

High-Speed Photocrosslinking of Thermoplastic Styrene–Butadiene Elastomers

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Received 2 June 1999; accepted 5 November 1999

ABSTRACT: Photoinitiated thiol/ene polymerization was used to crosslink a triblock styrene/butadiene/styrene (SBS) polymer of low vinyl content (8%). The crosslinking process was followed by infrared spectroscopy (loss of unsaturation), insolubilization, swelling, and hardness measurements. The photogenerated thiyl radicals react with both the vinyl and the 2-butene double bonds of the copolymer. Concentrations of less than 1 wt % in the trifunctional thiol crosslinker and in the acylphosphine oxide photoinitiator proved to be sufficient to create, within 0.5 s, a permanent chemical network in the elastomeric phase. This UV-curing technology was successfully applied to crosslink rapidly commercial SBS–Kraton® thermoplastic elastomers. It proved also effective in the case of the much less reactive triblock styrene/isoprene/styrene (SIS) polymer which contains no vinyl double bonds. The thiol/ene polymerization was shown to be a much more efficient process to crosslink SBS and SIS thermoplastic elastomers than was the copolymerization of the rubber double bonds with a diacrylate monomer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1902–1912, 2000

Key words: photochemistry; crosslinking; UV curing; thermoplastic elastomers; polybutadiene; thiol

INTRODUCTION

Thermoplastic interpenetrating polymer networks (IPNs) combine the properties of thermoplastic materials and of elastomers. They have found various industrial applications, in particular, for the manufacturing of molded articles, protective coatings, and pressure-sensitive adhesives. Thermoplastic elastomers are usually made of block copolymers containing glassy domains and elastomeric domains which tend to segregate and form a two-phase morphology.¹ A typical example is the polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS)² commercialized by Shell

under the trademark Kraton®. Typical SBS triblock thermoplastic elastomers exhibit high extensibility, elastic recovery, and resilience; they are resistant to water and alcohol, but remain soluble in ketones, esters, and hydrocarbons.

Because the network is made of physical crosslinks rather than chemical crosslinks, the glassy polystyrene (PS) domains lose their cohesion upon heating above the T_g (around 80°C) and the polymer starts to flow. Such IPNs are therefore ill-suited for producing hot-melt adhesives or flexographic printing plates which must exhibit a high resistance to elevated temperatures (>150°C) and to aromatic solvents as well. The physical network can be strengthened by creating a chemical network through permanent covalent bonds joining together the chains of the elastomeric phase to give an insoluble material.

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Contract grant sponsor: Shell Research, Louvain la Neuve, Belgium.

Journal of Applied Polymer Science, Vol. 77, 1902–1912 (2000)
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It was recently shown that such a crosslinking process is easily induced in SBS thermoplastic elastomers by UV irradiation in the presence of a radical-type photoinitiator.^{3,4} The shear adhesion failure temperature (SAFT) was found to increase from 80 to over 160°C upon UV curing, while the tack remained essentially unchanged.^{5,6} The network was considered to be formed by polymerization of the pendent vinyl double bonds, which are known to be more reactive than are the 2-butene double bonds of the polybutadiene chain. The crosslinking process can be markedly accelerated by the addition of multifunctional acrylate or thiol monomers that copolymerize with the polybutadiene unsaturations.^{4,7} The use of light to induce the chain reaction has several advantages, such as high cure speed, low-energy consumption, ambient temperature operations, dry processing without VOC emission, and selective curing in the illuminated areas. By performing the UV exposure through a mask, one can generate, after solvent development, the high-relief images which are needed for the manufacture of flexographic printing plates.

In a previous work, we showed that photoinitiated thiol-ene polymerization is an effective way to crosslink thermoplastic SBS rubbers, total insolubilization being achieved within less than 1 s.⁸ As thiyl radicals were found to be 16 times more reactive toward vinyl than were 2-butene double bonds, the first experiments were conducted on a specially designed SBS sample having a high vinyl content (59%). Crosslinking in the elastomeric phase was shown to still proceed when the polybutadiene vinyl content was decreased to 8%, as long as the thiol concentration was kept above 5 wt %. To reduce the bad smell associated with the use of mercaptans, an attempt was made to further lower the concentration of the thiol crosslinker. Another objective of this study was to reduce the photoinitiator concentration below 1 wt %, the lowest value used so far, in order to increase the penetration of UV radiation into the sample and be able to cure thick samples. Most of the experiments were carried out with a typical SBS sample, which, like most commercial SBS rubbers, contains a low amount of pendent vinyl groups. The crosslinking process was quantitatively studied by following the disappearance of the vinyl groups, as well as the insolubilization and the hardening of the SBS sample upon UV irradiation.

EXPERIMENTAL

Materials

The SBS from Shell used in this study was specially designed by Shell (Louvain-la Neuve, Belgium). It contained 8% pendent vinyl groups, the 2-butenylene units ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$) located on the polybutadiene backbone, representing 92% of the unsaturation content. Because of its relatively low styrene content ($\sim 20\%$), the SBS behaves similarly to a cured conventional vulcanized rubber. Some experiments were carried out with commercial SBS samples (Kraton® D-1102 and Kraton® D-1186 from Shell) that differ mainly by the molecular weight and the structure of the polybutadiene chain, which was linear or branched, respectively. The UV-curing performance of a polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) was also evaluated on a commercial sample (Kraton® D-1107 from Shell).

A trifunctional thiol was selected as the crosslinking agent, trimethylolpropane mercaptopropionate (TRIS), from Evans Chemetics (Lexington, MA). It was added to a toluene solution of SBS at a concentration between 0.2 and 3% by weight of SBS. Among the various radical-type photoinitiators tested, acylphosphine oxides proved to be the most efficient ones to photocrosslink the SBS samples. All the experiments were carried out using 2,4, 6-trimethylbenzoyl diphenylphosphine oxide (Lucirin TPO from BASF, Ludwigshafen, Germany) as the photoinitiator, at a typical concentration of 1 wt %. The chemical formulas of the three components used in this study are given in Figure 1.

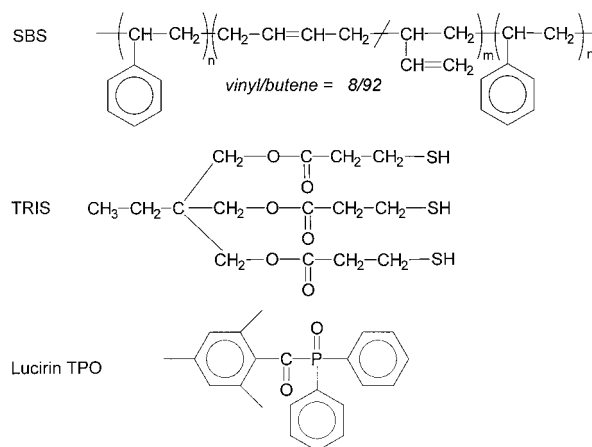


Figure 1 Chemical formulas of the SBS rubber, thiol, and photoinitiator used.

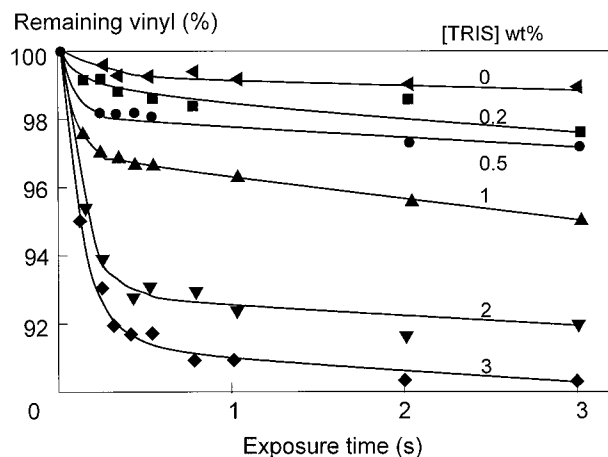


Figure 2 Influence of the thiol concentration on the vinyl polymerization of SBS upon UV exposure. [Lucirin TPO] = 1 wt %.

There are only a few reports in the literature on the photocrosslinking of the thiol-SBS system,^{7,8,11} with essentially no information on the reaction kinetics. We examined the influence of the thiol and photoinitiator concentrations on the UV curing of a low-vinyl SBS sample and on some commercial SBS rubbers as well.

Influence of the Thiol Concentration

Vinyl Consumption

The SBS samples containing 1 wt % of a photoinitiator (Lucirin TPO) and various concentrations of thiol ($0.2 \text{ wt \%} \leq [\text{TRIS}] \leq 3 \text{ wt \%}$) were exposed to UV radiation for different times up to 3 s. As the thiol consumption could not be followed by IR spectroscopy at the low concentration used, the polymerization reaction was monitored through the decrease of the vinyl IR band at 910 cm^{-1} . Although this decrease is quite small, it can still be quantified with great accuracy because each sample undergoing photocrosslinking was analyzed by the IR beam at exactly the same spot.

Figure 2 shows some typical kinetic curves of the vinyl group consumption upon UV exposure and the effect of the thiol content on the curing reaction which follows a two-step kinetics. The thiol-vinyl copolymerization proceeds rapidly during the first 0.3 s of irradiation, until the thiol monomer has been consumed. At a 5 wt % concentration of TRIS, the SH group was found to have essentially disappeared after a 0.3-s UV exposure. The slow decrease of the vinyl double bonds observed upon further irradiation parallels that in the thiol-free SBS and was

therefore attributed to the homopolymerization of these groups.

Although the decrease of the 2-butene double bond cannot be followed by IR spectroscopy because of *cis-trans* isomerization (bands at 3060 and 965 cm^{-1} , respectively), it is still possible to evaluate the contribution of the thiol-butene copolymerization to the crosslinking process from the difference between the loss of the thiol group $\Delta [\text{SH}]$ and that of the vinyl group $\Delta [\text{V}]$:

Loss of vinyl by copolymerization:

$$\Delta [\text{V}]_{\text{copo}} = \Delta [\text{V}]_{\text{SBS+TRIS}} - \Delta [\text{V}]_{\text{SBS}}$$

Loss of thiol group by copolymerization:

$$\Delta [\text{SH}] = \Delta [\text{V}]_{\text{copo}} + \Delta [\text{B}]_{\text{copo}}$$

Loss of butene group [B] by copolymerization:

$$\Delta [\text{B}]_{\text{copo}} = \Delta [\text{SH}] - \Delta [\text{V}]_{\text{SBS+TRIS}} + \Delta [\text{V}]_{\text{SBS}}$$

In Figure 3, the amounts of vinyl and butene groups which have copolymerized with the thiol after a 0.3-s exposure are plotted as a function of the SH concentration. The two quantities $[\text{V}]_{\text{copo}}$ and $[\text{B}]_{\text{copo}}$ were found to be quite similar and to increase linearly with the thiol content, as expected. The fact that a single curve was obtained implies that the rate constants k_v and k_b of the two copolymerization processes are in the reciprocal ratio of the vinyl and 2-butene concentrations:

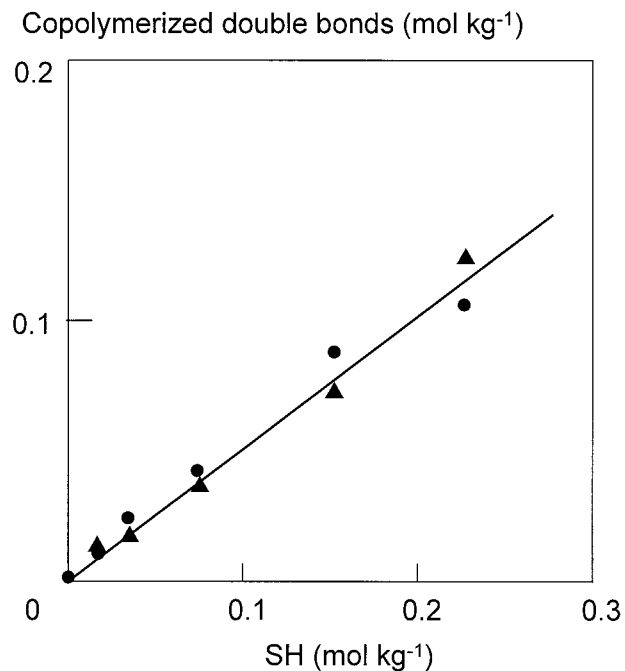


Figure 3 Thiol dependence of the amount of vinyl (●) and butene (▲) double bonds copolymerized after 0.3-s UV exposure of SBS. [Lucirin TPO] = 1 wt %.

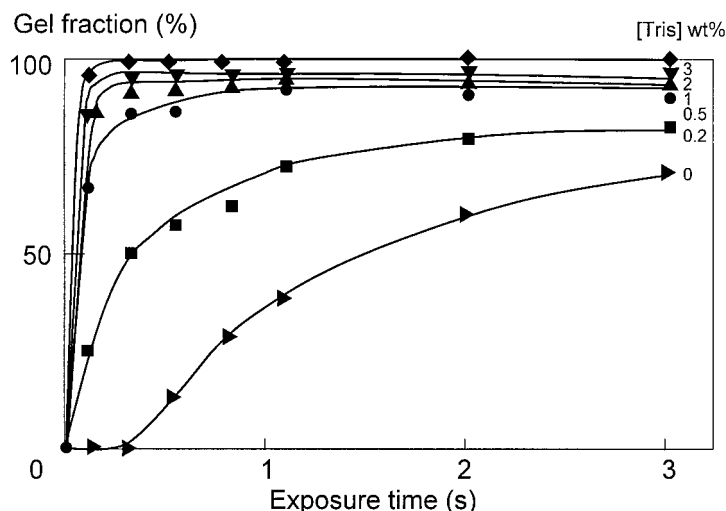


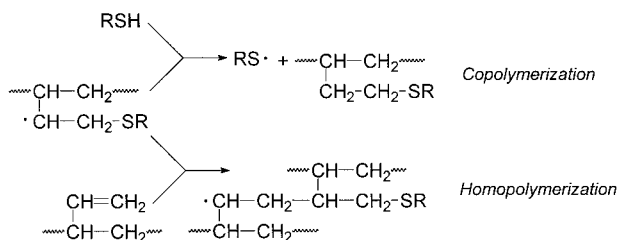
Figure 4 Influence of the thiol concentration on the insolubilization of SBS upon UV exposure. [Lucirin TPO] = 1 wt %.

$$k_v[V] = k_b[B]$$

$$\frac{k_v}{k_b} = \frac{[B]}{[V]} = 11.7$$

The higher reactivity of the vinyl double bond toward thiols is in good agreement with previous structure–reactivity studies on the addition of thiols on olefins.¹² It was attributed to an increase in electron density of the olefin which reacts with a relatively electrophilic thiyl radical.¹³

These data also show that the copolymerization of vinyl groups with a trithiol is favored over the homopolymerization ($\Delta [V]_{\text{copo}}/\Delta [V]_{\text{homo}} = 5.3$ at $[\text{SH}]_0 = 0.075 \text{ mol kg}^{-1}$), even though the vinyl concentration is much higher than is the thiol concentration ($[\text{vinyl}]_0/[\text{SH}]_0 = 16.8$ at 1 wt % TRIS). This means that the propagating alkyl radicals are much more reactive toward the thiol group than toward the vinyl double bond:



Insolubilization

The crosslinks created in the elastomeric phase by both copolymerization and homopolymeriza-

tion reactions led to insolubilization and solvent resistance of the UV-irradiated SBS–thiol system. Figure 4 shows some typical plots of the insoluble fraction as a function of the exposure time for different SBS formulations containing 1 wt % Lucirin TPO and increasing amounts of TRIS (from 0.2 to 3 wt %). For TRIS concentrations above 1 wt %, essentially all of the polymer was found to become insoluble after a 0.3-s irradiation. At lower TRIS contents, the SBS polymer remained partly soluble, the gel fraction increasing slowly upon further exposure due to homopolymerization of the vinyl groups, the small amounts of thiol having already been consumed.

From the quantity of reactive groups consumed after a 0.3-s exposure ($2.2 \times 10^{-2} < N < 23 \times 10^{-2} \text{ mol kg}^{-1}$), one can calculate the concentration of branch points in the elastomeric phase and the number of crosslinks (X) formed per SBS chain at the various thiol concentrations used:

$$X_{\text{total}} = ([\text{vinyl}]_{\text{homo}} + [\text{vinyl}]_{\text{copo}} + [\text{butene}]_{\text{copo}}) \frac{M_{\text{SBX}}}{1000}$$

the vinyl and butene concentrations being expressed in mol kg^{-1} . This number was found to increase linearly with the thiol content up to a value of 34 crosslinks per chain at $[\text{TRIS}] = 3 \text{ wt } \%$, as shown in Figure 5. Total insolubilization requires the formation of about 15 crosslinks per SBS chain. This is clearly apparent when the gel fraction, measured after a 0.3-s exposure, is plotted as a function of the number of crosslinks formed per SBS chain (Fig. 6).

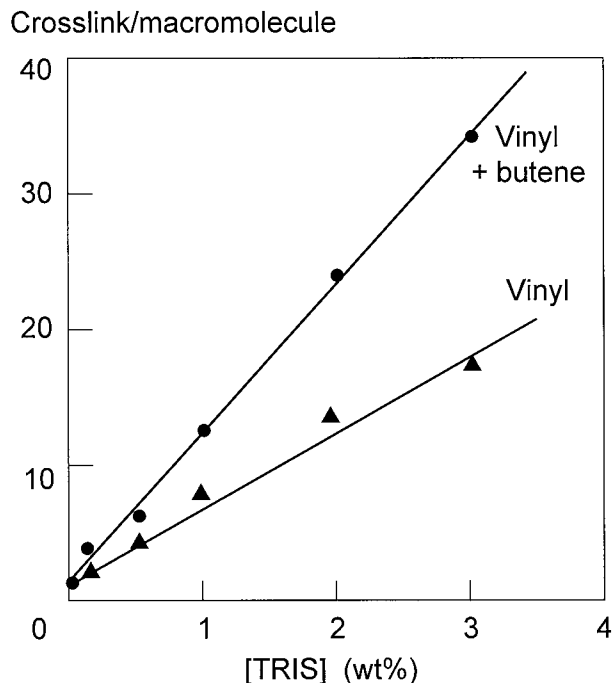


Figure 5 Thiol dependence of the amount of vinyl and butene crosslinks formed per chain after 0.3-s UV exposure of SBS. [Lucirin TPO] = 1 wt %.

For the SBS sample that contains no thiol, crosslinking results only from the homopolymerization of the few pendent vinyl double bonds, as 2-butene double bonds are much less reactive.¹³ After 0.3 s, the vinyl consumption was measured to be $7 \times 10^{-3} \text{ mol kg}^{-1}$, which corresponds to only one crosslink per SBS molecule. This explains why the polymer remains soluble at that stage (Fig. 4), insolubilization requiring the buildup of a least three bridges per chain.

The amount of solvent retained by the swollen polymer is directly related to the network crosslink density or to the number-average molecular weight of the network chain.¹⁴ Because the interaction parameter of the Flory swelling equation was unknown for the SBS/toluene couple studied, it was only possible to make a qualitative evaluation of the effect of the UV dose and the thiol content on the tightness of the polymer network formed. Figure 7 shows how the swelling ratio (SR = swollen solvent weight/dry polymer weight) varies with the exposure time for the various TRIS/SBS formulations. At very low TRIS concentrations (0.2 wt %), the SR value decreases from 35 to 15 with increasing exposure time, which indicates that a very loose polymer network has been formed. As the thiol concentration

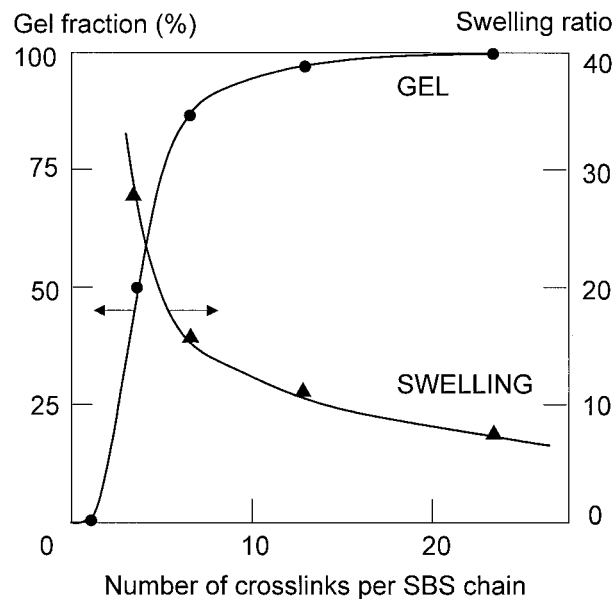


Figure 6 Dependence of the gel fraction and swelling ratio on the number of crosslinks per SBS chain after a 0.3-s exposure. [Lucirin TPO] = 1 wt %.

was increased to 3 wt %, a tighter network was formed, the swelling ratio decreasing to a minimum value of 5. Figure 6 shows the swelling ratio dependence on the number of crosslinks per SBS chain.

Hardening

The crosslinking caused by the thiol-ene polymerization during the first 0.3 s of UV exposure did not affect significantly the elastomeric character

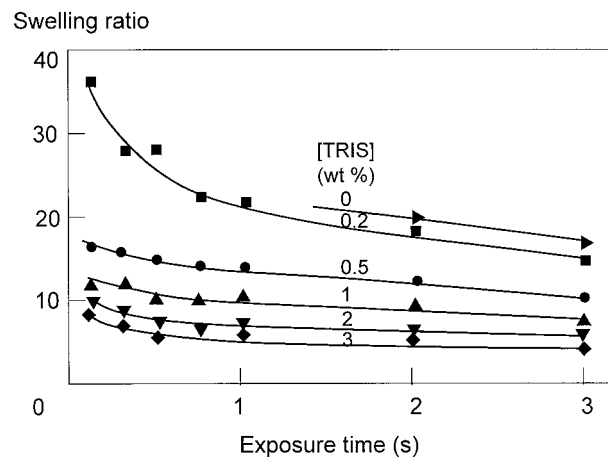


Figure 7 Influence of the thiol concentration on the swelling of a photocrosslinked SBS. [Lucirin TPO] = 1 wt %.

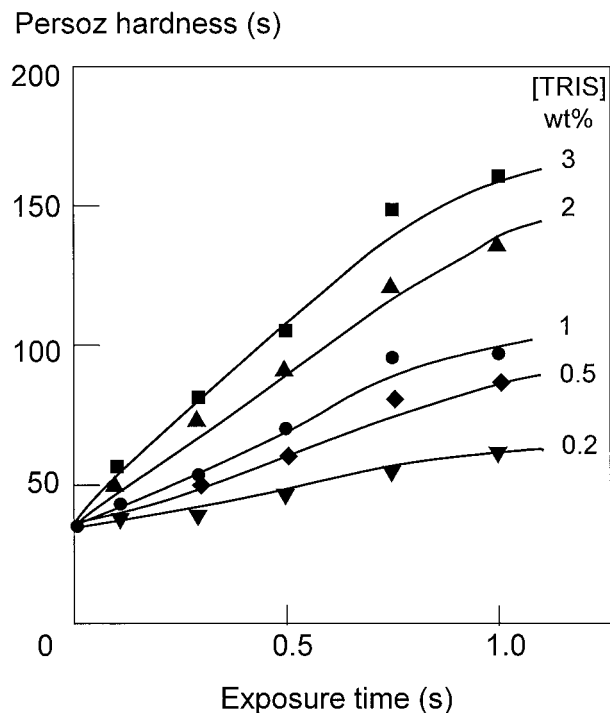


Figure 8 Influence of the thiol concentration on the hardness of a photocrosslinked SBS. [Lucirin TPO] = 1 wt %.

of the polymer, which remained soft and flexible as long as the TRIS concentration did not exceed 1 wt %. At higher concentrations, the Persoz hardness was found to increase from 40 to 75 s, as shown in Figure 8. As the UV irradiation was pursued, the SBS hardness increased further, es-

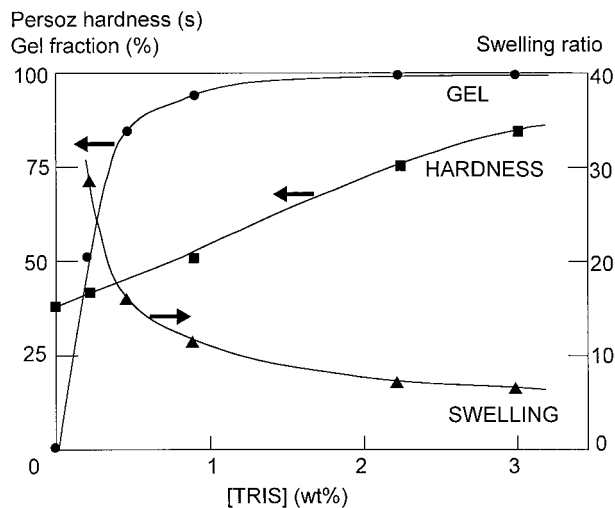


Figure 9 Influence of TRIS concentration on the photocrosslinking of SBS. [Lucirin TPO] = 1 wt %.

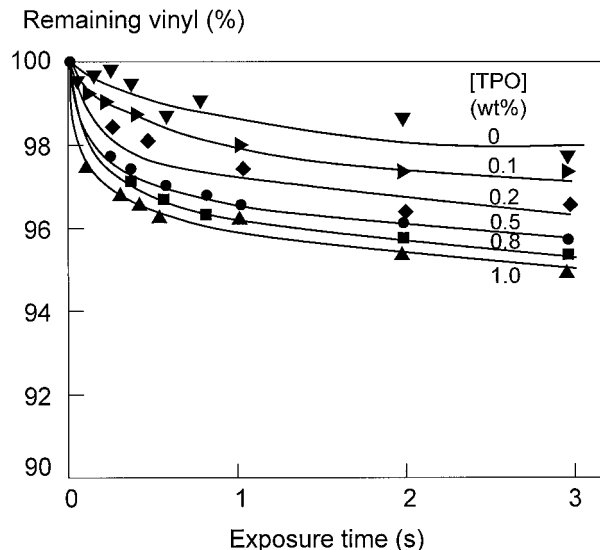


Figure 10 Influence of the photoinitiator concentration on the vinyl polymerization of SBS upon UV exposure. [TRIS] = 1 wt %.

pecially for [TRIS] > 1 wt %. This unwanted hardening may reduce the adhesive properties (tackiness) of the UV-cured polymer and should be strictly controlled.

The influence of the thiol on the photocrosslinking of the SBS elastomer is illustrated in Figure 9, which shows the variation with the TRIS concentration of the gel fraction, the swelling ratio, and the Persoz hardness of a sample UV-exposed for 0.3 s in the presence of Lucirin TPO (1 wt %). A TRIS concentration of 1 wt % and a UV dose of 0.3 s (which generates about 12 crosslinks per chain) appear as the best compromise for achieving a fast curing and still ensuring the high adhesion requested for pressure-sensitive adhesives.

Influence of the Photoinitiator Concentration

All the UV-curing experiments reported so far were performed with the same concentration of the photoinitiator, namely, 1 wt % Lucirin TPO. To increase the penetration of UV radiation for curing of thick samples and to reduce the formulation cost as well, the photoinitiator concentration was decreased to 0.1 wt %. This leads to a slowing of the polymerization reaction, as expected from the decreased initiation rate. Figure 10 shows the decay profiles of the vinyl double bond upon UV exposure of the SBS/TRIS (1 wt %) system at various concentrations in Lucirin TPO.

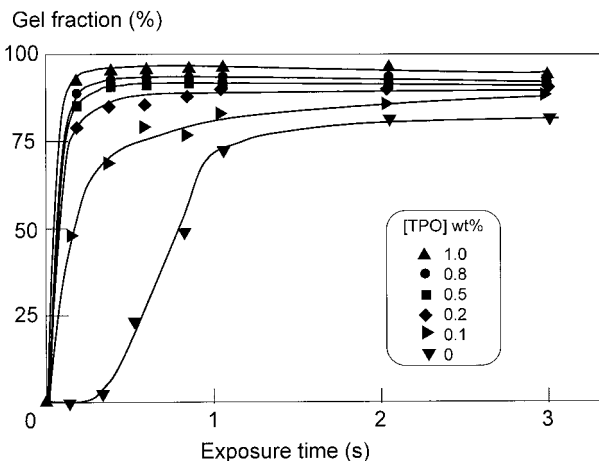


Figure 11 Influence of the photoinitiator concentration on the insolubilization of SBS upon UV exposure. [TRIS] = 1 wt %.

As expected, the vinyl conversion was found to be reduced when the photoinitiator concentration was decreased, but it was still sufficient to cause insolubilization of SBS, as long as [Lucirin TPO] \geq 0.2 wt %. Figure 11 shows the corresponding insolubilization profiles for TPO concentrations between 0 and 1 wt %.

One may notice that at a TPO content of 0.2 wt % the thiol-ene polymerization proceeds efficiently enough to yield a nearly completely insoluble material within 0.3 s. Very similar polymerization and insolubilization profiles were obtained by operating under the following experimental conditions: [TRIS] = 1 wt % and [TPO] = 0.2 wt %, or [TRIS] = 0.5 wt % and [TPO] = 1 wt %. The former formulation has the advantage of providing a more uniform deep-through cure, especially for thick samples, while being also more cost effective.

It can be seen in Figures 10 and 11 that curing occurs even in the absence of any added photoinitiator, although at a much slower pace. This is probably due to the presence in SBS of some impurities which act as initiating chromophores, but also to the high reactivity of the thiol radicals. Indeed, no crosslinking could be detected upon UV-irradiation of neat SBS under the selected experimental conditions.

The chemical network formed in the elastomeric phase of the SBS rubber has a loose structure when low concentrations of the photoinitiator were used. After a 0.3-s UV exposure, the value of the SBS swelling ratio was found to increase from 11 to 17 when [TPO] was decreased

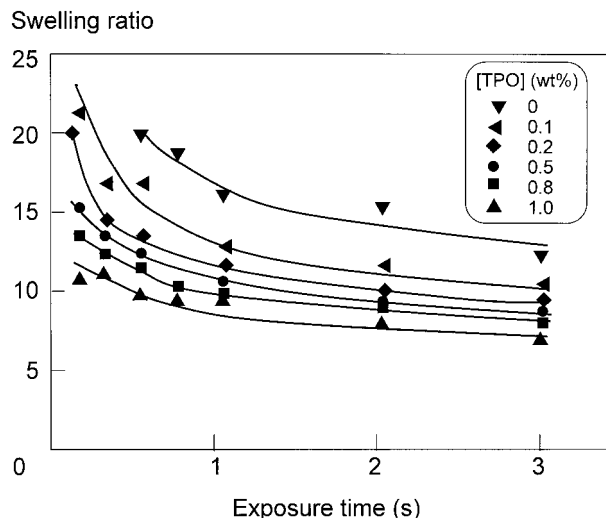


Figure 12 Influence of the photoinitiator concentration on the swelling of a photocrosslinked SBS. [TRIS] = 1 wt %.

from 1 to 0.1 wt %, as shown in Figure 12. The polymer hardening upon UV exposure is less pronounced at low photoinitiator concentrations, as expected, but it still occurs, even in the photoinitiator-free sample (Fig. 13). At [TPO] = 0.2 wt %, the Persoz value increased from an initial value of 35 to 60 s after a 1-s exposure, compared to 100 s at [TPO] = 1 wt %. Operating at such low photoinitiator concentrations, and at irradiation times below 1 s, is therefore recommended for adhesive applications, where the polymer should remain soft and flexible after crosslinking.

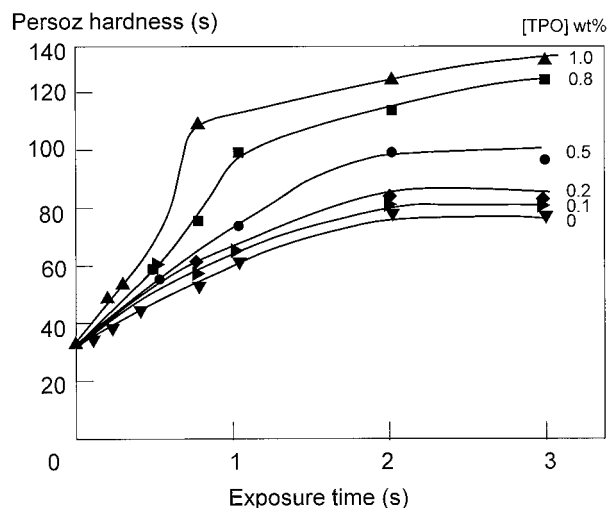


Figure 13 Influence of the photoinitiator concentration on the hardness of a photocrosslinked SBS. [TRIS] = 1 wt %.

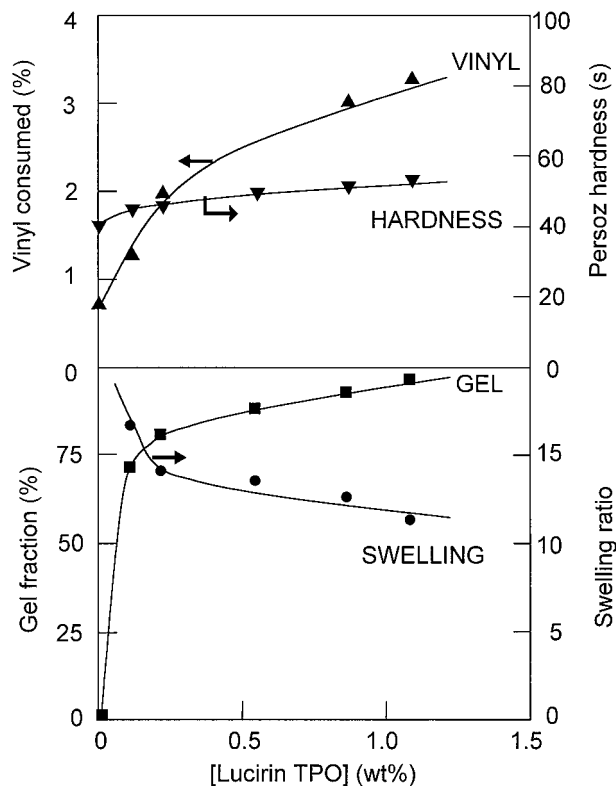


Figure 14 Influence of the photoinitiator concentration on the photocrosslinking of SBS. [TRIS] = 1 wt %. UV exposure: 0.3 s.

Figure 14 summarizes these results by showing the variation with the photoinitiator concentration of the vinyl double-bond consumption, gel fraction, swelling ratio, and Persoz hardness, in an SBS/TRIS (1 wt %) sample UV-irradiated for 0.3 s. A Lucirin TPO concentration of 0.2 wt % appears to be enough to obtain a crosslinked elastomer showing the required performance with respect to the photoreactivity, the viscoelastic properties, and the solvent and heat resistance. By operating at such low photoinitiator concentrations, a few millimeter-thick SBS samples were readily crosslinked by UV-irradiation. This is due to both an increased penetration of UV light and to a fast photobleaching of Lucirin TPO which promotes a frontal polymerization.¹⁵

Photocrosslinking of Kraton Thermoplastic Elastomers

A similar study was performed on two commercial thermoplastic styrene-butadiene elastomers, Kraton® D-1102 and Kraton® D-1186 from Shell. The styrene/butadiene ratio (30/70) and the poly-

butadiene vinyl content (~10%) were similar to that of the SBS sample previously studied. They differ mainly by the molecular weight of the polybutadiene block and its structure which was linear or branched, respectively.

Both samples proved to be very reactive when exposed to UV radiation in the presence of TRIS (1 wt %) and Lucirin TPO (1 wt %). Insolubilization was achieved within less than 1 s, with formation of a soft (Persoz hardness = 60 s) and loosely crosslinked (SR = 10) polymer. In the absence of thiol, the polymerization of the vinyl double bond proceeds less efficiently, so that insolubilization hardly occurs upon UV exposure, as shown in Figure 15 for Kraton® D-1102.

In the presence of 1 wt % TRIS, the branched SBS (Kraton® D-1186) was found to become more readily insoluble than was the linear SBS, so that the photoinitiator concentration could be decreased to 0.2 wt % and still achieve insolubilization within 0.3 s (Fig. 16). As expected, the branched structure of the elastomeric phase causes an increase of the crosslink density of the UV-cured rubber, as shown by the swelling data: an SR value of 8 for Kraton® D-1186 and of 13 for Kraton® D-1102. This trend was also found when neat SBS was UV-irradiated in the presence of a photoinitiator. After a 3-s exposure, the gel fraction was measured to be 70% for Kraton® D-1186 (Fig. 17), compared to only 20% for Kraton® D-1102 (Fig. 15).

To assess the efficiency of the thiol/ene system to crosslink SBS rubbers, in comparison to the

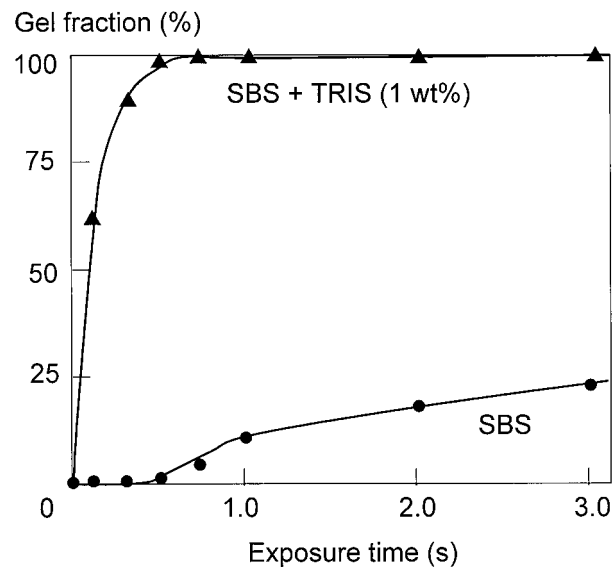


Figure 15 Photocrosslinking of Kraton® D-1102. Influence of the thiol. [Lucirin TPO] = 1 wt %.

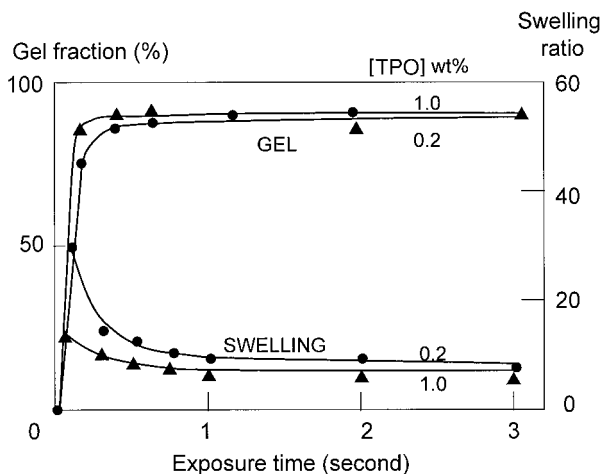


Figure 16 Photocrosslinking of Kraton® D-1186 in the presence of (●) 0.2 wt % or (▲) or 1 wt % Lucirin TPO. [TRIS] = 1 wt %.

usual acrylate-based system, we UV-irradiated a sample of Kraton® D-1186 containing hexanediol diacrylate (HDDA) as a crosslinking agent (20 wt %), under exactly the same conditions. It can be seen in Figure 17 that, in spite of the much higher crosslinker content, insolubilization takes place at a slower pace than for the sample containing 1 wt % TRIS. A gel fraction of 90% was reached after 3 s with the diacrylate and after only 0.3 s for the SBS/TRIS system. The crosslink density of

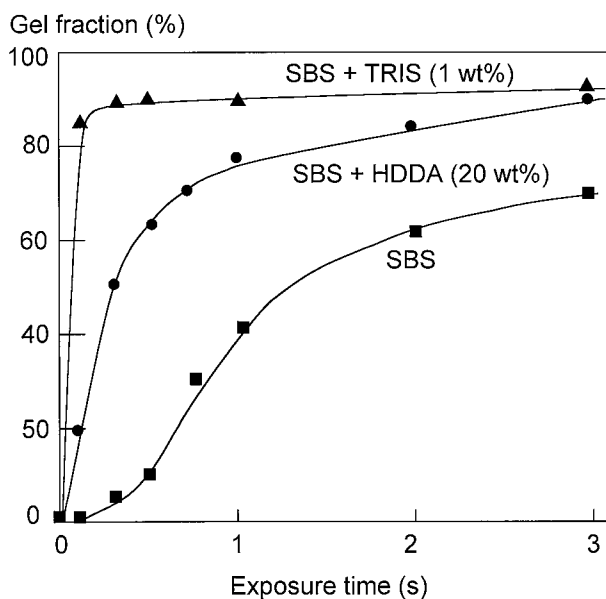


Figure 17 Influence of thiol and acrylate monomers on the photocrosslinking of Kraton® D-1186. [TRIS] = 1 wt %; [HDDA] = 20 wt %; [Lucirin TPO] = 1 wt %.

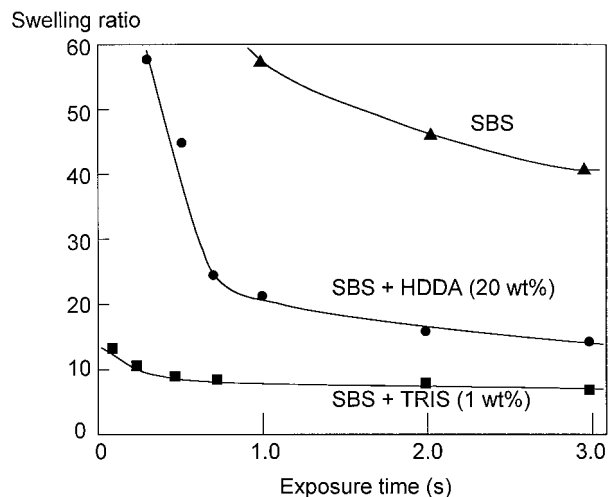


Figure 18 Influence of thiol and acrylate monomers on the swelling ratio of photocrosslinked Kraton® D-1186. [TRIS] = 1 wt %; [HDDA] = 20 wt %; [Lucirin TPO] = 1 wt %.

the UV-cured polymer is also much lower in the SBS/acrylate system, as shown by the swelling profiles (Fig. 18). After a 1-s exposure, the following SR values were measured: 70 for neat SBS, 22 for SBS/HDDA, and 8 for SBS/TRIS. The fact that the acrylate-based rubber is less crosslinked than is the thiol-based rubber was attributed to the competitive homopolymerization of the acrylate double bonds, which does not generate any additional crosslinks between the SBS chains.

Another type of thermoplastic rubber (SIS) consists of a styrenic triblock copolymer where the elastomeric midphase is made of a polyisoprene, such as Kraton® D-1107, which is commonly used in flexographic printing plates and adhesives applications. Its styrene/rubber ratio is 14/86, the linear polyisoprene chains containing no vinyl double bonds. SIS is therefore much less reactive than is SBS and remains completely soluble after a 5-s UV exposure in the presence of Lucirin TPO (1 wt %). The addition of a diacrylate monomer (20 wt % of HDDA) leads to partial insolubilization (Fig. 19), the crosslinks resulting from the copolymerization of the amylene and acrylate double bonds.^{16,17} Crosslinking was found to proceed much more efficiently in a SIS/TRIS (2 wt %) system, UV-irradiated in the presence of 1 wt % Lucirin TPO. Total insolubilization of SIS was achieved within 3 s (Fig. 19), by reaction of the thiol radicals with the amylene double bond:

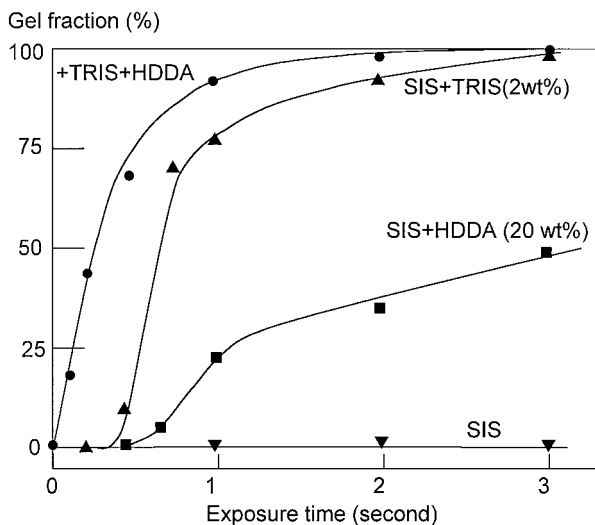
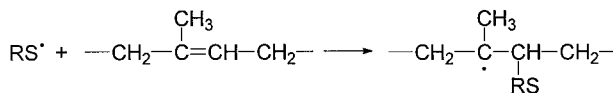


Figure 19 Influence of thiol and acrylate monomers on the photocrosslinking of Kraton® KX-601. [TRIS] = 2 wt %; [HDDA] = 20 wt %; [Lucirin TPO] = 1 wt %.



The best performance was obtained by combining the two crosslinking agents: 2 wt % of TRIS and 20 wt % of HDDA. It should be emphasized that this SIS-based formulation proved actually to be more reactive than the SBS-based formulation containing 20 wt % HDDA (Fig. 17), with formation of a tighter polymer network (SR values of 12 and 16, respectively).

CONCLUSIONS

Thermoplastic styrene/butadiene elastomers containing a low amount of the vinyl group (8%) can be readily crosslinked at ambient temperature by UV irradiation in the presence of very low amounts (≤ 1 wt %) of a trifunctional thiol crosslinker. Both the vinyl and butene double bonds of the polybutadiene chain participate in the thiol/ene polymerization which proceeds by step-growth addition, the thiol radicals acting as chain-transfer agents. The covalent bonds generated within the elastomeric phase led to a marked increase of the solvent and heat resistance of the UV-cured polymer. Insolubilization takes place within 0.3 s upon intense illumination, with formation of a soft and flexible material, well suited for adhesive and flexographic applications.

The photocrosslinking technology offers a number of advantages, such as on-line processing, high-speed curing, solvent-free formulations, low-energy consumption, low cost of chemicals, and selective cure in the illuminated areas. It is easily applicable to commercial styrene/butadiene thermoplastic elastomers, and even to the less reactive styrene/isoprene rubbers, by adding a diacrylate comonomer. The main applications of these photocurable rubbers are expected to be found in industrial sectors where cure speed and spatial control are a major concern, such as for the manufacturing of hot-melt adhesives and sealants, safety glasses, photoresists, and flexible printing plates.

The authors wish to thank Shell Research (Louvain la Neuve, Belgium) for a research grant.

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