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Mechanism for Long-Chain Branching in the Thermal Degradation of Linear High-Density Polyethylene

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ABSTRACT: A mechanism for long-chain branching in the thermal degradation of a linear high-density polyethylene (LHDPE) has been discussed on the basis of the changes in the contents of *trans*-vinylene groups and long-chain branches (LCB) in the polymer residues, especially the average number of LCB per molecule (L). From the *trans*-vinylene/LCB content ratios, the probability of the recombination termination reaction between primary and secondary macroradicals seems to be 2–5 times that of the disproportionation reaction. The above-mentioned ratio was about 0.3 at all temperatures, but the value of L increased with a decrease in temperature. The value of L at 350 °C suggests the formation of a branched polymer having one LCB per molecule. Moreover, these facts suggest the formation of branched polymers having several long branches and of cross-linked polymers at temperatures below 350 °C. It is thought that the branches are formed by recombination via intermolecular chain transfer of two radicals occurring by initiation in a cage and lead to molecular weight increases. Furthermore, if either of the radicals diffuses outside the cage, the usual propagations (depolymerization and intra- and intermolecular radical transfers) and terminations take place, leading to the formation of volatiles and a decrease in molecular weight. Thus both the molecular weight increase and the degradation reactions are considered to be dependent on the rate of diffusion, in relation to the viscosity of the media, of the two radicals outside the cage.

The mechanism of thermal degradation of polymers is an interesting subject not only from the standpoint of fundamentals of a polymer reaction but also with respect to understanding heat-resisting characteristics, polymer processes such as extrusion or injection molding, and the effective utilization of plastic wastes. Recently, the thermal degradation of polymers has been also widely reinvestigated to synthesize new compounds, including polymers, oligomers, and monomers,[1] and is very interesting from the standpoint of unit reactions in the synthetic chemistry.

The mechanisms of thermal degradation of polyethylene (PE) have been so far discussed as typical random scission type reactions from changes in their intrinsic viscosity and the chemical structures of the thermally degraded polymer or by observing changes in the volatilization and the compositions of the volatiles. In the initial stage of the reaction, a large decrease in the intrinsic viscosity of the thermally degraded polymer occurs. This phenomenon has been interpreted to be caused by the scission of the weak link in the polymer chain[2,3] or by a random intermolecular chain transfer of macroradicals followed by β scission.[4] Moreover, it has been interpreted from various experimental studies[5-7] that a small quantity of volatiles is formed by intramolecular chain transfer (back-biting) of macroradicals followed by β scission. Recently, however, a molecular weight increase reaction as well as the above-mentioned molecular weight decrease reaction has been reported. Witt et al.[8] and Tanaka et al.[9] have suggested by studying the melt viscosity of high-density polyethylene (HDPE) at about 200 °C that molecular weight increases when long-chain branches (LCB) are formed. Holmström et al.[10] carried out the heat treatment of low-density polyethylene (LDPE) and HDPE at temperatures between 284 and 355 °C under nitrogen containing 0.0005–0.16% oxygen. They observed both a molecular weight increase and formation of LCB on the basis of their studies of gel permeation chromatography (GPC) and intrinsic viscosities of the degraded PE. These facts are extremely important for the proposal of a detailed reaction mechanism, and the formation of a branched polymer having a controlled average number of LCB is expected.

We have established a quantitative method for determining the number of double bonds (terminal vinyl, *trans*-vinylene, and vinylidene groups), terminal methyl groups, and LCB by ^{1}H and ^{13}C NMR spectroscopies, taking into account the currently available information related to the structural changes in the thermally degraded polymer.[11] In this paper, a mechanism for the formation of LCB in the thermal degradation of a linear high-density polyethylene (LHDPE) is discussed on the basis of quantitative results of the contents of these functional groups, especially the average number of LCB per molecule (L) in the thermally degraded polymer.

Experimental Section

Material. The LHDPE sample used was a Phillips-type PE, which is free of branching and contains one terminal vinyl group per molecule.[11] The molecular weights were as follows: M_w = 15.0 × 10^4 (by light scattering); M_n = 1.4 × 10^4 (by osmometry). These data have been furnished by the supplier of the LHDPE sample.

Apparatus. Details of the apparatus used and the procedures used for this experiment have been described in a previous report.[11] One gram of sample was degraded under a pressure of 4 mmHg and flowing nitrogen (99.999% purity), which was reported to contain 0.0007% oxygen by volume. After the reaction,

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Table I
Changes in Volatilization, M_w, and M_n with Thermal Degradation of LHDPE

temp, °C	time, min	volatilization, %	M_w[a]	M_n[a]	M_n[b]
350	180	4.6	24000	5900	7900
	240	5.7	34000	5800	6800
	300	8.5	29000	3700	6500
370	60	4.1	14000	3600	7300
	120	6.1	12000	3200	5300
	180	8.3	9100	2100	3700
	240	14.5	7000	1900	3100
390[c]	30	5.1			5100
	60	5.7	5000	1800	3300
	120	11.4			1700
	180	16.8	2700	1200	1400

[a] By GPC. [b] By NMR. [c] From ref 11.

Table II
Double-Bond Distribution in Thermally Degraded LHDPE

temp, °C	time, min	terminal $-CH=CH_2$, mol %	trans $-CH=CH-$, mol %	$>C=CH_2$, mol %
350	180	58	30	12
	240	60	35	5
	300	53	36	11
370	60	70	26	4
	120	61	30	9
	180	62	25	13
	240	51	37	12
390[a]	30	74	21	5
	60	66	28	6
	120	76	22	2
	180	72	24	4

[a] From ref 11.

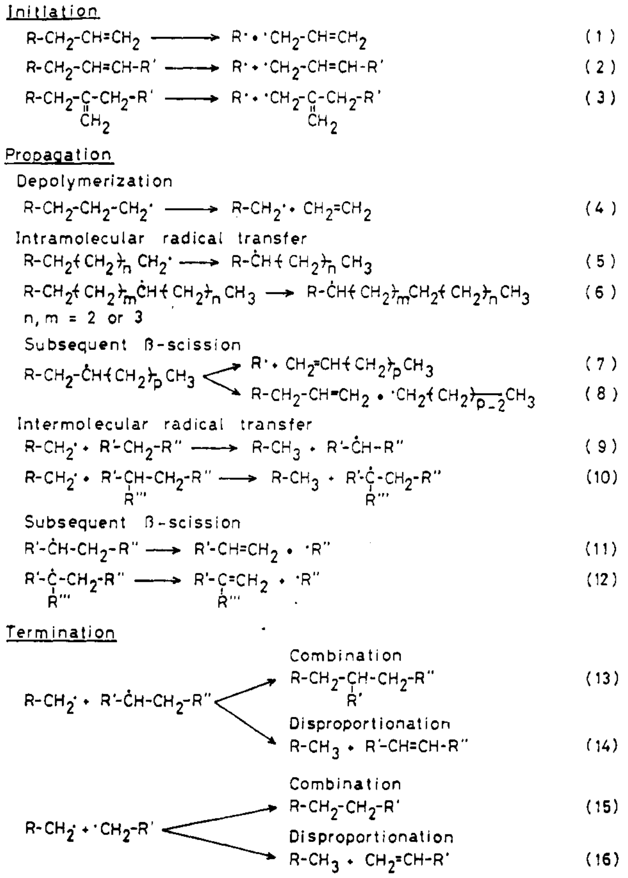

Figure 1. Reaction scheme for thermal degradation of polyethylene (from ref 10).

the thermally degraded polymer in the flask was dissolved in xylene and then reprecipitated with methyl alcohol. The reprecipitate was used as a sample for analysis after vacuum drying.

NMR Analysis. ^{13}C NMR spectra were measured with a JEOL JNM-FX100 spectrometer operating at 25.05 MHz and 110 °C with an internal lock. The protons were decoupled from the carbon nuclei using a random noise decoupling field. The concentration of the sample was approximately 10% (w/v) in a 1:3 (v/v) mixture of *o*-dichlorobenzene and benzene-d_6. Hexamethyldisiloxane (HMDS) was used as an internal standard (2.0 ppm from tetramethylsilane, Me_4Si). The 10-mm sample tubes were deaerated by several freeze-pump-thaw cycles and after nitrogen gas was admitted into the evacuated tube, sealed. Spectral widths were 2 kHz, with 8192 data points acquired on a JEC 980 computer. Pulse widths of 45° and approximately 6 μs and pulse repetition times of 20 s were used. A typical experiment was performed for about 10–45 h. These conditions assumed that equilibrium magnetization was attained and that saturation of a resonance would not occur.

^1H NMR spectra were measured with a JEOL JNM-FX100 spectrometer operating at 99.6 MHz and 110 °C with an internal lock. Although sample concentrations and the preparation of sample tubes were the same as those for carbon-13 nuclei, 5-mm sample tubes were used for ^1H NMR spectra. Spectral widths were 1 kHz, excluding the overflowing spectral region except for the chemical shift range of about 3–6 ppm, with 8192 data points acquired on a JEC 980 computer. Pulse widths of 8 μs (a 45° pulse) with a pulse repetition of 10 s and 5000–16 000 scans were used.

The number of double bonds, the concentration of terminal groups, and the LCB per 1000 C in the thermally degraded polymer were determined from the signal intensities of the individual methylene carbons of interest. The concentrations of each functional group, average number of double bonds per molecule (*f*), and average number of LCB per molecule (*L*) were calculated by the equations given in the previous report.[11]

Characterization. Number-average and weight-average molecular weights (M_n and M_w) and molecular weight distributions were measured by GPC (Toyo Soda HLC-811). The calibration line was produced by standard polystyrene, and 11.0 was used as the *Q* factor without intrinsic viscosity measurements.

Results and Discussion

A summary of changes in volatilization, M_w, and M_n with thermal degradation is given in Table I. The double-bond distribution and concentration of each functional group per 1000 C are given in Tables II and III, respectively.

Holmström et al.[10] have proposed a detailed radical chain mechanism, but only qualitatively, by considering the bond dissociation energy (*D*) of various C–C bonds and the activation energy (E_a) for various elementary reactions. This mechanism is given in Figure 1. By comparing the bond dissociation energies (*D* values), one can establish the most important initiation as the scission of the allylic C–C bond ($D \approx 61.5$ kcal/mol).[12] In the propagation stage, the activation energy for the formation of ethylene by depolymerization (eq 4) is about 26 kcal/mol with respect to the model compound[13] and those for the intermolecular radical transfer (eq 9 and 10) are about 10 kcal/mol for both reactions. Activation energies for the subsequent β scission are about 27 kcal/mol relative to eq 7, 8, and 11 and about 23 kcal/mol with regard to eq 12.[13] The recombination and disproportionation termination reactions shown in eq 13–16 have E_a values of ~0 kcal/mol.[14] From such considerations of energies of activation and bond dissociation, it appears that the back-biting reactions (eq 5 and 6) and intermolecular radical-transfer reactions (eq 9 and 10) are much more likely to occur than the depolymerization reaction (eq 4). The results obtained in this experiment can be approximately interpreted by using these elementary reactions. However, a quantitative explanation should be based upon the kinetic considerations

Table III

Changes in the Contents of Terminal Methyl Groups, Double Bonds, and Long-Chain Branching in Thermally Degraded LHDPE

temp, °C	time, min	terminal $-CH_3$ per 1000 C[a]	terminal $-CH{=}CH_2$ per 1000 C[a]	trans $-CH{=}CH-$ per 1000 C[b]	$>C{=}CH_2$ per 1000 C[b]	LCB $-\overset{|}{\underset{|}{C}}-$ per 1000 C[b]	$\frac{[-CH{=}CH_2]}{[-CH_3]}$	$\frac{[-CH{=}CH-]}{[-\overset{|}{\underset{|}{C}}-]}$	$\frac{[>C{=}CH_2]}{[-\overset{|}{\underset{|}{C}}-]}$	L[c]	f[d]
350	180	4.2	1.1	0.6	0.2	1.8	0.3	0.3	0.13	1.00	1.07
	240	5.0	1.0	0.6	0.1	1.9	0.2	0.3	0.05	0.91	0.84
	300	6.3	0.7	0.5	0.1	2.7	0.1	0.2	0.05	1.24	0.59
370	60	4.4	1.4	0.5	0.1	1.3	0.3	0.4	0.06	0.59	0.88
	120	6.1	1.2	0.6	0.2	2.1	0.2	0.3	0.08	0.79	0.74
	180	9.1	1.9	0.8	0.4	3.4	0.2	0.2	0.12	0.90	0.83
	240	12.4	1.2	0.9	0.3	4.6	0.1	0.2	0.06	1.02	0.27
390[e]	30	5.4	2.4	0.7	0.2	1.8	0.4	0.4	0.09	0.61	1.08
	60	8.6	2.2	0.6	0.1	2.3	0.3	0.3	0.04	0.54	0.69
	120	17.0	2.1	1.3	0.1	4.2	0.1	0.2	0.01	0.57	0.49
	180	20.1	4.8	2.8	0.2	6.1	0.2	0.5	0.02	0.65	0.83

[a] By ^{13}C NMR. [b] By ^{1}H and ^{13}C NMR. [c] Average number of LCB per molecule. [d] Average number of double bonds per molecule. [e] From ref 11.

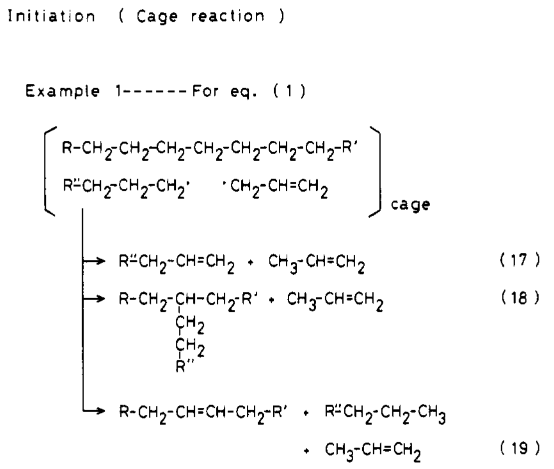

Figure 2. Reaction scheme for initiation in the cage.

of each elementary reaction. Mita[15] has inferred the energies of bond dissociation and activation and preexponential factors (A) for the polymeric elementary reactions from those for the reactions of model compounds and low molecular weight compounds and has kinetically described the effect of structures on thermal degradation of polymers. Adopting for our experiment the kinetic parameters $A = 10^{13}$ s^{-1} [15] and $E_a = D = 61.5$ kcal/mol for initiation, $A = 10^{13}$ s^{-1} [15] and $E_a = 26$ kcal/mol for depolymerization, and $A = 10^7$–10^8 L·mol^{-1}·s^{-1} [15] and $E_a = 10$ kcal/mol for intermolecular radical transfer, we can reasonably understand why propagation per initiation is overwhelmingly large. Terminations are recombination reactions and disproportionation reactions caused by bimolecular macroradicals. The zero activation energies for the two reactions means that the macroradicals can completely react with each other if they collide. In practice, however, the termination reaction is a diffusion-controlled reaction and the rate constant is effectively dependent on the rate of diffusion of the macroradicals in the media.[15] In thermal degradation of PE, the rate of termination can be expected to be remarkably small in the earlier stage of the reaction, whereas it is expected to be large in the later stage, but the dependence of the rate of diffusion on the termination in thermal degradation of polymers is not elucidated. As for the results obtained in this experiment, a small quantity of volatiles is formed by depolymerization and intramolecular radical-transfer reactions, especially the back-biting reactions (eq 5 and 6) followed by β scission, as mentioned above. The terminal vinyls, *trans*-vinylenes, vinylidenes, terminal methyls, and LCBs are formed by eq 7–16. The value of f should become 1, taking into account the random occurrence of the intermolecular radical-transfer reactions (eq 9–12) and the end groups of the original polymer, and should become greater than 1 with further contribution of the back-biting reaction (eq 8) and intermoleular chain transfer of small radicals formed by this reaction. Oakes et al.[2] have reported that the value of f for LDPE degraded between 295 and 360 °C under vacuum becomes about 1. However, the value of f in this experiment becomes less than 1, as shown in Table III. Although the LCB is formed according to a combination termination reaction (eq 13), the value of L should be remarkably small, taking into consideration that eq 13 is governed by a diffusion-controlled reaction. In this experiment, the most striking results are that the value of L is about 0.6 at 390 °C, 0.8 at 370 °C, and 1.0 at 350 °C, as shown in Table III. The results obtained at 350 °C show the formation of branched polymer having one long-chain branching.

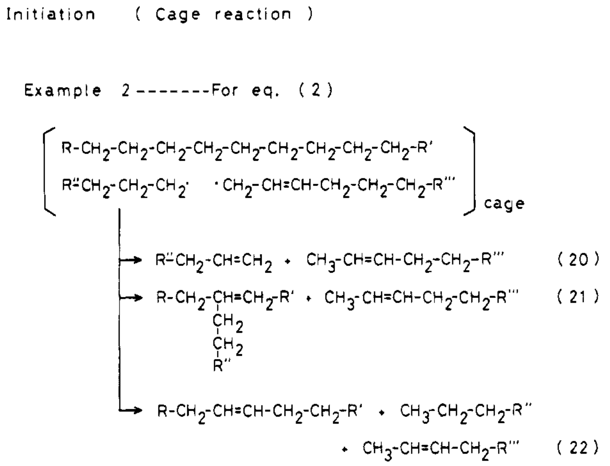

Figure 3. Reaction scheme for initiation in the cage.

Accordingly, the observed values of f and L cannot be appropriately interpreted by the usual mechanism related to especially the formation of LCB. Examples of the most probable cage reactions concerning initiation are shown in Figures 2 and 3. Here, "cage" implies the field of reaction made of the surrounding polymer segments. Figure 2 gives an initiation followed by intermolecular radical transfer and termination in the cage. This initiation is induced, predominantly via the degradation reaction, by the scission of the C–C bond at the allylic position to terminal vinyl groups that exist in the LHPDE sample used. Equation 17 corresponds to the direct disproportionation reaction. Equations 18 and 19 show that propylene and a secondary macroradical are produced via intermolecular chain transfer (hydrogen abstraction) of propenyl radical to the polymer segment forming the cage and that the produced secondary macroradical is terminated by a primary macroradical along with the recombination or disproportionation reaction. The LCB is produced in eq 18 (recombination), and *trans*-vinylene and terminal methyl groups are produced in eq 19 (disproportionation). In these cases the LCB and *trans*-vinylene groups are considered to exist in the central position of the polymer chain. With respect to the formation of propylene, Tsuchiya et al.[7] have reported that a large amount of propylene was observed in the volatile products obtained by thermal decomposition of HDPE at temperatures between 375 and 425 °C and that the propylene was produced via allylic scission of the terminal vinyl group, as represented in eq 1, followed by intermolecular radical transfer. Consequently, propylene is considered to be produced via the reactions shown in Figure 2. Figure 3 shows the initiation on eq 2 followed by a cage reaction. The LCB or *trans*-vinylene groups are produced in a manner similar to that of Figure 2. According to these reactions the *trans*-vinylene groups exist in the second position to the chain end. The three possible ways of cage reactions given in Figures 2 and 3 can also be expected in the case of occurrence of initiations by scission of the C–C bond of the polymer chain and of the α position to the branching point, but the two initiations rarely take place compared with that by the scission (eq 1–3) at the allylic position. Witt et al.[8] have reported that the melt flow index of PE having a terminal vinyl group decreases appreciably with an increase in time while that of PE having a *trans*-vinylene group does not vary. Thus PE having a *trans*-vinylene group in the immediate neighborhood of the chain end is considered to possess a relatively high thermal stability. Iida et al.[16] have observed about 5 wt % of the monoolefins having *trans*-vinylene groups in the neighborhood of the chain ends in the volatile products obtained by thermal decomposition of HDPE at 420 °C under a nitrogen atmosphere. These olefins are considered to be produced via the reactions shown in Figure 3. Consequently, in our experiment, the LCB is considered to be mainly produced via the cage reactions shown in Figure 2. According to the thermodynamic data, in both eq 18 and 19, the value of the activation energy for the hydrogen abstraction of a primary macroradical from the polymer segments forming the cage is somewhat lower than that of propenyl radical, and the abstraction of the former should be more favorable than that of the latter. However, the thermodynamic interpretations are in conflict with our experimental results. Recently, employing various solvents, Mita et al.[17] used the decay of delayed fluorescence after a 10-ns nitrogen laser pulse to study the effects of the degree of polymerization (DP) and solvent on the rate of intra- and intermolecular quenching of triplet anthryl groups attached to the chain end of polystyrene and reported that the intermolecular quenching rate constant decreases with DP and that the DP dependency is much greater than that for collision frequencies between reactive groups on the polymer chain and in low molecular weight compounds.[18] From these facts, we assume that the intermolecular hydrogen abstractions, which are generally regarded as activation-controlled reactions, produce a diffusion-controlled reaction in the molten polymer. As a result, it is expected, in contrast to the activation-controlled reaction, that the rate of hydrogen abstraction of propenyl radical is faster than that of the primary macroradical.

Thus the *trans*-vinylene/LCB ratios seem to express the results of competing reactions of disproportionation and recombination and apparently correspond to the ratios of kinetic constants for the two reactions. The ratio was about 0.3 at all temperatures. This suggests that the recombination reaction occurs more often than the disproportionation reaction. Arnett et al.[19] have undertaken a kinetic study of thermal degradation of HDPE at temperatures between 300 and 400 °C under vacuum, using the change in average molecular weights of the thermally degraded polymer. As for the termination reaction between primary macroradicals in eq 15 and 16, they have estimated that the probability of the occurrence of the recombination is about 10 times that of the disproportionation. In the present experiment, it is 2–5 times. Consequently, when the two radicals generated by initiation undergo a cage reaction, LCB is produced and leads to a molecular weight increase, whereas if either of the radicals diffuses outside the cage, the usual propagations take place and lead to the formation of volatiles and a drop in molecular weight. With respect to the molecular weight decrease, it is well-known that intermolecular chain transfer of macroradicals is important,[4] but chain transfer of small radicals such as allylic radicals formed via initiation and volatile radicals produced in eq 8 has been neglected. However, as mentioned above, the behavior of these small radicals is extremely significant. The rate of diffusion of the radicals formed outside the cage decreases with a decrease in temperature because of the increasing viscosity of the media. Consequently, the above cage reactions predominate with decreasing temperature. The large M_w/M_n ratio at the lower temperature, as shown in Table I, is also caused by the termination in the cage. Therefore it can be reasonably understood that the value of f becomes less than 1 and that the value of L increases with decreasing temperature. These facts suggest the formation of branched polymers having several long-chain branches and the formation of cross-linked polymers at temperatures below 350 °C.

In conclusion, the molecular weight increase and the decrease in the thermal degradation of PE are considered to be dependent on the rate of diffusion, in relation to the viscosity of the media, of the two radicals produced by initiation outside the cage.

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Cross-Link Formation in a Solid Photopolymer Based on the Chromophore 1,2-Diphenylcyclopropene

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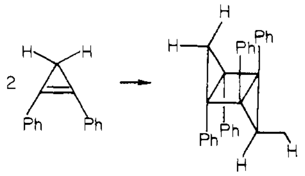
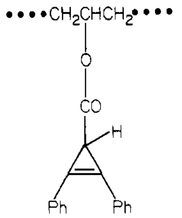
ABSTRACT: The absolute quantum yield of cross-link formation in a photopolymer based on the photoreactive chromophore 1,2-diphenylcyclopropene (CP) approaches the theoretical maximum for a single-step cross-linking process. In the matrix, only a small fraction of chromophores (~4%) are in reactive configurations, and it appears from the fluorescence behavior of the films that these are associated with excimers. Chemical analysis reveals the formation of tricyclic dimers in the irradiated films, as anticipated by DeBoer et al.,[2,3] which indicates that the primary cross-linking step is cycloaddition between the double bonds of two suitably oriented cyclopropene rings. The high initial quantum yield of the photoreaction coupled to a low concentration of reactive sites implies extensive energy migration in the system. From lifetime measurements, the migration range of the triplet excitation in the matrix is estimated at 150 Å.

In the course of work on the photochemistry of phenyl-substituted cyclopropenes[1,2] DeBoer and Breslow observed the facile dimerization of the excited triplet states of these molecules.



(2 + 2)Cycloaddition was the only reaction of the triplet state of 1,2-diphenylcyclopropene, and the corresponding tricyclic dimers were the principal products in the sensitized photolysis of 1,2,3-triphenylcyclopropene and of 1,2-diphenylcyclopropene-3-carboxylate.[2] The high quantum efficiency of the cycloaddition reaction in solution[1] suggested its use as a photo-cross-linking device. Incorporation of cyclopropene groups into suitable polymers did indeed produce highly photosensitive materials.[3-6]

We have now investigated a polymer (PCP) obtained by the partial esterification of poly(vinyl alcohol) with the acid chloride of 1,2-diphenylcyclopropene-3-carboxylic acid.



PCP

In the sample available to us 30% of the esterifiable positions were occupied by CP groups. The absolute

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