are expressed per 10 000 carbon atoms, eq 3 reduces to

$$f = 1 - \frac{1}{2}\frac{N_Y}{10^4 m(M^{-1} - M_0^{-1}) + N_Y + N_H} \tag{4}$$

where M_0 and M are the molecular weights of the unirradiated and irradiated polymers, respectively, and m is the molecular weight of the CH_2 groups. When the M_n's shown in Table IV are used together with the N_H and N_Y values given in Table III, f has been determined to be about 0.9 for the polyethylene fractions. Therefore, most of the fragments appear to be stabilized without the formation of the Y-branches. The N_S value can be also calculated for each irradiation using eq 2 and then the G-value for the chain scission is estimated to be 1.8. This value is somewhat large compared to the G-values of 0.50 and 0.52 obtained for n-$C_{16}H_{34}$ and n-$C_{17}H_{36}$ in liquids.[8,9] However, such an extent of discordance should be allowable in the case of the complicated polyethylene samples.

On the other hand, the methyl, ethyl, and butyl branches have almost no influence of the irradiation, whereas trans and cis double bonds significantly increase in concentration with increasing radiation dose. In particular, the amount of the trans double bonds increases to the level of the cis double bonds, although the trans double bonds are not included in the unirradiated fractions. Almost similar results were also obtained in the irradiation of the low molecular weight polyethylene (HW). These results are in good accord with those previously reported by Randal et al.[5-7] Further discussion will be given somewhere together with the results of the irradiation in the solid state.[10]

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Registry No. Polyethylene, 9002-88-4.

Gelation of Semidilute Polymer Solutions by Ion Complexation: Critical Behavior of the Rheological Properties versus Cross-Link Concentration

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ABSTRACT: The gelation of hydrolyzed polyacrylamide solutions by addition of chromium(III) has been investigated by using physicochemical and rheological approaches. First, we have studied the formation of cross-links by complexation using UV-visible spectroscopy and dialysis. Comparison with a low molecular weight model of the polymer has allowed us to understand the influence of specific polymer effects and to delimit the range of HPAM and Cr(III) concentrations within which the link concentration can be determined. Second, we have investigated the steady-state viscosity and the steady-state elastic modulus of samples of constant polymer concentration and various Cr(III) concentrations. In the vicinity of the gelation threshold, the variations of the rheological quantities versus the cross-link concentration have been interpreted in terms of critical behavior. The exponents have been found in good agreement with the scalar percolation predictions; the prefactors and the width of the critical region have been described in terms of the gelation of semidilute polymer solutions.

1. Introduction

Several works have been recently devoted to the study of gelation and, in particular, of the critical behavior of the rheological properties near the sol–gel transition.[1-5] In such studies, comparison of the experimental results with the models of the transition, classical theory, or percolation model requires a good knowledge of the number of cross-links formed in the medium, which is difficult to achieve for many gelling processes (copolymerization or polycondensation processes). In the present work,

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