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(45) The absorption spectrum differences shown in Figure 3 for the solid polystyrene samples that were prepared by two different techniques carried over into the spectra recorded when these samples were dissolved in benzene, indicating inherent differences in light absorbing chromophores in the two materials. In addition, the solid sample prepared by hot-pressing polystyrene scattered more light than did the bulk free-radical-polymerized sample. Thus, normalizing the data to an absorbance of zero at 500 nm gives rise to an apparent intersection between the two absorption curves at approximately 305 nm.
(46) The transient did not decay with simple first-order kinetics (see ref 40 for a discussion of this phenomenon). A biexponential fitting function adequately represented the data. One component of decay appeared to be independent of oxygen concentration and had a lifetime of ~170 μs. The lifetime of the second component decreased from 870 to 20 μs upon aeration of a deoxygenated sample.
(47) In $^1_0$polymer, the subscript denotes the ground electronic state. Superscripts denote spin multiplicities.
(48) To a good approximation, the lifetime of $^1\Delta_g O_2$ in solution can be related to the number and kind of C–H bonds present in the host medium[43,49,50] because C–H bonds (and O–H bonds, when present) are excellent sinks for the $^1\Delta_g O_2$ excitation energy in a process of electronic-to-vibrational energy transfer.[43,51] The *concentration* and type of C–H bonds in toluene and ethyl benzene liquids is approximately equivalent to that in polystyrene. To the extent that these solvents are indeed appropriate liquid phase analogues for solid polystyrene with respect to $^1\Delta_g O_2$ dynamics, it appears that the $^1\Delta_g O_2$ lifetime we measure in polystyrene (τ_Δ = 22 ± 2 μs) may be slightly shorter than those measured in the liquids [τ_Δ = 29 ± 1 μs (toluene) and 26 ± 1 μs [ethylbenzene]). These subtle differences could be due to a variety of factors, including $^1\Delta_g O_2$ quenchers unique to the polymer[40] or cage/reencounter effects more pronounced than those found in the liquids. This question is currently under investigation.
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(53) Polymer samples were equilibrated with ambient oxygen partial pressures ranging from 100 to 630 Torr. We have already discussed in detail why, over this pressure range and under our conditions, $^1\Delta_g O_2$ cannot originate through direct excitation of either $^3\Sigma_g^- O_2$ or $(^3\Sigma_g^- O_2)_2$.[11]
(54) In our earlier study on liquid samples,[11] we determined a $^1\Delta_g O_2$ quantum yield from the CT state (ϕ_Δ^{CT}) of approximately 0.2. Unfortunately, we have not yet been able to establish a ϕ_Δ standard in the solid polymers to serve as a reference in $^1\Delta_g O_2$ intensity measurements. At present, our efforts are limited by the inefficiency of triplet state sensitizer quenching by $^3\Sigma_g^- O_2$ in the glassy polymers.[40] Nevertheless, the $^1\Delta_g O_2$ intensity measurements made in polystyrene subsequent to CT excitation suggest that ϕ_Δ^{CT} (polystyrene) is not drastically different from ϕ_Δ^{CT} (liquid benzene).[11]
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Registry No. O_2, 7782-44-7; (polystyrene)·O_2, 39839-71-9; 1-phenylbutane, 104-51-8.

Photodecoupling of Cross-Links in Polymeric Gels

Min-Yu Li, Rong-Chang Liang,† and Arnost Reiser*

Institute of Imaging Sciences, Polytechnic University, 333 Jay Street, Brooklyn, New York 11201

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ABSTRACT: Poly(butyl methacrylate) gels with photolabile cross-linked acyloxime units were prepared. The acyloxime moieties are scissioned on exposure to UV radiation, the cross-links decouple, and the solid material is thereby solubilized. The quantum yield of cross-link decoupling is about Φ = 0.03. The physicochemical consequences of cross-link decoupling are investigated.

Introduction

While the phenomenon of photo-cross-linking has been investigated in detail,[1,2] the inverse phenomenon, namely the opening of cross-links by the action of radiation has received but little attention.[3] Yet the photodecoupling of cross-links is both of fundamental and potentially of practical interest. Photodecoupling of cross-links makes it possible to convert a three-dimensional network into an ensemble of linear chains by approaching the gel point of the system from the direction of higher cross-link densities. Apart from its inherent significance as a test for some aspects of gelation theory, photodecoupling may have interesting applications in lithography and in other imaging technologies. In fact, positive resists based on

† Present address: Mead Imaging, Newmark Drive, Miamisburg, OH 45342.

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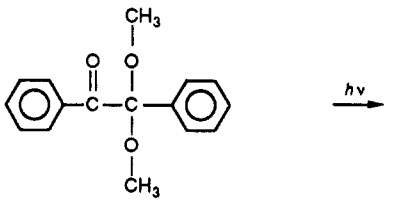
cross-link decoupling would have several practical advantages:

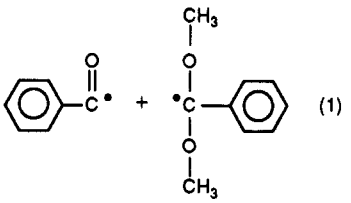
First, there is the possibility of higher sensitivity (photographic speed). In conventional positive resists a large number of functional groups must react before an appreciable differential in solubility is achieved. In a de-cross-linking system, image discrimination is based on the transition from a cross-linked gel to an ensemble of disconnected polymer chains, a sol, and that transition can be achieved by a comparatively small number of decoupling events. Second, because the developed image is a cross-linked polymer, it will have higher thermal and mechanical stability and better resistance against plasma etching than conventional resists.[3]

This paper is concerned with a particular implementation of the idea of cross-link decoupling. It explores the possibility of incorporating photolabile cross-links into simple acrylic polymers, and it investigates the mechanism of cross-link decoupling and the physicochemical consequences of the decoupling process.

Photolabile Cross-Links. In looking for reactive structures that could serve as photolabile cross-links, we considered the large class of photoinitiators that produce free radicals by a bond-scission process. A classical example is the benzoin ethers, such as DMPA, which undergo carbon–carbon bond scission on irradiation.[4]



2,2-dimethoxy-2-phenylacetophenone (DMPA)

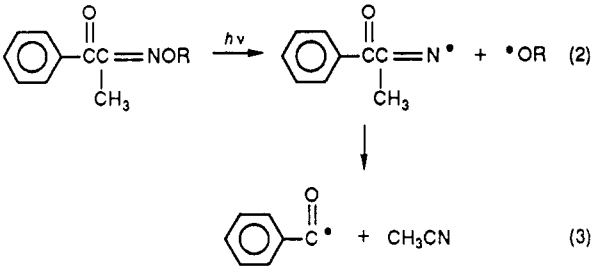


(1)

In principle, such a system would be suitable as a photolabile cross-link, and DMPA units were used in our preliminary experiments. However, in the scission reaction of DMPA two carbon radicals are formed in close proximity of each other (some 1.5 Å apart) in a "solvent cage", and as a result many of the radical pairs will recombine and lead the system back to its initial state. In fluid solution cage recombination is moderate, and as a result the quantum yield of photofragmentation can be high. For example, in benzene solution[5] the quantum yield of radical production by DMPA is of the order of 40%. Cage recombination becomes more important in viscous media and it dominates the behavior of the system in solid polymer films. We have prepared linear polymers with DMPA units in their backbone and have exposed solid films of these materials to UV radiation. Even on prolonged irradiation, the molecular weight of the polymer did not change significantly. However, irradiation of the same polymers in solution did lead to chain fragmentation.

In light of these observations we have chosen the acyloxime unit as the photosensitive moiety for this investigation, because here the final radicals are separated by a slightly larger distance, and there is hope that recombination would not be complete and that some cross-link opening would occur in these systems.

The acyloximes, introduced by Delzenne et al.[6] in 1970, have proven to be highly effective in photogenerating free radicals (quantum yields of radical formation are of the order of 90%). Part of their success is based on the fact that primary bond fission is followed in these systems by a facile second-fragmentation step.



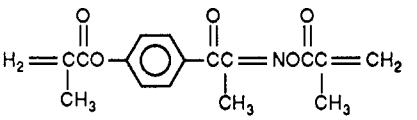
(2)

(3)

It will be noted that here the final radicals in (2) and (3) are at least 4.5 Å apart, which puts them just outside the primary cage.

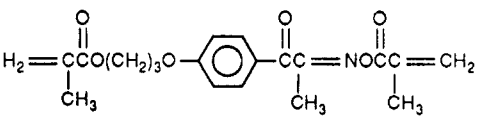
Acyloximes as part of the backbone of a photodegrading polymer chain have been studied by Smets.[7] Delzenne and his colleagues have likewise investigated the photofragmentation of linear polymers containing acyloxime moieties in the main chain.[8] Reichmanis and co-workers[9] and others at Bell Laboratories[10] have used acyloxime groups in the side chain to initiate the photodegradation of polyacrylates and -methacrylates by a Norrish type 1 mechanism.

The first successful cross-linker of this project was prepared with the acyloxime structure shown below.

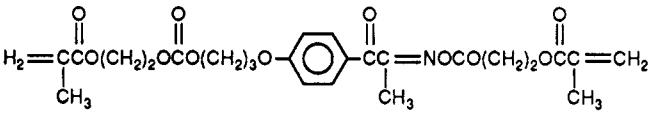


C-1

With cross-linker C-1 it was possible to obtain positive images on imagewise irradiation of poly(butyl methacrylate) gels. Since the secondary reaction step (eq 3) requires a certain degree of flexibility in the environment of the photoreactive moiety, it was thought that better results could be achieved if the central unit of the photosensitive cross-linker was separated from the adjoining chains by flexible spacers. With the idea in mind, the cross-linkers C-2 and C-3 were prepared.



C-2



C-3

Polymer Gels. Cross-linked polymer gels were prepared by polymerizing a mixture of butyl methacrylate (BMA) with one of the bifunctional cross-linkers (photoreactive bismethacrylates) C-1, C-2, or C-3, using AIBN as a radical initiator. The components, together with 2% free methacrylic acid, were dissolved in toluene, 1% of AIBN was added, and varying amounts of the chain-transfer agent *n*-dodecanethiol (*n*-DCT) were produced; a typical quantity was 0.5% by weight of *n*-DCT. The

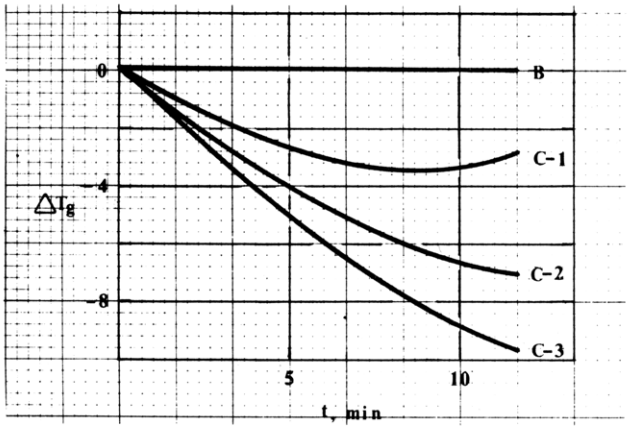


Figure 1. Effect of exposure on T_g of poly-BMA gels containing cross-linkers C-1, C-2, or C-3. Composition of monomer feed: 3% of cross-linker, 2% of methacrylic acid, 0.5% *n*-DCT. 2% BHT was added to the gel. B is a blank, which is not radiation sensitive and which was produced by using 1,6-hexanediol diacrylate (HDDA) as the cross-linker.

solution was brought to 60–65 °C and kept there for about 6 h (oil bath). The set gels so formed were cut into small pieces and washed with fresh solvent to remove any excess of the thermal initiator. The gel was then dispersed with a high-shear rotary blender and coated on glass or quartz slides. After evaporation of the solvent, clear glossy polymer films were obtained. These were dried overnight in a vacuum oven.

The swollen gels could be perfused with various additives, the most important being radical scavengers, in order to partially suppress the recombination of the primary radicals formed on exposure. The effect of irradiation on the cross-link density in the films was monitored in several ways: by measuring T_g, by determining the swelling volume before and after exposure, by monitoring the absorption spectrum of the photoreactive chromophore during irradiation, and, finally, by testing the solubility of the irradiated material.

Early experiments showed that films with a fairly low content of cross-linkers did become soluble on irradiation and showed also appreciable changes in T_g. As it was hoped, the cross-linkers C-2 and C-3 produced somewhat more sensitive gels than cross-linker C-1 (see Figure 1). The cross-linker C-2 represents a compromise between efficiency of de-cross-linking and ease of preparation; cross-linker C-3 is only slightly better than C-2, but it is much more cumbersome to synthesize. For this reason cross-linker C-2 was used in all subsequent experiments.

It also became apparent that the presence of a radical scavenger, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT), was much more important than the choice of cross-linker. This point is illustrated in Figure 2 where the effect of BHT content on the degree of cross-link decoupling, as measured by the change in T_g is shown. It can be seen that the T_g vs irradiation time curve flattens out at about 10-min irradiation time and then ascends again. Evidently, cross-link decoupling competes with the formation of new cross-links, and in the ascending branch of the curves cross-link formation overtakes cross-link decoupling. The plateau at 10-min irradiation time corresponds to the maximum extent of net cross-link opening that can be achieved in the given system.

Cross-Link Density in the Gels. The measurement of swelling volumes affords a means for determining cross-link density in the gels. The theory of the method is summarized in the Flory–Rehner equation,[11] which, for

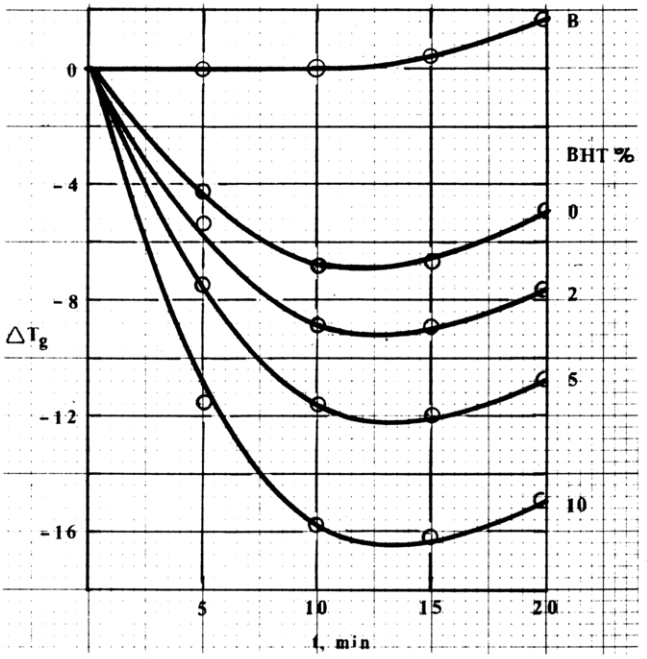


Figure 2. Effect of the added radical scavenger BHT on the T_g of poly-BMA gels cross-linked with 3% of C-2 in the presence of 0.5% of *n*-DCT. B is a blank as in Figure 1.

Table I
Cross-Link Density in Poly-BMA Gels

feed compositn	M_c	ρ	ρ(theor)	ρ/ρ(theor)
1.5% C-2	15 300	5.37×10^{-3}	11.3×10^{-3}	0.47
2.0% C-2	15 100	5.54×10^{-3}	15.1×10^{-3}	0.37
3.0% C-2	12 400	7.53×10^{-3}	22.7×10^{-3}	0.33
5.0% C-2	10 000	10.28×10^{-3}	38.1×10^{-3}	0.27

a low degree of cross-linking, as it applies in our case, can be put into the form

$$q^{5/3} = \frac{\upsilon M_c}{1 - 2M_c/M} \frac{0.5 - X_1}{\upsilon_1} \tag{4}$$

Here q is the ratio of the volume of the swollen to the unswollen gel, υ is the specific volume of the polymer, υ_1 is the molar volume of the solvent, M is the molecular weight of the linear polymer without cross-linking, M_c is the molecular weight of the chain between cross-links, and X_1 is the Flory–Huggins interaction parameter of the solvent with the polymer.[12]

Swelling volumes can be determined gravimetrically, M is available from GPC experiments, and if X_1, υ, and υ_1 are known, M_c can be calculated. The cross-link density, i.e., the fraction of monomer units in the gel that are involved in cross-links, is related to M_c by the expression

$$\rho = \frac{1 - M_c/M_w}{M_c/M_o} \tag{5}$$

where M_o is the molecular weight of the monomer unit and M_w is the weight average molecular weight of the (notional) linear polymer before cross-linking. As a result of the determination of the cross-link density from swelling volumes, it was found that less than half of the cross-linker molecules in the initial feed of the polymerization reaction did in fact form intermolecular cross-links. (See Table I.)

The measurement of the glass transition temperature is another, less cumbersome, way of monitoring changes in cross-link density. For a given type of polymer system T_g can be calibrated in terms of absolute cross-link

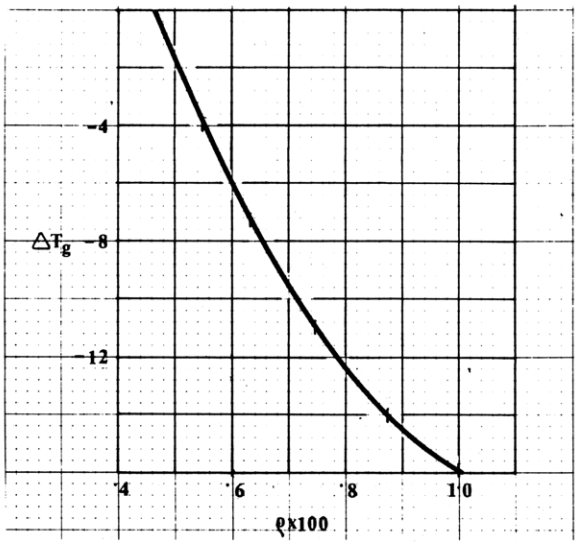


Figure 3. Calibration of the glass transition temperature change ΔT_g in terms of cross-link density as derived from swelling experiments. This calibration is valid for poly-BMA gels cross-linked with C-2 in the presence of 0.5% *n*-DCT.

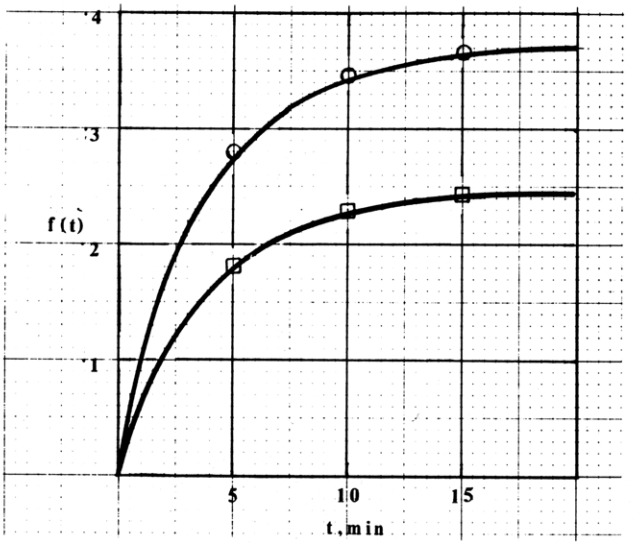


Figure 4. Plot of net fraction of cross-links decoupled on irradiation as a function of exposure time. Upper curve: in the presence of 5% BHT as radical scavenger. Lower curve: no radical scavenger.

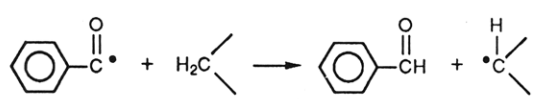
density by using the results of swelling experiments on the same system. Figure 3 shows such a calibration curve for cross-linked poly(butyl methacrylate) gels.

Conditions for Complete Solubilization. Many factors besides the exposure dose play a role in making a gel soluble. Solubilization corresponds to a transition from the gel to a sol, and it was found that the content of cross-linker in the polymerization feed and the concentrations of chain-transfer agent and radical scavenger both play an important role. In order to find the minimum exposure dose needed to make a particular film soluble, the problem is best approached through determination of the fraction of cross-links opened by the irradiation dose.

If the cross-link density of the unirradiated gel is $\rho(0)$ and the cross-link density remaining after an exposure time t is $\rho(t)$, the fraction of cross-links opened at time t is given by

$$f(t) = \frac{\rho(0) - \rho(t)}{\rho(0)} \tag{6}$$

The fraction of cross-links opened in the gel can be monitored by swelling experiments or by T_g measurements. It is found that the decoupling effect saturates on irradiation to a medium-pressure mercury lamp (200 W) at a distance of 1 ft for 10–15 min. This is caused by the appearance of side reactions whereby the photogenerated primary radicals abstract hydrogen from a nearby chain.



The carbon-centered radicals may recombine and form cross-links that can no more be opened by light. The gradual accumulation of nonopenable cross-links counteracts the primary decoupling reaction. In the systems investigated in this project the two processes balance when about 38% of cross-links are opened. This is illustrated in Figure 2 where it can be seen that after some 12 min of exposure the glass transition temperature of the film levels out and later starts to increase, having fallen dramatically in the early stages of irradiation. Figure 4 shows that even in the presence of a radical scavenger not more than 38% of cross-links can be opened by irradiation. Data obtained by swelling experiments and by the measurement of T_g are given in Table II and validate our previous calibration of the T_g method.

Table II
Fraction of Cross-Links Opened As Derived from Swelling Volumes and from T_g

compositn	t, min	M_c	T_g	$\rho \times 10^3$	$f(T_g)$	$f(M_c)$
3% C-2	0	12 400	0	7.53	0	0
	5	14 200	4.0	5.45	0.150	0.19
	10	14 600	6.0	5.75	0.24	0.23
3% C-2, 5% BHT	0	12 300	0	7.64	0	0
	5	15 100	6.0	5.75	0.25	0.28
	10	16 000	10	5.00	0.35	

To accomplish the full transition from a gel to a set of linear polymer chains (the sol), the system must reduce its cross-link density to that of the gel point before the limit of the maximum openable fraction of cross-links has been reached. The cross-link density at the gel point is given by the Stockmayer equation[13]

$$\rho_G = M_o/M_w \tag{7}$$

and the critical fraction of cross-links that must be opened to reach gel point is

$$f_c = (\rho(0) - \rho_G)/\rho(0) \tag{8}$$

For example, in a gel prepared with 1.5% by weight of cross-linker C-2 the initial cross-link density was found to be $\rho(0) = 5.4 \times 10^{-3}$. The cross-link density at the gel point is

$$\rho_G = 142/36500 = 3.9 \times 10^{-3}$$

and the critical fraction of cross-links to be opened to achieve solubilization is therefore

$$f_c = (5.4 - 3.9)/5.4 = 0.28$$

This value is comfortably below 0.38, which is the fraction of cross-links that can in practice be opened by irradiation. As a result, this particular gel produces clean wash-off images of good quality.

In summary, it is noted that the most important factors in deciding whether a given gel can be solubilized by irradiation are (a) the cross-linker content and the

Table III
Critical Fraction of Cross-Links To Be Opened for Solubilization

% *n*-DCT	M_v	$\rho(0) \times 10^3$	$\rho_G \times 10^3$	f_c
0	128 700	6.61	1.10	0.83
0.5	36 500	7.53	3.89	0.48
1.5	15 100	11.36	9.40	0.17

Table IV
Quantum Yield of Net Cross-Link Opening (Poly-BMA Gels, 3% C-2, 0.5% *n*-DCT)

compositn	t, min	w, mg	$\rho \times 10^3$	$Q \times 10^5$, einstein	Φ
no BHT	5	28.5	1.28	1.35	0.019
	10	43.0	1.75	2.70	0.020
5% BHT	5	15.8	2.00	0.675	0.033
	10	22.7	2.64	1.350	0.031

content of chain-transfer agent, which set the initial cross-link density of the gel, and (b) the concentration of radical scavengers in the film, which sets the maximum openable fraction of cross-links in the system. The strong effect of chain-transfer agent on the critical fraction of cross-links to be opened is shown in Table III.

Critical Exposure Dose and the Quantum Yield of Cross-Link Decoupling. The critial exposure dose, E_c, is defined as the incident minimum dose of radiation that transforms the gel into a sol. It can be expressed in terms of the cross-link densities of the unexposed system and the cross-link density at the gel point in the form

$$E_c = \frac{\rho(0) - \rho_G}{A\Phi} \frac{w}{M_0} \tag{9}$$

where w is the weight per unit area of the film and M_0 is the molecular weight of the monomer unit. For a typical gel made with 3% of cross-linker C-2 in the presence of 0.5% of chain-transfer agent *n*-DCT and exposed at 313 nm, the critical exposure dose was found to be E_c = 110 mJ/cm^2. This value was not changed appreciably by the addition of up to 5% plasticizer.

A more fundamental quantity characterizing the photoresponse of the material is the quantum yield of cross-link decoupling, Φ, defined by the expression below.

$$\Phi = \frac{n_x}{Q} = \frac{\Delta\rho}{Q} \frac{w}{M_0} \tag{10}$$

Here n_x is the number of cross-links opened by the absorbed dose Q (photons or einstein); w is the mass of the gel sample irradiated (say, the unit area of film). The results shown in Table IV were obtained with BMA gels cross-linked with 3% of cross-linker C-2 in the presence of 0.5% of *n*-DCT and containing either no radical scavenger or 5% of BHT.

It can be seen from these results that in solid films photodecoupling of cross-links is not a very efficient process; the quantum yield is between 2 and 3%. There can be two reasons for this lack of efficiency: either most radicals formed on excitation recombine in the primary cage or there is extensive formation of secondary cross-links. This would mean that radicals escape from the primary cage but interact with the polymer and form new cross-links by a route other than the recombination of the original radicals. Which of the two mechanisms predominates can be decided by comparing the quantum yield of disappearance of the photolabile chromophore (i.e., the quantum yield of primary cross-link opening) with the (net) quantum yield of cross-link decoupling.

The quantum yield of primary cross-link opening can be determined as the quantum yield of chromophore conversion by monitoring the change of the absorption spectrum of the system during irradiation. The primary quantum yield, ϕ, can be calculated from the rate of change of the optical density at the wavelength of irradiation via the expression

Table V
Comparison of Quantum Yield of Net and of Primary Cross-Link Opening

compositn	Φ	ϕ	$(\phi - \Phi)/\phi$
2% C-2	0.020	0.027	0.025
3% C-2 + 5% BHT	0.032	0.037	0.13

$$\phi = \frac{10^{-3}}{I_0 A \Delta e} \frac{dD}{dt} \tag{11}$$

where D is the optical density at the wavelength of irradiation, I_0 is the incident quantum flux, A is the fraction of quanta absorbed by the chromophore, Δe is the change of extinction coefficient between reactant and product, and t is time of exposure to the quantum flux I_0. A comparison of Φ and ϕ in Table V shows that the fraction of primary radicals which eventually form secondary (unopenable) cross-links in the absence of a radical scavenger is 25% and falls to 13% in the presence of 5% of the radical scavenger BHT. It must be concluded from this that in these systems the low efficiency of cross-link decoupling is caused not so much by secondary cross-link formation outside the cage but mainly by cage recombination of the primary radicals.

Experimental Part

Synthesis of Cross-Linker C-1. A total of 0.12 mol of *n*-butyl nitrite was added dropwise to a solution of 0.1 mol of 4-hydroxypropiophenone in 95 mL of anhydrous ether while gaseous HCl was passed through the solution. The mixture was then cooled to 0 °C, treated with additional HCl, and stored for 9 h. The solution was washed with water and extracted with ice-cold aqueous 5% NaOH. The extracts were poured into cold HCl solution (100 mL of water and 75 mL of HCl). The precipitates were collected, washed with water, and further purified by recrystallization: mp 179 °C (DSC, onset), yield 56%.[14]

A total of 0.05 mol of the acyloxime was dissolved in a mixture of 0.16 mol of dry pyridine and 150 mL of dry THF. The solution was stirred at 0 °C while 0.15 mol of methacryloyl chloride was added dropwise. The mixture was stirred for an additional 10 h at room temperature, the solvent was removed, and the residue was dissolved in CH_2Cl_2. The solution was washed in turn with 1.5% NaOH, 1.5% HCl, and water and finally dried over $MgSO_4$. After the solvent was removed, the product was purified by chromatography: mp 49 °C (DSC onset), yield 90%.

Synthesis of Cross-Linker C-2. A trace of KI was added to a solution of 0.25 mol of 4-hydroxypropiophenone in 150 mL of absolute alcohol containing 0.275 mol of KOH, and the mixture was heated and stirred. After 1 h 0.25 mol of 1-chloro-3-hydroxypropane was added dropwise, and the solution was refluxed for 15 h. The solvent was removed and the residue dissolved in ether. The ether solution was washed with water and finally dried over $MgSO_4$. Ether was then removed and a pure product obtained by vacuum distillation (180–182 °C (2.2 mmHg), yield 92%). The acyloxime was then treated in the way described for cross-linker C-1. The resulting product had an mp of 48 °C (DSC onset) and a yield of 94%.

Synthesis of Cross-Linker C-3. A total of 0.325 mol of *n*-butyl nitrite was added dropwise to a mixture of 0.25 mol of the substituted propiophenone (the intermediate in the synthesis of cross-linker C-2) and a solution of 0.25 mol of metallic sodium in 150 mL of absolute alcohol held at 5–10 °C. The mixture was then stirred at room temperature for another 2 h. The solvent was removed and the residue dissolved in 25 mL of cold water. This solution was poured into a HCl solution (200 mL of ice-water and 100 mL of 37% HCl), and the precip-

itate was collected, washed with water, and purifed by recrystallization: mp 119 °C (DSC onset), yield 50%.

In a separate run 0.02 mol of HEMA was added dropwise to a solution of 0.024 mol of *p*-nitrobenzyl chloroformate and 0.024 mol of dry pyridine in 50 mL of dry THF at 0 °C. The solution was stirred for 15 h, THF was removed, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with 1.5% $NaHCO_3$, 1% HCl, and finally water and dried over $MgSO_4$. After CH_2Cl_2 was removed, 0.015 mol of this intermediate product was taken up into 10 mL of dry THF and this solution was added dropwise to a mixture of 0.005 mol of the acyloxime described above, 3 g of K_2CO_3, and 0.19 g of 18-crown-6 in 30 mL of dry THF. This mixture was stirred for 15 h. The solvent was removed and the residue dissolved in a mixture of CH_2Cl_2 and water. The organic layer was washed with 1.5% $NaHCO_3$, 1.5% HCl, and water and finally dried over $MgSO_4$. After the solvent was removed, the final product was purified by chromatography: mp 57 °C (DSC onset), yield 40%.[15]

Determination of Molecular Weight. The viscosity-average molecular weight of poly(butyl methacrylate) was determined by viscometry at 30 °C, in benzene. The Mark–Houwink relation, $[\eta] = KM^a$, was used to calculate molecular weight, with $K = 4.0 \times 10^{-3}$ mL/g and $a = 0.77$.[16] A Cannon–Fenske viscometer was used to measure the intrinsic viscosity.

Actinometry. The intensity of the incident radiation was determined by ferrioxalate actinometry following the procedure described by Kurien.[17]

Coating Thickness. The coating thickness was of the order of 2 μm. It was derived from the weight of the polymer layer and the area covered. A density of 1 g/cm^3 was assumed for all films.

Measurement of T_g. The glass transition temperature of the polymers was determined by DSC using a Du Pont 1090 thermal analyzer equipped with a Du Pont 910 DSC cell. The midpoint af the trace of the transition was taken.

Light Sources. Exposures of the polymer coatings were carried out using either a 02-XBO 150-W xenon lamp coupled to a Bausch and Lomb monochromator or a Hanovia medium-pressure mercury arc of 250 W.

Swelling Experiments. The swelling volumes of the various gels were determined by gravimetry. The gels were washed and dried and their weights determined. They were then swollen in benzene at 25 °C, and when equilibrium had been established, excess solvent was removed and the swollen gel weighed. From the swelling volume the molecular weight between cross-links (M_c) and finally the cross-link density were determined by the Flory–Rehner equation as described in the text of the paper. The following parameters taken from the literature[16] were used: X = 0.41 in benzene at 25 °C; d = 1 g/cm^3 for the polymers, d = 0.874 g/cm^3 for benzene, and the molecular weight is 78.11. M was taken to be the viscosity-average molecular weight as determined in our experiments.

References and Notes

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Registry No. C-1, 24561-51-1; (C-1)(BMA) (copolymer), 126297-36-7; C-2, 126297-34-5; (C-2)(BMA) (copolymer), 126297-37-8; C-3, 126297-35-6; (C-3)(BMA) (copolymer), 126297-38-9; *n*-butyl nitrite, 544-16-1; 4-hydroxypropiophenone, 70-70-2.