Conclusions

The "alternating" copolymers of 2VN and MAn contain a small but significant fraction of the 2VN–2VN and MAn–MAn diad sequences regardless of the monomer feed ratio. The 2VN–2VN diad sequence provides excimer forming sites, and a small difference in this diad fraction is dominantly reflected in the fluorescence spectra of the 2VN–MAA copolymers in aqueous solution. Alternating sequences that result in crowded naphthalene residues in a compact polymer structure in aqueous solution (particularly at acidic pH's) would provide blue-shifted excimers with a range of stabilities. Since the number of the excimer forming sites in a polymer chain are extremely small as compared to the total number of the naphthalene residues, the efficient down chain energy migration through the alternating 2VN–MAA sequences plays an important role in concentrating the excitation energy onto the excimer traps.

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Registry No. (2VN)(MAn) (copolymer), 106821-90-3; (2VN)(DMM) (copolymer), 117652-10-5; 2VN, 827-54-3; MAn, 108-31-6.

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Photocross-Linking of EPDM Elastomers. Reactions with Model Compounds Studied by Electron Spin Resonance

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ABSTRACT: The initial radical reaction to occur in photocross-linking of EPDM elastomers was studied by ESR on model compounds (ethylidenenorbornane, dihydrodicyclopentadiene, *trans*-2-heptene, and *cis*-2-heptene). After cleavage of 1-hydroxycyclohexyl phenyl ketone to benzoyl and hydroxycyclohexyl radicals, the benzoyl radical abstracts the most labile hydrogens on the model compounds to form allylic radicals. These radicals were trapped using pentamethylnitrosobenzene as a spin-trapping agent. When *trans*-2-heptene was used, the benzoyl radical added to the unsaturation to some extent to form a rather stable radical. This would explain the measured lower reactivity in cross-linking of its EPDM than with the other diene elastomers.

Introduction

By copolymerization of ethylene, propylene, and a diene, elastomeric products (EPDM) can be produced, which unlike polydiene rubbers contain a saturated backbone. This is an advantage with respect to oxidative and photolytic aging which in polydienes leads to cleavage of the main chain. The unsaturation is pendant on the main chain and incorporated by copolymerization with either hexadiene, ethylidenenorbornene, or dicyclopentadiene.

It is possible to cross-link the EPDM rubbers by using ultraviolet light and radical-producing photoinitiators.[1] The advantage of photocross-linking is primarily the saving of energy. In conventional systems with thermal initiation, the energy is applied to both the rubber and the initiator. In photocross-linking, the energy can be transferred selectively to the photoinitiator. A secondary advantage is

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that less toxic compounds are used and that lower amounts of volatile products are formed than in conventional vulcanization.[2]

In earlier work, it has been reported that the order of reactivity in thermally initiated cross-linking with benzoyl peroxide of the three types of EPDM rubber are ethylidenenorbornene ≥ dicyclopentadiene > hexadiene[3] and that the same order is found in photocross-linking.[4]

It has further been reported that no photocross-linking of saturated EPM rubbers with hydroxyalkylacetophenone-type initiators occurs.[4] The photoinitiated cross-linking reaction evidently takes place at the diene units, but how?

The aim of this work is to determine the mechanism of the cross-linking reaction. This is done by studying the radicals formed on model compounds using electron spin resonance.

Experimental Section

2-Heptene (cis and trans) from Aldrich was used as received. Ethylidenenorbornane (ENA, 2-ethylidenebicyclo(2.2.1)heptane), which was distilled twice, was kindly supplied by Exxon Research and Engineering Co., Linden, NJ. Dihydrodicyclopentadiene (2H-DCPD) was synthesized according to ref 5. Benzil from Aldrich was recrystallized twice from acetone. The photoinitiator 1-hydroxycyclohexyl phenyl ketone from Ciba Geigy (Fribourg, Switzerland) was used as received. For the spin-trapping experiments, pentamethylnitrosobenzene was synthesized according to ref 6 with the specification that $Tl(OCOCF_3)_3$ was dissolved in trifluoroacetic acid, the pentamethylbenzene was dissolved in acetonitrile, the temperature of the reaction was 0 °C and the thallium–pentamethylbenzene was precipitated during evaporation of the solvent. All samples were placed in 3-mm Suprasil quartz ESR tubes (PQ 706, Wilmad Glass Co., Inc., Buena, NJ) evacuated with the freeze–thaw method with a vacuum of 5×10^{-6} torr and sealed, under red light. The samples for the spin-trapping experiments were used immediately, and the samples for laser irradiation with 1 wt% benzil were kept in darkness until used. The ESR instruments used were a Varian Century Series Model 115 ESR spectrometer equipped with an XeCl 308-nm laser (150 mJ, 9 mW with a pulse rate at 1.5 Hz) and a Bruker EPR 420 equipped with a Philips SP 500-W Hg lamp with the beam focused into the cavity. A 295-nm shortcut filter from Oriel Corp. (Stamford, CT) was placed in front of the cavity in the spin-trapping experiments to avoid unwanted reactions.

As a first experiment, the spin trap itself, pentamethylnitrosobenzene (1×10^{-3} g) dissolved in the model compounds (0.1 mL), was irradiated with UV light, and a diaphragm was used to prevent detectable amounts of radicals forming after at least 10 min of irradiation. This setup was used for all spin-trapping experiments.

Then the photoinitiator (1×10^{-4} g) and spin trap (1×10^{-4} g) were dissolved in dichloromethane (0.1 mL) and irradiated for durations ranging from 0.1 s to 3 min. Photoinitiator (1×10^{-5} g) and spin trap (1×10^{-5} g) were dissolved in model compounds (0.1 mL) to produce three samples which were irradiated as before. Spectra was recorded before irradiation, after each irradiation, and finally during a last irradiation.

Result and Discussion

Most of the conventional photofragmenting initiators form benzoyl as one of the radicals. In the system used, benzoyl is the only sufficiently reactive radical to abstract hydrogen or to add to unsaturation. It would therefore be desirable to selectively produce this radical to get as simple spectra as possible.

Laser Experiments. Laser irradiation (308 nm) of benzil dissolved in model compounds showed a broad ESR singlet at low temperatures (183 K). The signal disappeared at higher temperatures except for *trans*-2-heptene, which showed a 12-line spectrum (Figure 1) at −11 °C. This spectrum could be seen for approximately 15 min and is attributed to the 2-benzoylheptyl radical (I) shown in Table I. The formation of this radical essentially goes by at least three steps. Step 1. Cleavage of benzil to form two benzoyl radicals:

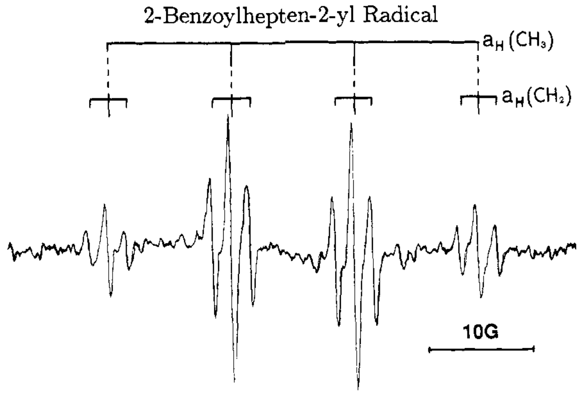


Figure 1. ESR spectrum of 2-benzoyl-3-heptyl radical produced by laser irradiation (308 nm) of a solution of benzil and *trans*-2-heptene at 262 K.

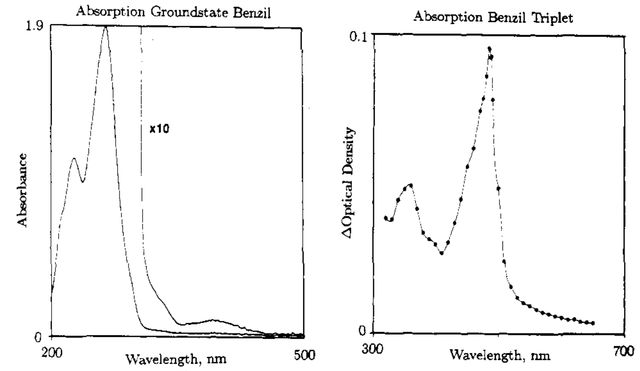
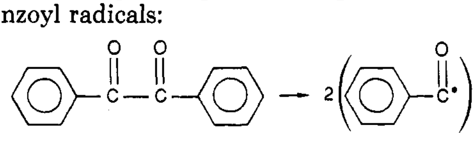
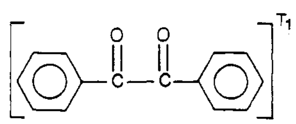


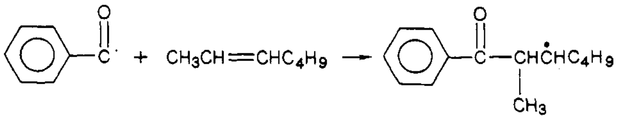
Figure 2. Ultraviolet absorption spectrum of benzil (left) and absorption spectrum of benzil in the first excited triplet state (right) (recorded by Scaiano and McGimpsey and published by permission from ref 7).


(1)

This cleavage does not occur upon normal UV irradiation. In such a case, one photon is absorbed to produce the first excited triplet state of benzil:



This species does not cleave, and consequently benzoyl radicals cannot be formed. But, if laser light is used, it may cleave benzil by a biphotonic process[7] if the absorbtion spectra of benzil in the ground state and the absorption spectra of benzil in the first excited triplet state show an overlap of the emitted light. These spectra (Figure 2) show an overlap. The excited triplet of benzil may then absorb one more photon and form a higher excited triplet state with enough energy to cleave the central bond. When the addition has formed the new benzoylheptyl radical, step 2, no further additions can take place.

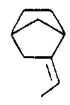
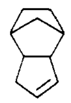
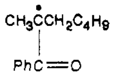
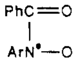
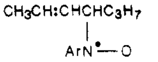
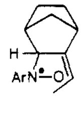
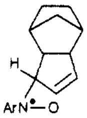
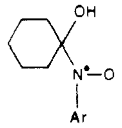
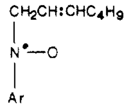
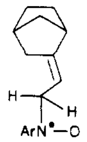

(II)

(2)

There are only two possibilities:

Table I

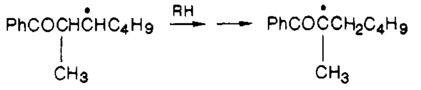
Radical Adducts, Conditions of Irradiation, and Irradiated Samples (Hyperfine Couplings in Gauss)

	model compounds			
conditions	$\mathrm{CH_2Cl_2}$ (inert solvent)	$\mathrm{CH_3CH{:}CHC_4H_9}$[a]	 [b]	 [c]
laser (308 nm), benzil		 $\mathrm{CH_3\dot{C}(C(=O)Ph)CH_2C_4H_9}$ trans I $a_H(\mathrm{CH_3})$ = 11.1, $a_H(\mathrm{CH_2})$ = 1.8, g = 2.00	no	no
Hg lamp (spin trap)	 $\mathrm{PhC(=O)-N^{\bullet}(-O)Ar}$ III a_N = 8.6, g = 2.0068	 $\mathrm{CH_3CH{:}CHCH(C_3H_7)-N^{\bullet}(-O)Ar}$ V *trans*: a_N = 12.8, a_H = 6.6, g = 2.0060 cis: a_N = 13.4, a_H = 7.8, g = 2.0060	 VIII a_N = 12.8, a_H = 3.6, g = 2.0060	 X a_N = 13.5, a_H = 9.4, g = 2.0060
	 IV a_N = 13.1, g = 2.0060	 $\mathrm{CH_2CH{:}CHC_4H_9-N^{\bullet}(-O)Ar}$ trans VII a_N = 13.1, a_H = 6.6, g = 2.0060	 IX a_N = 13.1, a_H = 5.5, g = 2.0060	

[a] *cis*- and *trans*-2-heptene. [b] Ethylenenorbornane. [c] Dihydrodicyclopentadiene.

I. Combination of radicals. This is inhibited somewhat by the external magnetic field which causes the spin of the unpaired electrons to orient in the same direction. Recombination, which requires opposite directions of the electron spins, is thereby prevented. (Outside the magnetic field there is no such effect.)

II. Intermolecular abstraction of hydrogen until the most stable radical possible in the system is produced. The radical first produced (II) will abstract a hydrogen from the surroundings. Any radical in the system may now abstract the labile hydrogen attached to the carbon bearing the benzoyl group and form the identified radical (I), step 3.



$$\mathrm{PhCOCH(CH_3)\dot{C}HC_4H_9} \xrightarrow{RH} \mathrm{PhCO\dot{C}(CH_3)CH_2C_4H_9} \qquad (3)$$

(II) (I)

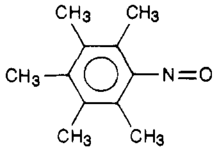
Spin Trap. To reach a sufficient concentration in our experiments, the other radicals have to be spin trapped. Spin trapping was first carried out by Lagercrantz and Forshult[8] and Janzen and Blackburn[9] in 1968, who used C-nitroso compounds and nitrones as spin traps:

$$\mathrm{R^{\bullet} + ST \rightarrow R{-}ST^{\bullet}} \qquad (4)$$

The radical adds to the spin trapping agent (ST) and produces a radical adduct stable from minutes up to days in detectable concentrations.

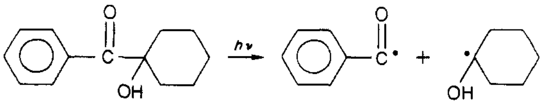
In our system, we could not obtain any information from their spin traps. *tert*-Butyl nitroxide suffers from instability and is probably decomposed by excited photoinitiator as previously reported.[10] The nitrones give sextets with unique parameters for every radical. To prove the existence of a certain radical, it has to be synthesized by other methods. Nitrosobenzene (NB) does not suffer from these insufficiences but gives a large number of lines due to coupling with all five hydrogens. A spectrum consisting several trapped unknown radicals is difficult to interpret even with computer simulation. If, however, NB is substituted in both the ortho and para positions by *tert*-butyl groups, the number of lines decreases.

Unfortunately no information was obtained here, either because of low reactivity of the trap or because the peaks from the photoinitiator obscured the peaks from the trapped model compound. In 1977 Doba et al.[11] describe a new spin trap, pentamethylnitrosobenzene, which was shown to be useful in our experiments.



(ArNO)

Photoinitiator. In these experiments, pentamethylnitrosobenzene is used as a spin-trapping agent and 1-hydroxycyclohexyl phenyl ketone as a radical source. The photoinitiator is excited by ultraviolet light and produces two radicals by a Norrish type I clevage:[12]



(III) (IV) (5)

These radicals are trapped to produce a spectrum (Figure 3) with two triplets arising from trapped benzoyl radicals (III) and trapped hydroxycyclohexyl radicals (IV), Table I. As the benzoyl group is electron withdrawing, it will have a small hyperfine coupling (hfc) with nitrogen. The adducts of trapped radicals III and IV have no hydrogens in the β position so there will be no further splitting.

Heptene. When the photoinitiator was dissolved together with the spin trap in *trans*-2-heptene, it produced

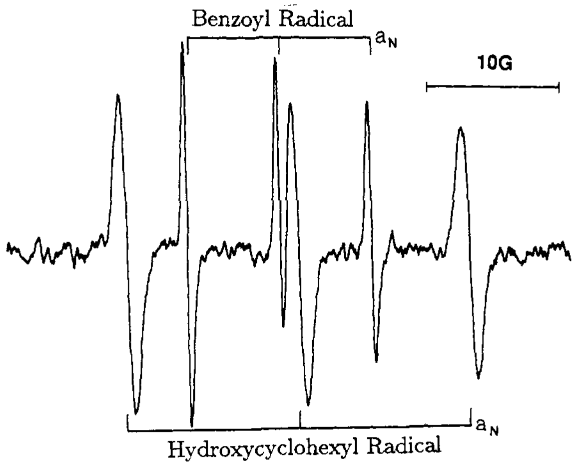


Figure 3. ESR spectrum of spin-trapped hydroxycyclohexyl and benzoyl radicals formed when 1-hydroxycyclohexyl phenyl ketone in dichloromethane was irradiated with UV light.

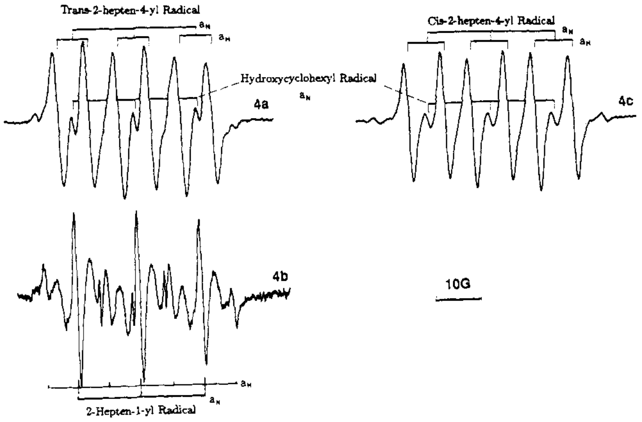


Figure 4. ESR spectra of radicals trapped when 1-hydroxycyclohexyl phenyl ketone was UV irradiated in a solution of 2-heptene and spin trap: (a) short time of irradiation of *trans*-2-heptene, (b) longer irradiation, and (c) the same in *cis*-2-heptene.

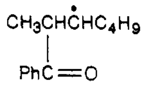
a spectrum after a short time of irradiation (0.1 s) (Figure 4a) with the hydroxycyclohexyl radical triplet and a broad six line pattern arising from the following:

1. The trapped 2-hepten-4-yl radical (V), Table I. This is formed after hydrogen abstraction of the labile allylic hydrogen.

$$\mathrm{CH_3CH{=}CHC_3H_7} \xrightarrow{\mathrm{Ph{-}\dot{C}{=}O}} \mathrm{CH_3CH{=}CH\dot{C}HC_3H_7} \quad \text{(6)}$$

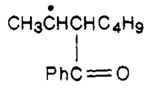
(V)

2. The adducts formed when the benzoyl radicals add to the unsaturation in heptene (VIa, VIb).



$$\mathrm{CH_3CH\dot{C}HC_4H_9} \atop {|\atop \mathrm{PhC{=}O}}$$

(VIa)



$$\mathrm{CH_3\dot{C}HCHC_4H_9} \atop {|\atop \mathrm{PhC{=}O}}$$

(VIb)

The small peaks at the sides are due to a triplet of triplets formed by hydrogen abstraction from the allylic methyl group and subsequent trapping (VII) (Table I). This adduct is formed to a larger extent upon longer irradiation (spectrum in Figure 4b).

$$\mathrm{CH_3CH{=}CHC_4H_9} \xrightarrow{\mathrm{Ph\dot{C}{=}O}} \mathrm{{}^{\bullet}CH_2CH{=}CHC_4H_9} \quad \text{(7)}$$

(VII)

The abnormal shape of the doublets of triplets is interpreted as due to all three radicals (V, VIa, VIb) which are formed, but radical V is expected to dominate. They differ just a little in splittings and g values and cannot be resolved in these spectra.

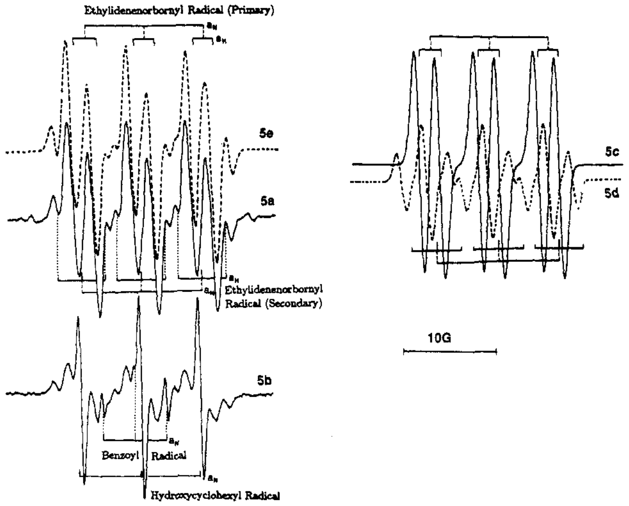
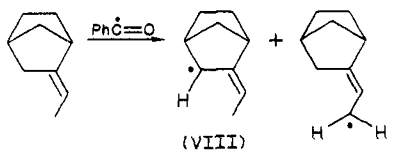


Figure 5. ESR spectra of radicals trapped when 1-hydroxycyclohexyl phenyl ketone was UV irradiated in a solution of ethylidenenorbornane and spin trap: (a) short time of irradiation and (b) longer irradiation. Simulation of spectrum a shows that it is formed by overlapping a triplet of doublets, c, with a triplet of triplets, d, to form e.

cis-Heptene gave almost the same spectrum as *trans*-heptene, Figure 4c. This spectrum is interpreted in the same way as with *cis*-heptene but with slightly different parameters (Table I).

Ethylidenenorbornane. When ENA was used, spectra 5a,b in Figure 5 were produced. These are interpreted (Table I) as due to abstraction of hydrogen in the allylic positions, followed by trapping. The spin trapping gives a six-line pattern due to radical VIII and a nine-line pattern due to radical IX (Table I).



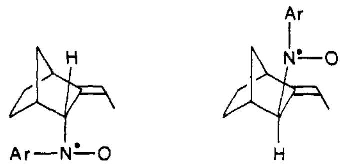
(VIII) (IX) (8)

After longer periods of irradiation, the photoinitiator radicals are also trapped (spectrum 5b).

To ensure the right interpretation, spectrum 5a was simulated using the parameters in Table I. Radical VIII with one hydrogen in the β position will give a triplet of doublets (Figure 5c). Radical IX with two hydrogens in the β position will give a triplet of triplets (Figure 5d). When 5c and 5d are superimposed, they form a spectrum (5e) in good agreement with the recorded spectrum (5a).

When hydrogen is abstracted in the allylic position, there will be an sp^2-hybridised carbon bearing one hydrogen and two carbons in one plane. Perpendicular to this plane, the half-filled p orbital will point outward.

The spin trap may then add from either side of the molecule, and a pair of diastereomers will be formed.



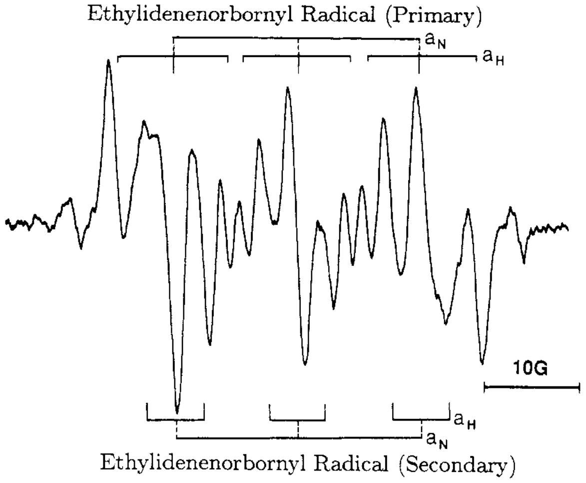


Figure 6. Spin trapping of ethylidenenorbornyl radicals at elevated temperature (343 K) giving more narrow peaks than at room temperature. Elevated temperatures also favor trapping at the methyl group before the methylene group.

Both the radical center and the β hydrogen will be in different environments. Although nonequivalent hydrogens will give different hfcs,[13] these radicals will have almost the same hfc because of the very small difference in environment.

The half-filled p orbital could overlap with the two p orbitals, forming the π bond, so another pair of enantiomers could be formed by spin trapping. This would require a change in hybridization on one of the carbons in the five-membered ring from sp^3 to sp^2, and an unfavorable strain would result. The shape of the ESR peaks reveals that there is only one type of radical present.

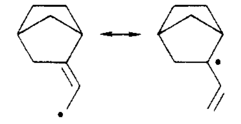
The two radicals have one β hydrogen, they will form a triplet of doublets, and they will overlap. The magnitude of the hfc by β hydrogens follows approximately the cos^2 law:

$$\text{hfc} = \text{constant} \times \cos^2 \theta$$

where θ is the dihedral angle between the half-filled p orbital and the C–H(β) bond.

The rotation of the spin trap part around the N–C bond is not fast enough to average out. On the ESR time scale, this will be seen as a number of different θ angles around the most preferred conformation and hence a line broadening.

When one allylic hydrogen on the methyl group is abstracted, the radical will be located on the methyl group carbon and on the methine carbon by resonance.


(9)

However, spin trapping does not occur of the tertiary radical, although this form is dominant. The reason for this behavior is believed to be sterical hindrance. Trapping does occur on the methyl carbon. The spin trap part will not be able to rotate at ESR frequency because of the bulky groups.

Raising the temperature (343 K) favors formation of the spin adduct, increases the rate of rotation, and causes some narrowing (Figure 6).

If addition of the benzoyl radical to the double bond does occur, a tertiary radical would be formed that could, according to earlier reasoning, not be trapped. Formation of this radical must be considered as possible.

Dihydrodicyclopentadiene. When 2H-DCPD is irradiated with photoinitiator and spin trap, it produces a spectrum (Figure 7). This spectrum consists of a triplet of doublets formed when one of the hydrogens in the allylic position is abstracted and the so-formed radical (X) is trapped (Table I).

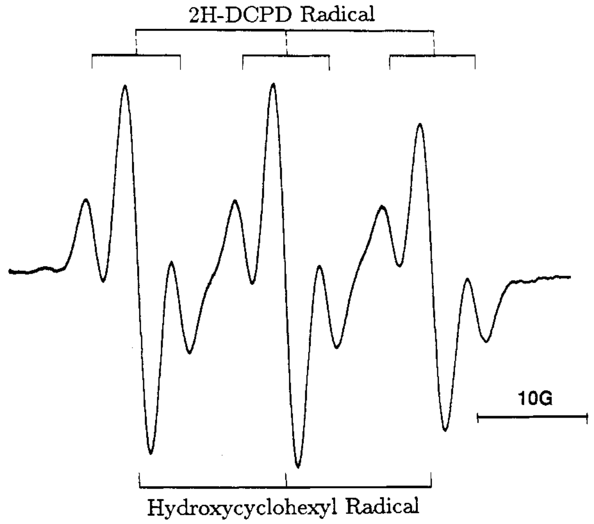
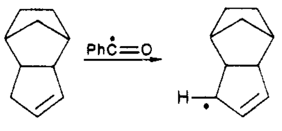
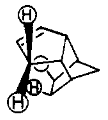


Figure 7. ESR spectrum of radicals trapped when 1-hydroxycyclohexyl phenyl ketone is UV irradiated in a solution of dihydrodicyclopentadiene.



(10)

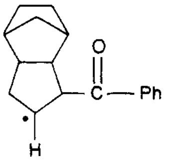
^{13}C NMR spectrum of 2H-DCPD shows 10 peaks (32.2, 130.3, 132.9, 52.9, 39.6, 25.2, 22.0, 41.2, 42.5, 41.0 ppm, TMS) which clearly indicates the endo form.[14]



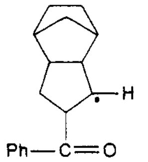
10

Here again it can be seen that the hydrogens are not equivalent. Once the allylic radical has been formed, the spin trap can only approach from one side due to sterical hindrance on the other side. Only one radical adduct is formed.

The two unsaturated carbons have almost the same probability of adding a benzoyl radical. This should result in two different radicals after spin trapping.



(XI)



(XII)

Radical XI could possibly be trapped from both sides (although one with preference) and radical XII only from one side. Three different adducts should form and result in a distorted peak. It is therefore believed that abstraction is dominating. This can possibly be shown by reacting a hydrogen abstracting species with the 2H-DCPD.

The peak to the right in the hydroxycyclohexyl triplet (Figure 7) is somewhat distorted and proves that there is something more hidden behind. It may be the adducts formed by addition to 2H-DCPD.

In most cases, an allylic radical is formed. This is not surprising. More reactive radicals in the system may quickly rearrange to form the more stable allylic types.

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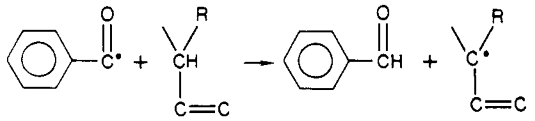
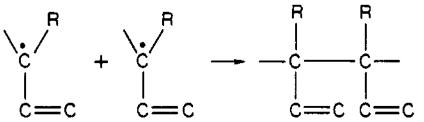
This means that for every radical formed one benzoyl radical is necessary:


(11)

Cross-linking may only occur when two allylic radicals recombine:


(12)

Hence, for every cross-link to be formed, two initiator molecules are necessary.

Conclusions

From studies with model compounds, it is concluded that macroradicals are formed when photocross-linking EPDM rubbers are mainly of the allylic type, which are formed by hydrogen abstraction by benzoyl radicals. The cross-links are formed when these allylic radicals combine.

However, rubbers containing 1,4-hexadiene as a third unsaturated comonomer are cross-linked more slowly. This is explained by the fact that the relatively stable benzoylheptenyl radical is formed which cannot combine with itself. This radical can probably act as a trap for the reactive benzoyl radical which would otherwise give cross-linking.

This latter mechanism may also explain the poor results achieved when polyisoprenes or polybutadienes have been cross-linked with hydroxyalkylacetophenone-type photoinitiators.

Acknowledgment. This work was supported by STU, the Swedish Board for Technical Development, which is gratefully acknowledged by the authors.

Registry No. ENA, 2146-40-9; 2H-DCPD, 4488-57-7; *cis*-2-heptene, 6443-92-1; *trans*-2-heptene, 14686-13-6; benzil, 134-81-6; 1-hydroxycyclohexyl phenyl ketone, 947-19-3; pentamethylnitrosobenzene, 65594-36-7.

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Fluorescence Polarization Study of the Poly(acrylic acid)/Poly(ethylene oxide) Interpolymer Complex in Aqueous Solution

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ABSTRACT: Fluorescence polarization studies of acenaphthylene (ACE) labeled poly(acrylic acid) (PAA) have demonstrated that the complexation between PAA and poly(ethylene oxide) (PEO) results in a tightly packed, sterically restricted conformation in which the mobility of the PAA segments is inhibited. Complexation is maximized when the PAA and PEO repeat unit concentrations are equal, while neutralization of <10% of the carboxylic acid groups restores the initial (uncomplexed) fluorescence polarization of the ACE probe. Time-resolved measurements indicate that the motion of the polymer-bound ACE probe is anisotropic, and information concerning the conformational dynamics of the PAA/PEO complex at various extents of association has been obtained.

Introduction

In nature, interactions between macromolecules play an important role in determining the structures and functions of biological systems.[1] However, the inherent complexities of biological systems make their direct investigation difficult. It is for this reason that synthetic polymers of known structure have been widely used as simple models for biological macromolecules.[2] Particular interest has been directed at synthetic water-soluble polymers, with polyelectrolytes being an important class of such polymers that have been studied by many researchers.[3–5]

One of the most studied systems is the hydrogen-bonded interpolymer complex formed in aqueous solution between poly(ethylene oxide) (PEO) and the polyelectrolyte poly(acrylic acid) (PAA). The bulk properties of this system have been well characterized.[6–9] Complex formation is known to result in a rise in solution pH and a decrease in solution viscosity.[6,9] The significant dependence of the solution properties of the complex on the chain length of the interacting polymers suggests a cooperative complexation process occurs in this system.[7]

Recently, a number of researchers have used fluorescence probe techniques to study the complexation between PAA and PEO and also other related systems.[10–15] The advantage of fluorescence probe measurements is that information about the behavior of the polymers on a molecular level can be obtained, as compared to the bulk properties determined by nonspectroscopic methods.[16]

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