

Photocrosslinking of Functionalized Rubbers. X. Butadiene–Acrylonitrile Copolymers

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ABSTRACT: The photocrosslinking of polyacrylonitrile-*block*-polybutadiene-*block*-polyacrylonitrile (ABA) was shown to proceed within seconds at ambient temperature upon UV exposure in the presence of an acylphosphine oxide photoinitiator. The curing process was followed by infrared spectroscopy, insolubilization, and hardness measurements. Complete insolubilization could not be achieved with the neat ABA rubber because of the poor reactivity of the 2-butene double bond and the low vinyl content of the polybutadiene chain. The addition of multifunctional acrylate monomers (20 wt %) causes a substantial increase of both the reaction rate and the crosslink density of the polymer, which becomes completely insoluble in toluene in less than 1 s upon UV irradiation. An even greater effect was observed by using small amounts (1 wt %) of a trifunctional thiol crosslinker. Both the thiol and the photoinitiator concentrations were shown to affect the kinetics of the thiol–ene polymerization and the polymer network crosslink density. A direct relationship was found to exist between the swelling degree of the UV-cured rubber and the interchain molecular weight of the network. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2204–2216, 2001

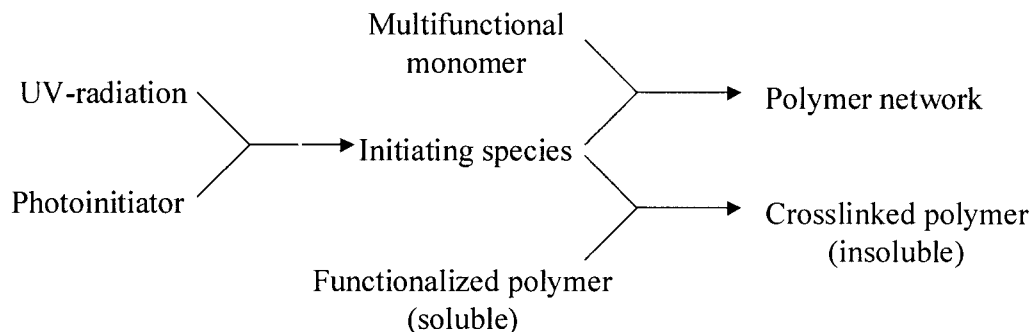
Key words: photopolymerization; crosslinking; polybutadiene; acrylate; thiol

INTRODUCTION

UV-radiation curing has become a well-proven technology which has found a large variety of industrial applications because of its distinct advantages. Highly crosslinked polymers can be generated within seconds at ambient temperature by UV irradiation of a solvent-free formulation.^{1–3} This environment-friendly technology is used mainly to transform a liquid resin into a solid polymer material, in particular, to achieve an ultrafast drying of varnishes and printing inks or a quick setting of adhesives or composite materials.⁴ It can also be applied to produce highly crosslinked polymer networks by the pho-

tocrosslinking of functionalized polymers. In all these UV-curable systems, the role of light is only to generate the initiating species, free radicals, or cations, by photolysis of radical-type or cationic-type photoinitiators (Scheme 1).

Different kinds of linear polymers have been rendered insoluble by a short UV exposure, in particular, rubber-type elastomers bearing epoxy groups,^{5–8} acrylate double bonds,^{9,10} or vinyl groups¹¹ on their backbone. The most promising results were obtained with a styrene–butadiene block copolymer (SBS) which was readily crosslinked by homopolymerization of the few pendent vinyl double bonds of the polybutadiene chain.¹² Insolubilization of this thermoplastic elastomer was substantially accelerated by the addition of either a multifunctional acrylate monomer, which copolymerizes with the poly-



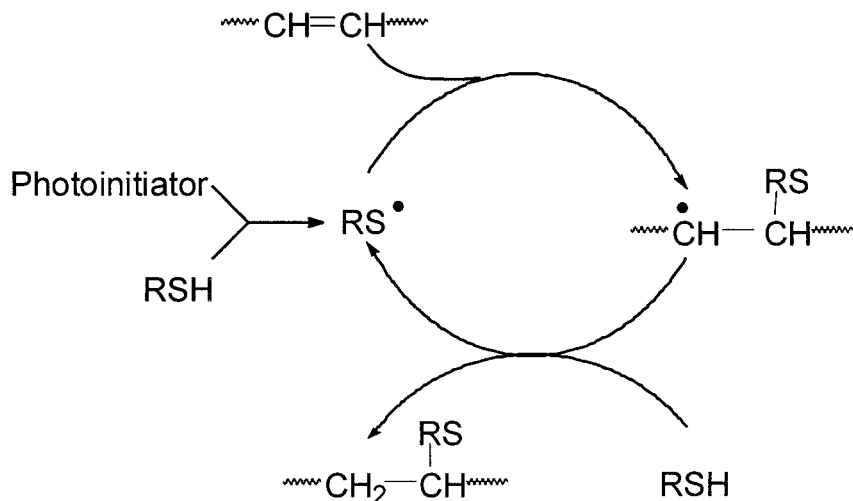
Scheme 1

butadiene unsaturations,¹² or a multifunctional thiol (RSH), which undergoes a step-growth addition polymerization with the alkene double bonds.¹³ The thiol-ene polymerization is considered to proceed by a chain-transfer reaction involving thiyl radicals (RS^\bullet) as propagating species, according to Scheme 2.

Crosslinks between polybutadiene chains are formed only if the thiol contains at least two functional groups. A thiol concentration of 1 wt % proved to be sufficient to generate, within less than 1 s, a tightly crosslinked polymer network showing excellent resistance to organic solvents and a greater thermal stability than those of the original SBS, the shear adhesion failure temperature increasing from 80 to over 160°C.^{14,15}

The objective of the present study was to apply the same UV technology to an acrylonitrile-butadiene block copolymer (ABA) to achieve readily crosslinking and thus improve its chemical and physical characteristics. This

triblock copolymer consists of a main chain made of the soft 1-4 polybutadiene rubber ($T_g = -106^\circ\text{C}$) and of end chains made of the stiff polyacrylonitrile (PAN; $T_g = 97^\circ\text{C}$). Because PAN is a highly polar material with strong interaction between nitrile groups, ABA block copolymers are considered to have a two-phase morphology, with glassy PAN domains dispersed in the elastomeric matrix. Upon heating above 100°C, the glassy domains lose their cohesion and the polymer starts to flow. This kind of physical network can be strengthened by creating a chemical network through permanent covalent bonds joining together the polybutadiene chains. UV irradiation in the presence of a photoinitiator proved to be an easy way to achieve an effective crosslinking. This process was quantitatively studied by following the disappearance of the polybutadiene unsaturation, as well as the insolubilization and hardening of the ABA sample upon UV exposure.

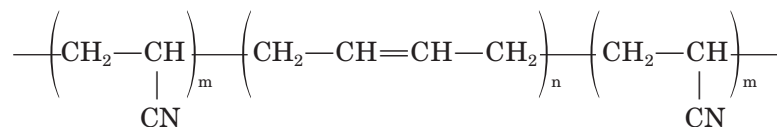


Scheme 2

EXPERIMENTAL

Materials

The PAN-*block*-polybutadiene-*block*-PAN (ABA) used in this study was a commercial material



with $m = 50$ and $n = 195$. Based on the infrared spectrum, the polybutadiene chain contains essentially butene-2 double bonds arising from the 1-4 polymerization of butadiene and only a few pendent vinyl double bonds. From the value of the IR absorbance at 1827 cm^{-1} of the ABA sample and its comparison with that of a styrene-butadiene (SBS) polymer containing 8% vinyl double bonds, the vinyl content was evaluated to be on the order of 3%, that is, only six vinyl double bonds per polymer chain.

The following acrylate monomers were introduced into the ABA rubber at a concentration of 20 wt % to speed up the crosslinking process: ethyldiethylene glycol monoacrylate (EDGA), hexanedioldiacrylate (HDDA), and trimethylolpropane triacrylate (TMPTA), all from UCB Chemicals (Drogenbos, Belgium). For the thiolene polymerization, a trifunctional thiol was selected as a crosslinking agent: trimethylolpropane mercaptopropionate (TRIS) from Evans Chemetics (Lexington, MA). It was added to a toluene solution of ABA at a concentration between 0.2 and 2% by weight of ABA.

Different radical-type photoinitiators were introduced into the polymer, at a typical concentration of 3 wt % ABA, namely, 2,2'-dimethoxy-2-phenylacetophenone (Irgacure 651), 2-benzoyl-2-hydroxypropane (Darocur 1173), a morpholinoketone (Irgacure 369), and a bisacylphosphine oxide (Irgacure 819), all from Ciba Specialty Chemicals (Basle, Switzerland), and 2,4,6-dimethylbenzoyl(diphenyl)phosphine oxide (Lucirin TPO from BASF, Ludwigshafen, Germany). The formulas of the main compounds used in this study are given in Chart 1.

Irradiation

In a typical UV-curing experiment, a 20- μ -thick film was cast from a toluene solution onto either a KBr crystal for infrared analysis or a glass plate for insolubilization and hardness measurements.

produced by Polysar (Sarnia, Canada) under the trade name KRYNAC. Its number-average molecular weight is relatively low, $\bar{M}_n = 16,000 \text{ g}$, and the PAN content is 34 wt %. The ABA formula is the following:

Samples were exposed to the unfiltered UV radiation of an 80-W/cm medium-pressure mercury lamp (IST), in the presence of air and at ambient temperature. The web was operated at a speed of 1 m/s, which corresponds to an exposure duration of 0.1 s per pass. The maximum UV light intensity at the sample position was measured by radiometry (IL-390 light bug) to be 520 mW cm^{-2} .

Analysis

Infrared spectroscopy was used to follow the crosslinking reaction, by monitoring the decrease upon UV exposure of the IR band at 1638 cm^{-1} , corresponding to the polybutadiene unsaturation (Perkin-Elmer spectrophotometer 1600). It should be noted that the IR spectrum of ABA hardly

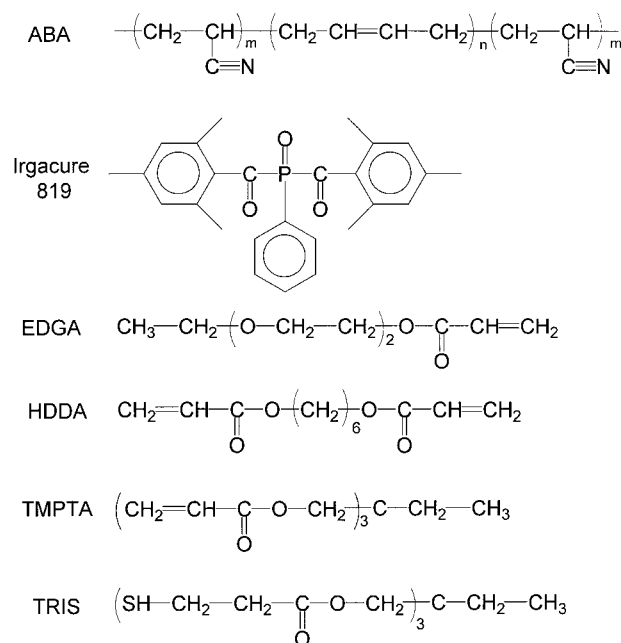
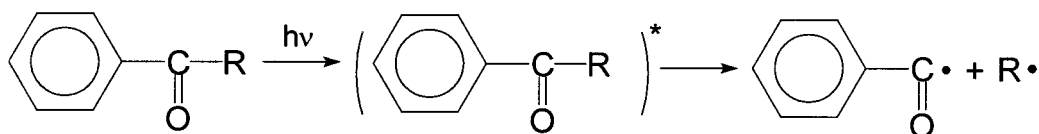


Chart 1 Chemical Formulas of the Various Compounds Used



Scheme 3

changes upon UV irradiation. Very small variations of the IR band intensity can still be monitored accurately because the analysis is performed on the same sample exposed to UV light for various durations, exactly on the same spot. In formulations containing an acrylate monomer (20 wt %), the disappearance of this double bond was followed at 810 cm^{-1} ($\text{CH}_2=\text{CH}$ twisting). The degree of conversion (x) was calculated from the ratio of the corresponding IR absorbance before and after UV exposure (A_0 and A_t) by using the following equation:

$$x(\%) = [1 - (A_t/A_0)] \times 100$$

The thiol monomer was introduced at a concentration which was too low (2 wt % maximum) to allow us to monitor accurately its disappearance through the IR absorbance of the SH group at 2569 cm^{-1} .

The gel fraction and the degree of swelling (SR) of the irradiated polymer were determined by soaking the sample in toluene for 1 day at room temperature. The insoluble polymer was recovered by filtration and dried at 70°C to a constant weight. The hardness of the coating was evaluated before and after irradiation by monitoring the damping time of the oscillations of a pendulum (Persoz hardness). The hardness was shown to be strongly dependent on the glass transition temperature,¹⁶ with Persoz values ranging typically from 30 s for soft elastomeric materials to 300 s for hard and glassy polymers.

RESULTS

In the first approach, we tried to crosslink the neat ABA block copolymer by UV irradiation in

the presence of an adequate photoinitiator. However, because the polymer used contains essentially no vinyl double bonds, known for their high reactivity,¹² but mainly the poorly reactive 2-butene double bonds, relatively long exposure times were required to achieve crosslinking, and the UV-cured polymer was only partly soluble. To make the process more efficient, we introduced into the ABA rubber some multifunctional acrylate monomers to promote a copolymerization reaction with the 2-butene unsaturations. But the best results were obtained by using a thiol crosslinker which proved to be very reactive toward the polybutadiene double bonds, even in minute amounts, thus allowing us to get a highly crosslinked material within a fraction of a second.

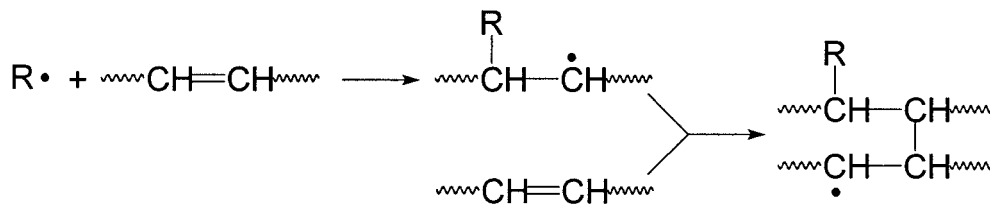
Photocrosslinking of a Neat ABA Rubber

Influence of the Photoinitiator

The photoinitiator (PI) plays a key role in light-induced polymerization by controlling both the reaction kinetics and the cure-depth profile. The radical-type photoinitiators typically used in UV-curable systems are aromatic ketones which undergo a fast carbon-carbon cleavage upon UV exposure, with formation of a benzoyl radical and an alkyl radical (Scheme 3).

These free radicals are expected to react with the unsaturations of the polybutadiene chain (Scheme 4).

Crosslinks will only be formed if the alkyl radical reacts with a butene double bond located on another polybutadiene chain. Intramolecular reactions will generate loops, without the desired effect on the chemical and heat resistance of the UV-cured polymer.



Scheme 4

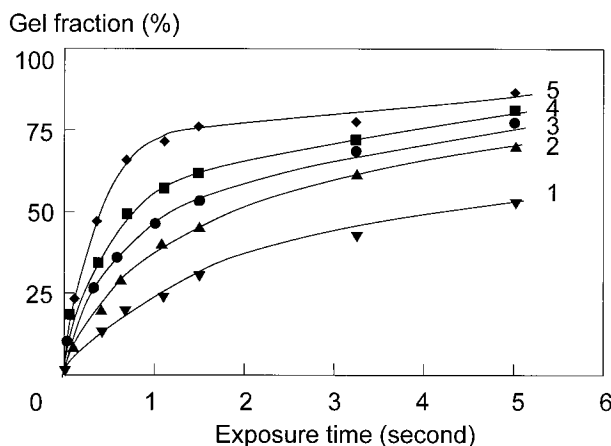


Figure 1 Influence of PI (3 wt %) on the insolubilization profile of a 20- μm -thick ABA film exposed to UV radiation ($I = 520 \text{ mW cm}^{-2}$): (1) Irgacure 369; (2) Darocur 1173; (3) Irgacure 651; (4) Lucirin TPO; (5) Irgacure 819.

The initiation efficiency depends on the PI light absorbance, its rate of photolysis, the cleavage quantum yield, and the reactivity of the radical fragments. To select the best-performing system, insolubilization of the ABA rubber was followed upon UV irradiation in the presence of different types of PIs, at a concentration of 3 wt %. Figure 1 shows some characteristic curves obtained by plotting the gel fraction as a function of the exposure time. These commercial PIs can be classed in the following order of increasing efficiency:

Irgacure 369 < Darocur 1173 < Irgacure 651
< Lucirin TPO < Irgacure 819

The two acylphosphine oxides appear to be the most efficient PIs, partly because of their greater UV absorbance. Irgacure 819 was chosen for our further studies on ABA photocrosslinking. It can be noted that, even with the best-performing PI, total insolubilization of the ABA rubber could not be achieved after a 5-s exposure to high-intensity UV radiation. This result is in marked contrast with the behavior observed with the SBS rubber, UV-irradiated under the same conditions, where complete insolubilization was achieved in less than 2 s.¹² It is probably due to the much lower content of vinyl groups (3%) in the ABA sample, together with the poor reactivity of the 2-butene double bonds and the five times lower molecular weight. Figure 2 shows the decay upon UV curing of these functions, which levels off at a maximum

loss of 6%. From this value, one can calculate that 12 double bonds, on average, have reacted on each polymer chain. This should be amply enough to ensure a complete insolubilization of the polymer. The fact that the polymer is still partly soluble at that stage implies that an intramolecular polymerization process is taking place between the butene double bonds located on the same polybutadiene chain. If neighboring double bonds are involved in this process, cyclic structures will be formed along the polybutadiene chain, which would, therefore, remain soluble. The reaction can be formally written in Scheme 5.

Except for the minor decrease of the double-bond IR band at 1638 cm^{-1} , the infrared spectrum of the sample remained unchanged after UV irradiation, which means that the PAN moiety is not affected by the photocrosslinking process.

As polymerization proceeds, the polymer network becomes increasingly crosslinked and the degree of swelling decreases concomitantly, as shown in Figure 3. At the same time, the soft rubberlike material becomes somewhat harder (Fig. 4). It can be seen in Figures 1–4 that the same classification of the PIs was obtained by following either one of the four parameters: gel fraction, double-bond consumption, swelling ratio, and hardness.

Influence of the PI Concentration

The PI concentration [PI] controls not only the rate of initiation but also the penetration of UV light. An increase of [PI] will both accelerate the

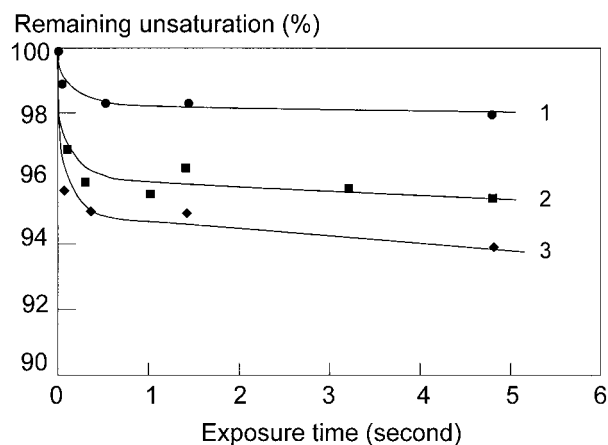
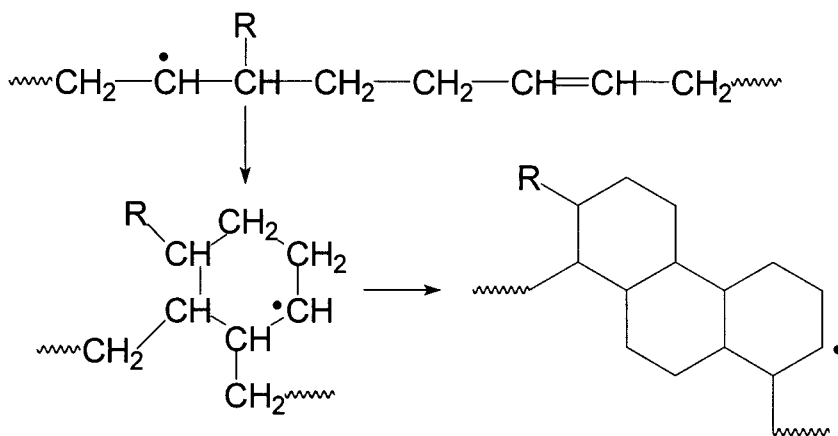


Figure 2 Loss profiles of polybutadiene double bonds upon UV exposure of an ABA rubber in the presence of various PIs (3 wt %): (1) Darocur 1173; (2) Irgacure 651; (3) Irgacure 819.



crosslinking reaction and steepen the cure depth gradient. Figure 5 shows the insolubilization profiles of a 20- μm -thick ABA film containing 1–5 wt % Irgacure 819 exposed to UV radiation for up to 5 s. A concentration of 1 wt % is already enough to achieve an effective curing, the maximum speed being reached for a PI concentration of 3 wt %. At higher [PI], the crosslinking becomes less effective because of the reduced penetration of the incident light in the deep-lying layers (inner filter effect).

An increase of the PI concentration leads also to the formation of a tighter polymer network, because of the increased number of initiating radicals. The swelling ratio of the UV-cured ABA was found to decrease from 10 to 4 when [Irgacure

819] was increased from 1 to 3 wt %. A similar but more pronounced trend was observed by monitoring the hardening of UV-irradiated samples containing various concentrations of the PI (Fig. 6). Here, again, the 3 wt % value proved to be the optimum [PI] concentration, for a 20- μm -thick film. As the film thickness l is increased, this value will decrease concomitantly because the determining factor of the inner filter effect is the light absorbance which is proportional l [PI]. Working at a concentration of 1 wt % will be recommended if such UV-curable systems are to be used for adhesive applications, because the cured elastomer needs to remain very soft. Moreover, the maximum efficiency will then be reached for a 60- μm -thick film, which is a typical thickness for the adhesive layer.

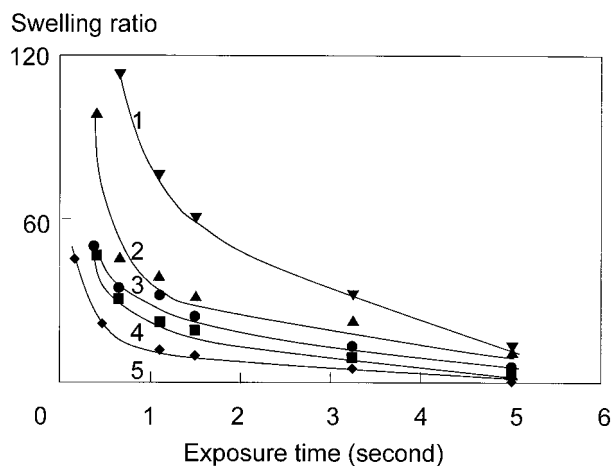


Figure 3 Influence of PI (3 wt %) on the swelling of a 20- μm -thick ABA film exposed to UV radiation ($I = 520 \text{ mW cm}^{-2}$): (1) Irgacure 369; (2) Darocur 1173; (3) Irgacure 651; (4) Lucirin TPO; (5) Irgacure 819.

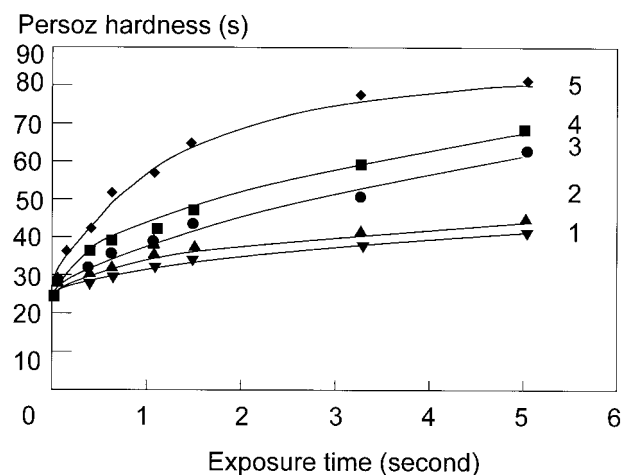


Figure 4 Influence of PI (3 wt %) on the hardening of a 20- μm -thick ABA film exposed to UV radiation ($I = 520 \text{ mW cm}^{-2}$): (1) Irgacure 369; (2) Darocur 1173; (3) Irgacure 651; (4) Lucirin TPO; (5) Irgacure 819.

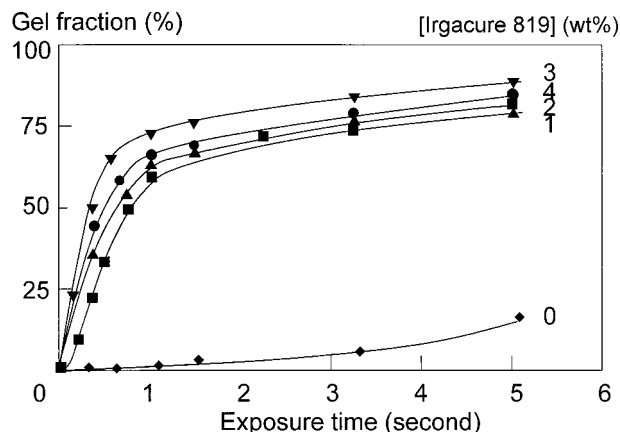


Figure 5 Influence of PI concentration (Irgacure 819) on the insolubilization profile of a 20- μm -thick ABA film exposed to UV radiation.

Photocrosslinking of ABA/Acrylate Blends

An effective way to speed up the curing reaction and increase the crosslink density is by introducing into the rubber some multifunctional monomers capable of copolymerizing with the polybutadiene unsaturations. The very reactive acrylate monomers were shown to fulfill perfectly well this objective in the case of polyisoprene⁹ and for SIS¹⁷ and SBS¹³ block copolymers. This is also true for the ABA copolymer which was readily crosslinked upon UV irradiation in the presence of di- or triacrylate monomers. Figure 7 shows the insolubilization profiles obtained upon UV exposure of the ABA rubber containing 20 wt % of EDGA, HDDA, or TMPTA, Irgacure 819 (3 wt %)

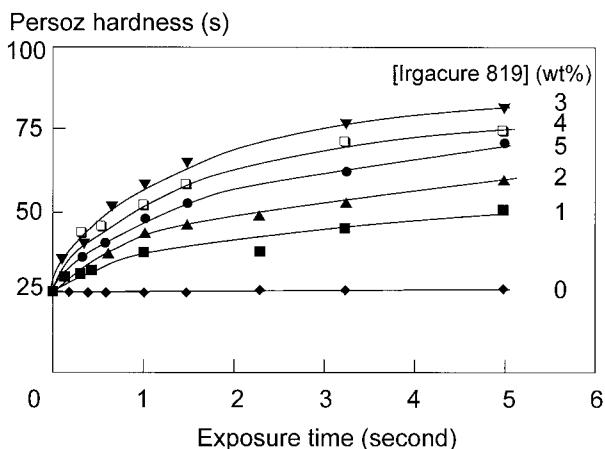


Figure 6 Influence of PI concentration (Irgacure 819) on the hardening of a 20- μm -thick ABA film exposed to UV radiation.

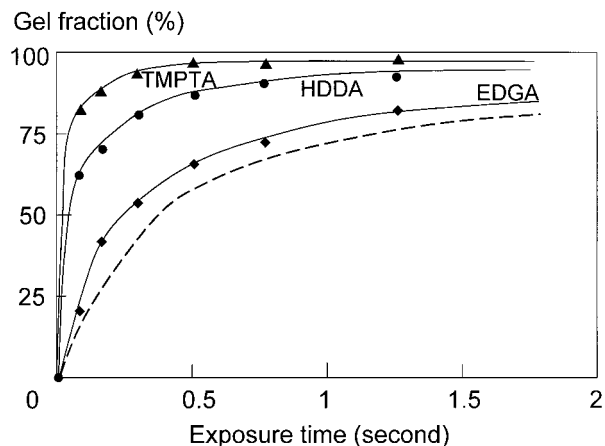


Figure 7 Photocrosslinking of a 80/20 mixture of ABA rubber and acrylate monomer. PI: [Irgacure 819] = 3 wt %. (---) Neat ABA.

being used as the PI. As expected, the triacrylate TMPTA was found to be more efficient than was the diacrylate HDDA, nearly total insolubilization of ABA being achieved in less than 1 s, while the monoacrylate EDGA had hardly any effect.

The polymerization of these monomers can be quantitatively followed by infrared spectroscopy, through the decrease of the IR band at 812 cm^{-1} , which is characteristic of the acrylate double bond (Fig. 8). A faster but less complete polymerization was observed when the monomer functionality was increased, in full agreement with previous observations.¹⁸ It is quite remarkable that the molecular mobility in the solid elastomer cured in the presence of HDDA is still great enough to allow 92% of the acrylate double bonds to poly-

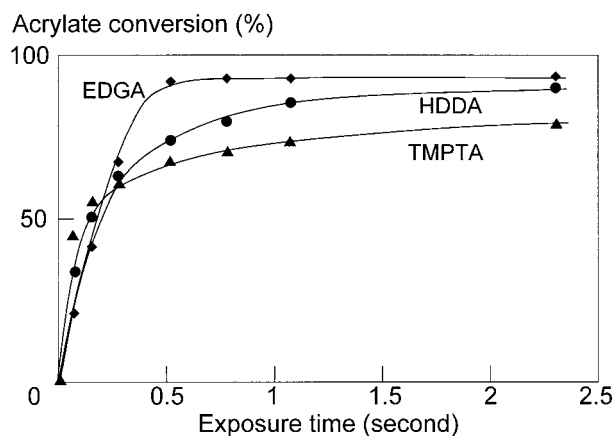


Figure 8 Polymerization profiles of acrylate monomer upon UV exposure of a 80/20 ABA/acrylate mixture. [Irgacure 819] = 3 wt %.

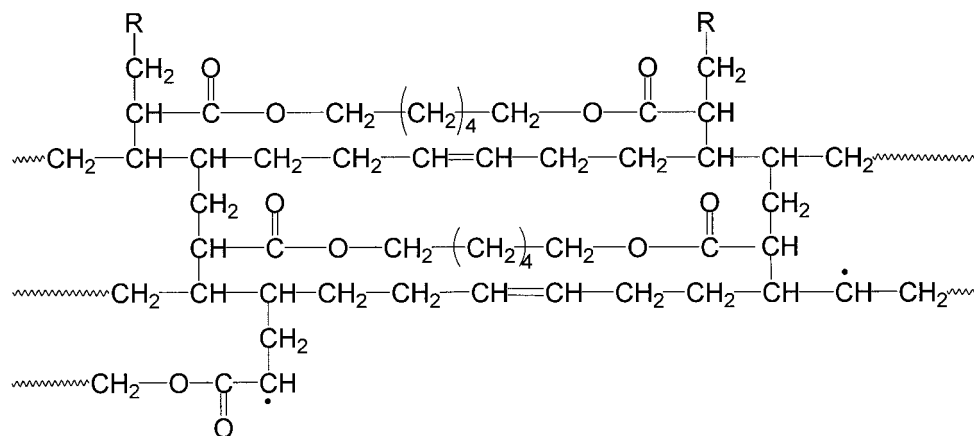


Chart 2 Copolymer Network Formed by UV Irradiation of the ABA Rubber and the HDDA Monomer

merize within a 2-s UV exposure. The copolymer formed is represented schematically in Chart 2.

That a tight polymer network was formed in the ABA rubber UV-cured in the presence of diacrylate or triacrylate monomers was confirmed by swelling measurements (Fig. 9). After a 0.5-s exposure, the swelling ratio of the insoluble polymer formed was found to drop from a value of 17 for the neat ABA to a value of 2.7 for the sample containing HDDA and down to 1.2 in the case of TMPTA. Upon further UV irradiation up to 3 s, these values decreased to 6, 1.7, and 0.4, respectively. Due to its very low swelling in organic solvents, the UV-cured ABA/TMPTA rubber shows the best chemical resistance. From all these kinetic results, we can conclude that the

incorporation of multiacrylate monomers is a quite efficient method to achieve a fast and extensive photocrosslinking of an acrylonitrile-butadiene block copolymer.

It should be noted that the addition of these acrylate monomers (20 wt %) had no major effect on the hardness of the UV-cured rubber which remained soft and flexible, even after extensive UV exposure (Persoz hardness value between 50 and 70 s). The elastomeric character, in particular, the impact resistance and the adhesives properties (tackiness), was thus retained in the photocrosslinked ABA copolymer, thus making it well suited for adhesives and safety-glass applications.

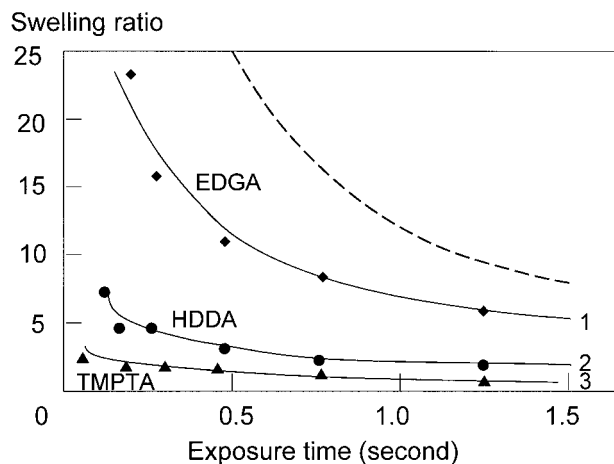


Figure 9 Swelling profiles of an 80/20 ABA/acrylate mixture exposed to UV radiation: (1) EDGA; (2) HDDA; (3) TMPTA. (---) Neat ABA. PI: [Irgacure 819] = 3 wt %.

Photocrosslinking of the Thiol-Polybutadiene System

Thiol-ene polymerization is known to proceed more efficiently with olefins in which the double bond is located at the end of the monomer molecule than in its backbone.¹⁹ This process was successfully used to photocrosslink polybutadiene chains containing pendent vinyl double bonds.¹³ As these functional groups are hardly present in the ABA sample used in this study, it was far from certain that this process would also work in the present case.

The first UV-curing experiments carried out in the presence of 2 wt % of a trifunctional thiol (TRIS) revealed that the in-chain polybutadiene double bonds react readily with the thiyl radicals formed by UV irradiation of this mercaptan. After a 0.1-s exposure, as many as 6% of the butene

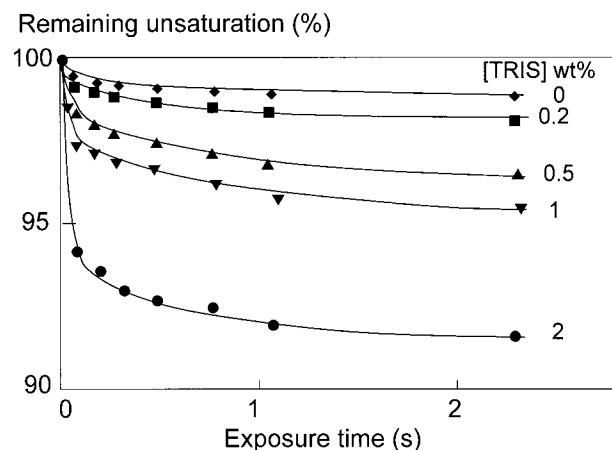


Figure 10 Influence of thiol content on the loss profiles of the polybutadiene double bonds upon UV exposure of ABA-TRIS mixtures. [Irgacure 819] = 1 wt %.

groups had already disappeared, compared to less than 1% for the neat ABA sample. Further experiments were therefore performed at even lower concentrations of thiol: 0.2, 0.5, and 1 wt %. Figure 10 shows the influence of the TRIS concentration on the decay profile of the butene double bond, characterized by its IR absorbance at 1639 cm^{-1} . The initial sharp drop is due to the reaction of the butene double bond with the thiol, which is rapidly consumed. Because of the low TRIS concentration, it was not possible to follow its consumption by IR spectroscopy, but we found in a previous study on the photocrosslinking of SBS that, at a concentration of 5 wt %, the thiol was already consumed after a 0.3-s UV exposure under the same conditions.¹⁵ The slow decay observed later on can be attributed to the homopolymerization of the vinyl and butene double bonds.

In spite of their very low concentration (3%), vinyl double bonds are still likely to contribute to the curing process because of their higher reactivity toward thiyl radicals than that of the butene double bonds (by a factor 16).¹³ By taking this reaction into account, we calculated that about one-third of the crosslinks involves vinyl groups, and two-thirds the butene double bonds.

From the amount of double bonds consumed, one can evaluate the number of branch points on the polybutadiene chain. Its value increases with the exposure time and depends on the thiol concentration, as shown by the values reported in Table I. Under optimum conditions, there are as many as 15 attachments per ABA chain. From these values, we calculated the average molecular

Table I Influence of the TRIS Concentration on the Crosslink Density of UV-Cured ABA Rubber

Exposure Time	[TRIS] wt %				
	0	0.2	0.5	1	2
	No. Crosslinks per ABA Chain				
0.1 s	—	1.5	3.0	5.1	11.2
0.3 s	1.3	1.9	4.2	6.1	13.1
2 s	1.9	3.3	6.7	8.6	15.8

weight \bar{M}_c between two branch points, which was then plotted as a function of the thiol concentration in Figure 11, for three exposure times. The \bar{M}_c value decreases rapidly with an increase of the crosslinker concentration, to reach values as low as 600 g for 2 wt % TRIS, thus indicating that a very tight polymer network was formed. The tri-dimensional polymer network formed by the thiol-ene polymerization in the ABA rubber is represented schematically in Chart 3.

As expected, such an efficient crosslinking process leads to a rapid insolubilization of the ABA rubber. Figure 12 shows the insolubilization profiles obtained at various thiol concentrations upon UV exposure of the ABA sample in the presence of 1 wt % Irgacure 819. At a TRIS concentration of 2 wt %, a single pass under the lamp at a speed of 30 m/min proved to be sufficient to obtain a 95% insoluble material, compared to only 8% for the

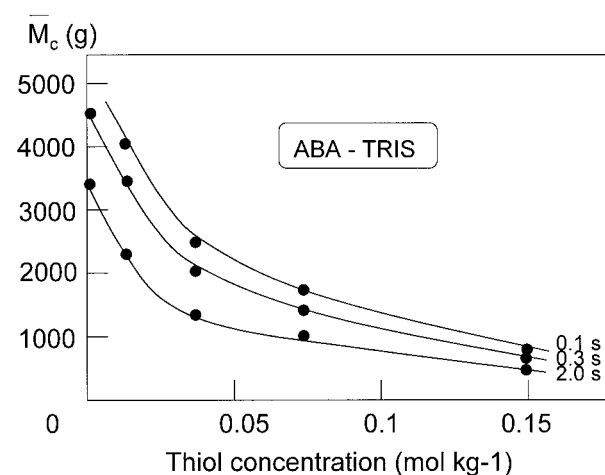


Figure 11 Dependence of average interchain molecular weight of the network on the thiol concentration in photocrosslinked ABA-TRIS mixtures. UV exposure time: 0.1, 0.3, and 2 s. [Irgacure 819] = 1 wt %.

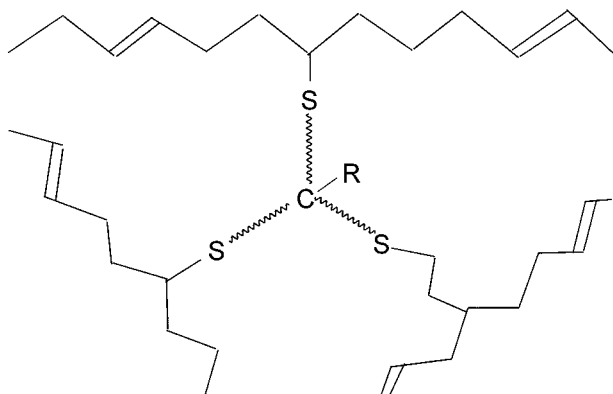


Chart 3 Schematic Representation of the Photocrosslinked ABA/TRIS Polymer Network Formed

neat rubber. The increase of the crosslink density of the UV-cured polymer with the TRIS concentration was confirmed by swelling measurements.

Figure 13 shows the variation of the swelling ratio as a function of the irradiation time. After a 1-s exposure, the SR value was found to decrease from 14 to 3 when the TRIS concentration was increased from 0.2 to 2 wt %. The amount of the solvent retained by the swollen polymer is directly related to the average molecular weight of the network chain \bar{M}_c .²⁰ Because the interaction parameter of the Flory equation was unknown for the ABA/toluene couple studied, we could only make a qualitative evaluation of the effect of the UV dose and the thiol content on the polymer network crosslink density. By plotting the swelling ratio versus the \bar{M}_c values determined from the butene consumption (Fig. 14), we still have

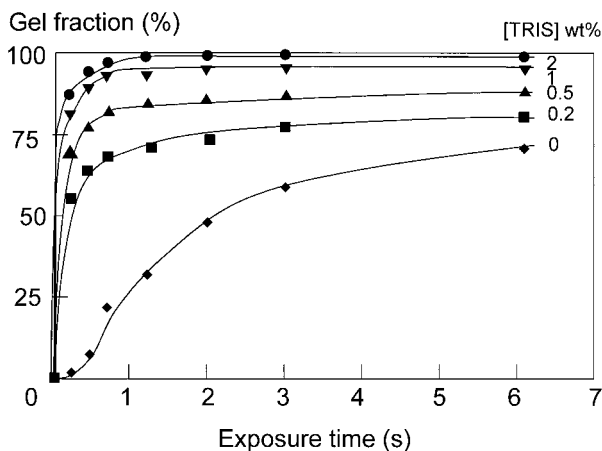


Figure 12 Influence of thiol content on the insolubilization profile of ABA-TRIS mixtures exposed to UV radiation. [Irgacure 819] = 1 wt %.

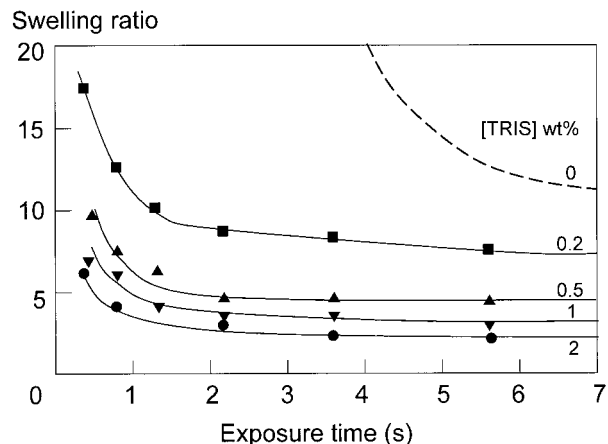


Figure 13 Influence of thiol content on the swelling of ABA-TRIS mixtures exposed to UV radiation. [Irgacure 819] = 1 wt %.

been able to show that these two quantities are, indeed, directly correlated over a relatively large range ($3 \leq SR \leq 12$).

To know how many crosslinks are needed to obtain a completely insoluble polymer, we plotted in Figure 15 the gel fraction as a function of the number of branching points, for the various samples UV-exposed for different times. It can be seen that the ABA rubber starts to become insoluble as soon as two branch points are formed on the polybutadiene chain. Insolubilization proceeds further as additional crosslinks are formed, complete insolubilization of the rubber requiring about 10 crosslinks per chain. Also shown in Figure 15 is

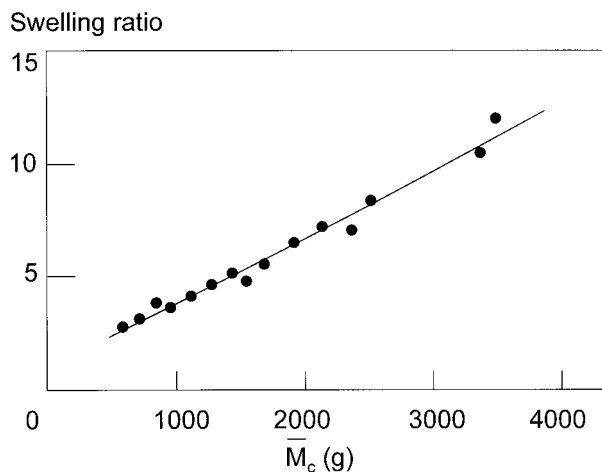


Figure 14 Relationship between swelling ratio and average interchain molecular weight of the network for a photocrosslinked ABA-TRIS polymer.

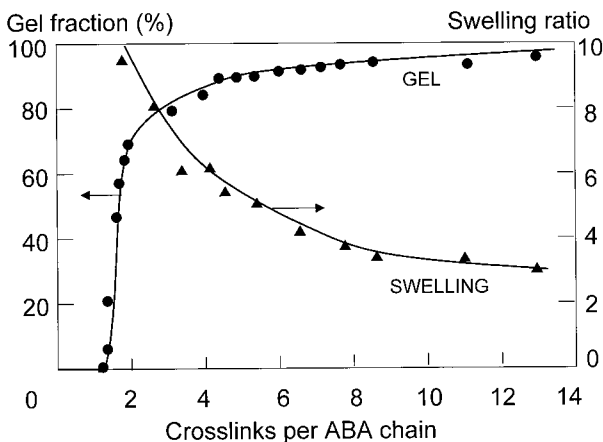


Figure 15 Dependence of gel fraction and swelling ratio on the number of crosslinks per ABA chain for a UV-cured ABA-TRIS polymer.

the decrease of the swelling degree of the cured polymer with the increasing amount of crosslinks.

The crosslinking caused by the thiol-ene polymerization leads to a moderate hardening of the rubber, which remains soft and flexible, as shown in Figure 16. Even at a TRIS concentration of 2 wt %, the Persoz hardness did not exceed 60 s, thus making the UV-cured rubber well suited for adhesive applications. The fact that the elastomeric character was retained is a distinct advantage of the ABA rubber over the SBS rubber where the hardening upon UV irradiation in the presence of 2 wt % TRIS was much more pronounced (Persoz hardness of 140 s).¹⁷ The influence of the thiol crosslinker on the UV curing of the ABA elastomer is illustrated in Figure 17, which shows the

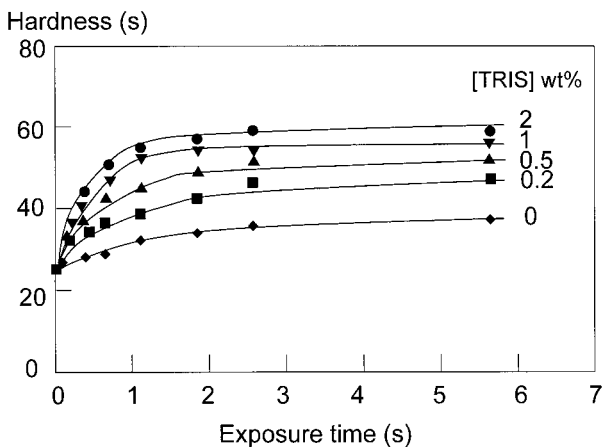


Figure 16 Influence of thiol content on the hardening of ABA-TRIS mixtures exposed to UV radiation. [Irgacure 819] = 1 wt %.

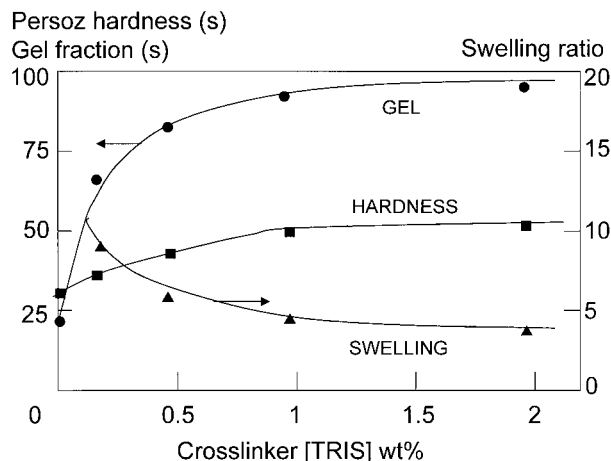


Figure 17 Influence of TRIS concentration on the photocrosslinking of ABA rubber. Exposure time: 0.3 s. [Irgacure 819] = 1 wt %.

variation with the TRIS concentration of the gel fraction, the swelling ratio, and the hardness of a sample UV-exposed for 0.3 s in the presence of Irgacure 819 (1 wt %). A TRIS concentration of 1 wt % appears to be ample enough to get the optimum performance.

All the UV-curing experiments of the ABA/TRIS system reported so far were performed at the same PI concentration (1 wt % Irgacure 819). To increase the penetration of UV radiation and to be able to cure thick samples, the PI concentration was reduced, down to 0.15 wt %, maintaining the TRIS concentration constant at 1 wt %. As expected, the thiol-ene polymerization proceeds then less rapidly, but it was still possible to get an 80% insoluble polymer within 0.3 s, as shown in Figure 18. The swelling measurements indicate that the polymer network is nearly as tight as at higher PI concentrations (SR = 7 instead of 5 at [PI] = 1 wt %), while it is as soft as the uncured rubber.

The influence of the PI concentration on the properties of the polymer material obtained after a 0.3-s UV exposure of the ABA-TRIS (1 wt %) system is illustrated in Figure 19. An Irgacure 819 concentration of 0.15 wt % is already sufficient to get the expected performance. This formulation presents the following advantages:

- high reactivity upon UV exposure;
- low cost of the tiny amounts of additives used;
- no residual thiol and PI in the UV-cured rubber;

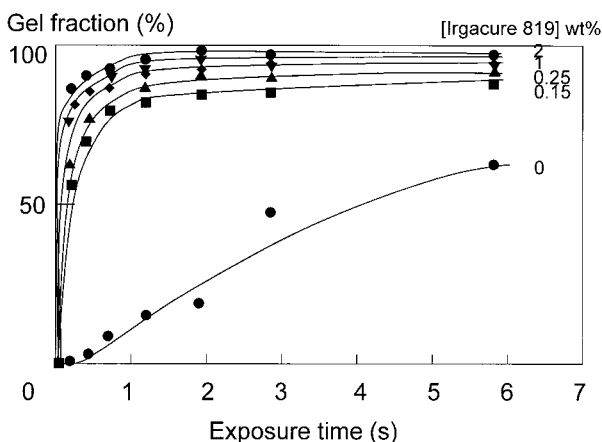


Figure 18 Influence of PI concentration on the insolubilization profile of an ABA-TRIS mixture exposed to UV radiation. [TRIS] = 1 wt %.

- deep-through cure of thick samples;
- low-modulus polymer well suited for adhesive applications.

Two pieces of glass coated with an ABA-TRIS film were tightly bond together by a 1-s UV irradiation. This was made possible because the phosphine oxide PI used here still absorbs the UV radiation filtered by glass. This process was successfully applied to glass/metal bonding, which is sometimes difficult to achieve. An even better adhesion was reached by placing, between the two coated pieces of the assembly, a liquid UV-curable urethane-acrylate resin, as was done previously with SBS-based systems.²¹ Here, also, an efficient

curing was achieved by simple exposure to sunlight for a few seconds. The main interest of this solar technology is to be a cheap process requiring no special irradiation device and consuming no energy, while it allows, at the same time, large-dimension items (several square meters) to be rapidly processed, as, for instance, safety-glass panels.

To illustrate the superior performance of the thiol/ene system for achieving an efficient crosslinking of acrylonitrile-butadiene rubber, we compared, in Figure 20, the insolubilization profiles of the neat ABA, ABA-HDDA (20 wt %), and ABA-TRIS (2 wt %) samples, which were exposed to UV radiation under the same conditions (1wt % Irgacure 819). After a 0.8-s exposure, gel fraction values were measured to be 22, 83, and 98%, respectively, thus clearly showing the outstanding efficiency of the thiol-ene polymerization in this elastomer. The polymer network is also more tightly crosslinked, as shown by the swelling ratio values of samples UV-irradiated for 1 s: 14, 5, and 3.3, respectively.

CONCLUSIONS

Acrylonitrile-butadiene rubbers can be readily crosslinked at ambient temperature by UV irradiation in the presence of a phosphine oxide PI. The polymer network generated in the polybutadiene phase by reaction of the vinyl and butene double bonds increases the chemical and heat resistance of the rubber which remains soft and

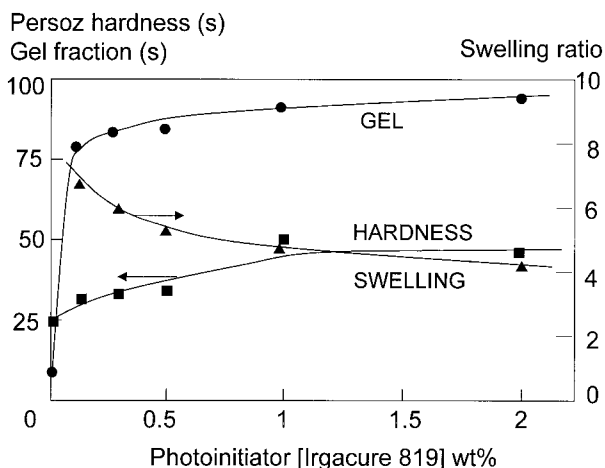


Figure 19 Influence of PI concentration on the photocrosslinking of an ABA-TRIS mixture. Exposure time: 0.3 s. [Exposure 819] = 1 wt %.

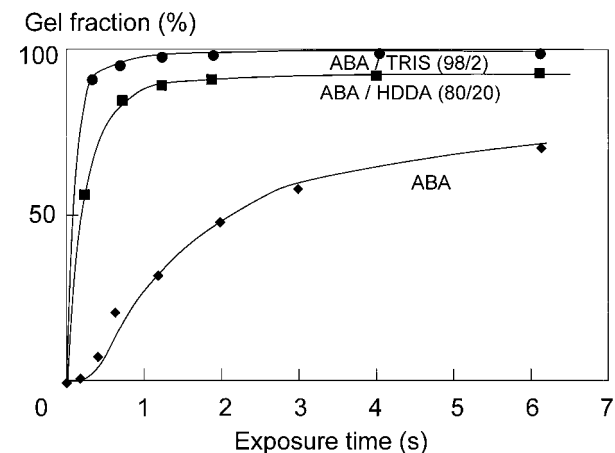


Figure 20 Influence of thiol and acrylate monomers on the photocrosslinking of an ABA rubber. [TRIS] = 2 wt %; [HDDA] = 20 wt %; [Irgacure 819] = 1 wt %.

highly flexible. The addition of diacrylate or triacrylate monomers (20 wt %), which copolymerize with the polybutadiene double bonds, proved to be an efficient way to both speed up the curing process and increase the crosslink density. Even better performance was achieved by incorporating into the rubber small amounts (<2 wt %) of a trifunctional thiol. Under intense illumination, the curing reaction proceeds within a fraction of a second by a step-growth-addition mechanism, with formation of an insoluble polymer network. Crosslinking occurs predominantly by reaction of the thiyl radicals with the 2-butene double bonds and the few pendent vinyl double bonds of the polybutadiene chain.

Hardening is hardly taking place during UV curing, so that the ABA rubber retains its viscoelastic properties, while becoming more resistant to heat and chemicals. The soft and highly flexible polymers thus obtained are well suited for the manufacturing of hot-melt adhesives and sealants, safety glass, photoresists, and flexible printing plates. Because of its process facility and efficiency, the UV technology has been revealed as a powerful tool to crosslink a commercial rubber and modify, selectively in the illuminated areas, its physicochemical characteristics. As the thiol-ene polymerization was previously found to work equally well in SBS thermoplastic elastomers,^{15,17} we can reasonably expect this UV-curing process to be also quite efficient to crosslink acrylonitrile-butadiene-styrene (ABS) rubbers within seconds at ambient temperature.

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