Sulfur Vulcanization of Polyisoprene Accelerated by Benzothiazole Derivatives. III. The Reaction of 2-Bisbenzothiazole-2,2'-disulfide with Sulfur and ZnO in Polyisoprene

M. H. S. GRADWELL and W. J. MCGILL*

Polymer Chemistry, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, 6000, South Africa

SYNOPSIS

The sulfur vulcanization of polyisoprene accelerated by 2-bisbenzothiazole-2,2'-disulfide (MBTS) was investigated. Rubber compounds were heated in a DSC and removed at various temperatures along the DSC thermal curve. The rubber vulcanizate was analyzed for cross-link density and for residual reactants and extractable reaction products. MBTS reacts readily with sulfur, and the polysulfidic accelerator complexes react with the rubber chain to form pendent groups. Crosslinking results from hydrogen abstraction, by the benzothiazole pendent group, from a neighboring chain. 2-Mercaptobenzothiazole, a product of cross-linking, also acts as an accelerator in the later stages of the reaction. MBTS has been shown not to react with ZnO and the higher crosslink densities obtained when ZnO is present are attributed to ZnO aiding the abstraction of the benzothiazole pendent group to give zinc mercaptobenzothiazole. A mechanism for the MBTS acceleration of sulfur vulcanization is proposed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The 2-bisbenzothiazole-2,2'-disulfide (MBTS)-accelerated sulfur vulcanization of rubber has been studied by various authors.[1-7] Campbell and Wise[1] found that, in the vulcanization of natural rubber (NR), MBTS reacted with the sulfur to form 2-bisbenzothiazole-2,2'-polysulfides (MBTPs). The concentration of MBTPs increased to a maximum at the end of the cure delay period and decreased rapidly after the onset of crosslinking. When MBTS was replaced by MBTP in the vulcanization of NR, the cure delay time was shortened by the time required for the formation of the maximum amount of the polysulfidic intermediate in the MBTS cure. This led them to suggest that the polysulfidic MBTS species were, in fact, the active accelerators. A mechanism for the formation of MBTPs from a re-

action between MBTS and sulfur, in the absence of rubber, was proposed.[8]

Dogadkin et al.[2] found that MBTS increased the absorption of sulfur by rubber, but, in contrast to Campbell and Wise,[1] they claimed that the thiol formed from MBTS, namely, 2-mercaptobenzothiazole (MBT), reacted with the sulfur and was therefore the actual accelerator. Tutorskkii et al.[3] found that when vulcanizing with MBTS and sulfur the MBTS added to the rubber, but only until the sulfur was used up. A linear relationship was found between the amount of bound sulfur and bound MBTS. MBTS is said to dissociate on heating to form radicals,[2,7] the molecule splitting symmetrically or unsymmetrically. This is in agreement with Shelton and McDonel[9] who found MBTS vulcanization to be a combined free-radical and ionic mechanism. Radical scavengers retard the crosslinking reaction of MBTS.

While some authors[10] suggested that interaction between ZnO and MBTS can occur, X-ray studies by Gradwell and McGill[11] and DSC work by Kruger and McGill[12] showed that MBTS does not react with
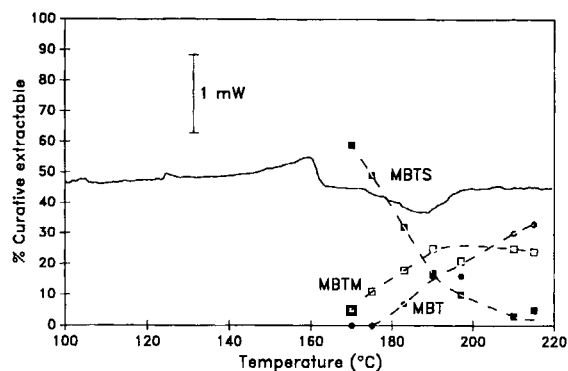
Figure 1 Analysis of the IR/MBTS vulcanization system. DSC curve, heating rate 2.5°C/min, M_i = 27.6574 mg, M_f = 27.6265 mg. (----) % Curative extractable.

ZnO to form zinc mercaptobenzothiazole [Zn(mbt)$_2$]. MBT, which forms in the compound during vulcanization with MBTS,[1] readily reacts with ZnO, but the formation of Zn(mbt)$_2$ delays the onset of crosslinking in MBT-accelerated systems.[13,14] Thus, the role of the zinc–accelerator complex, often claimed to be the active accelerator,[15] must be questioned. This article reinvestigated the MBTS-accelerated sulfur vulcanization of polyisoprene (IR), aimed to clarify the role of MBT in the reaction, and compared the reactions that occur in the presence and absence of ZnO.

EXPERIMENTAL

The 2-bisbenzothiazole-2,2'-disulfide (MBTS) was produced by Orchem (South Africa). The experimental procedures were described in previous articles in the series.[13,14] The data for MBTPs in this text is the total MBTP concentration; it includes the trisulfide, tetrasulfide, and any higher polysulfides that were detected by HPLC. 2-Bisbenzothiazole-2,2'-monosulfide (MBTM) was synthesized according to the method of D'Amico et al.[16]; NMR

and sulfur analysis of the product confirmed the structure of MBTM. MBTS polysulfides were prepared by the method of Levi.[17]

RESULTS

IR/MBTS

MBTS is relatively insoluble in rubber.[4] The DSC curve of the IR/MBTS system exhibits a broad endotherm peaking at 159°C, attributable to the melting/dissolution of the MBTS (Fig. 1). A decomposition exotherm, associated with the formation of MBTM, starts at T_0 = 173°C and has a peak at T_p = 188°C. The first crosslinks are found at 190°C and the crosslink density increases very slowly, reaching the very low value of $\frac{1}{2}$ M_c = 6.27 × 10^{-7} mol/mL at 215°C, which is to be expected in the absence of elemental sulfur. The bulk of the MBTS reacts before any crosslinking is observed. The products of these reactions are MBTM and, once crosslinking starts, MBT.

In an isothermal study of this vulcanization reaction, the rubber compound was heated for various times, from 5 to 30 min at 172°C (Table I). A similar result to that found above was obtained, where the MBTS had reacted almost entirely before crosslinking took place. A gel was formed after 15 min, at which point 41% of the MBTS had been converted to MBT and MBTM and 23% was unextractable.

The formation of carbon–carbon crosslinks was proposed by Dogadkin et al.[2] To determine the presence of any carbon–carbon bonds, a vulcanizate, which had been heated to 220°C, was treated with a chemical probe.[18] The vulcanizate dissolved completely after treatment with the methyl iodide, indicating that there were no C — C crosslinks in the vulcanizate.

Table I   Analysis of the IR(100)/MBTS(12.3) Vulcanization System Heated at 172°C for Different Times

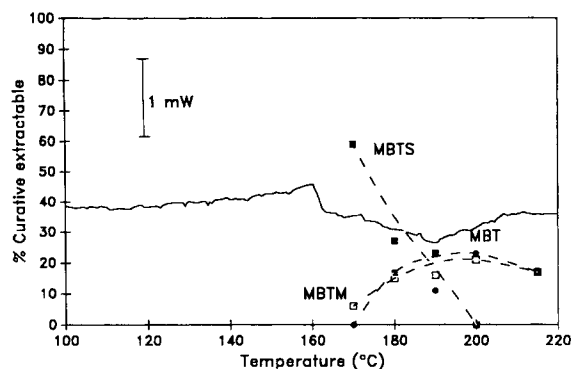| Time (min)	Crosslink Density $1/2M_c$ (× 10^5 mol/mL)	% Curative Extractable				S Atoms/Crosslink
		MBT	MBTM	MBTS	MBTP	
5	0	0	6	75	0	
10	0	3	20	58	0	
15	Gel	13	28	33	0	
30	0.02	25	23	2	0	298

Figure 2 Analysis of the IR/MBTS/ZnO vulcanization system. DSC curve, heating rate 2.5°C/min, M_i = 22.8852 mg, M_f = 22.6851 mg. (----) % Curative extractable.

IR/MBTS/ZnO

The combination of IR/MBTS/ZnO shows a similar DSC curve to the IR/MBTS system (Fig. 2). The DSC exotherm has T_0 = 172°C and T_p = 189°C with the MBTS melt/dissolution at 160°C. This is identical to the IR/MBTS system, and, once again, crosslinking does not begin until after the maximum of the exotherm. Although still small, the maximum crosslink density obtained at 215°C is more than double that without ZnO ($\frac{1}{2} M_c$ = 0.056 × 10⁻⁵ mol/ mL). The extractable product spectrum is similar to that found in the absence of ZnO (cf. Figs. 1 and 2), the extractable MBTS concentration decreases more rapidly than in the absence of ZnO, MBTM is formed, and some MBT appears above 180°C, in this case prior to the detection of a loose gel.

IR/MBTS/Sulfur

The MBTS/sulfur melt/interaction occurs at 147°C (Fig. 3). The vulcanization exotherm exhibits two exothermic events: The first exotherm starts at 153°C and the second exotherm at 165°C, with the peak at 173°C.

The crosslinking reaction is more rapid than with MBT as the accelerator[14] and starts at 155°C, i.e., at the beginning of the first exotherm, at which point 56% of the MBTS is unextractable. The end of the first exotherm coincides with the MBTS being used up. The maximum crosslink density ($\frac{1}{2} M_c$ = 6.48 × 10⁻⁵ mol/mL) occurs at this point (165°C) and the Moore–Trego efficiency is at its optimum (19 sulfur atoms per crosslink). However, when the MBTS has been consumed, 43% of the sulfur remains as well as 74% of the benzothiazole groups, now converted to MBT (Fig. 3). MBT is produced very rapidly once crosslinking begins. During the

second exotherm, the remaining sulfur is used without any further increase in the overall crosslink density, reversion reactions dominating. When using half of the sulfur loading, a much lower sulfur concentration remained when the MBTS had been consumed and the second exotherm above 165–170°C, attributed to the MBT/sulfur reaction, is not evident.

Unlike in the IR/MBTS system, MBTPs are detected, although, as they are very reactive, the amounts extracted at any point in the vulcanization process are very low. At 150°C, just prior to crosslinking, some 45% of the MBTS added to the compound was unextractable and presumed bound to the rubber chain as pendent groups. To investigate the role of such groups in crosslinking, a sample was heated to 150°C in the DSC, extracted with acetone to remove residual MBTS and sulfur, and reheated to 220°C. No exotherm was evident, and on addition of benzene, the sample formed a highly swollen gel of very low crosslink density. To another sample, heated and extracted as above, 33.5 × 10⁻⁵ mol of sulfur per mL of rubber was added. When reheated in the DSC, the vulcanization exotherm obtained was not that of an IR/sulfur system as would be expected if the pendent groups were inactive. Instead, the onset and peak of the exotherm occurred at lower temperatures, indicating interaction between pendent groups and the added sulfur.

An isothermal study, at 131°C, of the early stages of reaction of this compound also showed that much of the MBTS and sulfur are bound before any significant crosslinking starts. A sample that had been heated for 40 min had only 8% MBTS and 37% sulfur extractable, although the crosslink density was still only 0.23 × 10⁻⁵ mol/mL.

The possibility of carbon–carbon crosslinks was investigated by heating samples to 165°C and reacting them with methyl iodide. No carbon–carbon crosslinks were found in this vulcanization system.

IR/MBTS/Sulfur/ZnO

The DSC curve for this combination is very similar to that of the IR/MBTS/sulfur vulcanization (Fig. 4). The MBTS/sulfur melt interaction occurs at 147°C, T_0 = 151°C and T_p = 173°C. The vulcanization cure curve again exhibits a double exotherm, but after the first shoulder becomes much more exothermic, the second starting at 164°C when all of the MBTS has been consumed. Crosslinking starts at 155°C, at which point 40% of the MBTS is no longer extractable.
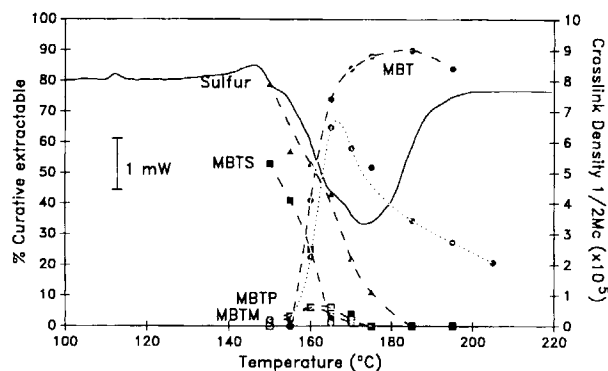
Figure 3   Analysis of the IR/MBTS/sulfur vulcanization system. DSC curve, heating rate 2.5°C/min, M_i = 23.9907 mg, M_f = 23.9547 mg. (· · · ·) Crosslink density $\frac{1}{2} M_c$ (×10⁵. (----) % Curative extractable.

Plots of extractable sulfur and MBTS vs. temperature (Fig. 4) suggest that these are consumed slightly more slowly. MBT is released quickly once crosslinking starts but much more slowly than in the absence of ZnO and it does not reach the same concentration. As in other systems containing zinc,[13] ZnO leads to a higher crosslink density ($\frac{1}{2} M_c$ = 9.48 × 10⁻⁵ mol/mL at 165°C).

DISCUSSION

IR/MBTS

On heating MBTS in the presence of IR, the amount of extractable MBTS decreases progressively (Fig. 1) while the MBTM concentration in the extract increases. This is consistent with the decomposition of MBTS in the absence of rubber.[11] While some MBTPs form on heating MBTS, no MBTPs were extracted from the IR/MBTS system, presumably as any small amount of these highly reactive polysulfides[1] would readily bind to the rubber chain.

The total amount of extractable mercaptobenzothiazole groups decreases as the temperature is increased and it is noticeable that this is not associated with the formation of MBT. In the IR/TMTD and IR/TMTD/sulfur systems[19] and in the reaction of TMTD/sulfur with the model compound 2,3-dimethyl-2-butene (TME),[20] the formation of polysulfidic accelerator-terminated pendent groups is accompanied by the generation of dimethyldithiocarbamic acid, i.e., addition of the accelerator to the rubber is a substitutive process, the H atom abstracted binding to half an accelerator molecule to give the acid. The addition of MBTS or MBTP to the polymer appears to be an additive process. It

is not implied that MBTP adds to the double bond; addition may occur elsewhere on the polymer chain and be accompanied by a shift of, say, H atoms to the double bond. This aspect is being further investigated. MBT is generated rapidly only once crosslinking commences (Fig. 1). It is generally[21] suggested that crosslinking in accelerated sulfur vulcanization either involves reaction between pendent groups or reaction of a pendent group with a neighboring chain. As MBT formation, rather than the regeneration of MBTS, accompanies crosslinking, reaction between pendent groups and neighboring chains would appear the more reasonable mechanism with MBTS. Hydrogen abstraction most probably occurs via the more electronegative nitrogen atom in the benzothiazole group:
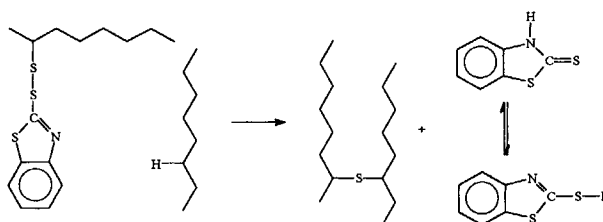
The number of crosslinks formed (<0.05 × 10⁻⁵ mol/mL) is far less than the amount of MBT generated (20 × 10⁻⁵ moles/mL). An analogous intramolecular abstraction to the above would lead to the formation of cyclic sulfides in the chain and would account for the high yield of MBT compared to the number of crosslinks formed.

At 215°C, 62% of the original MBTS is extractable as MBTS, MBTM, or MBT (Fig. 1). The remainder is probably bound to the polymer as unreactive monosulfidic pendent groups.
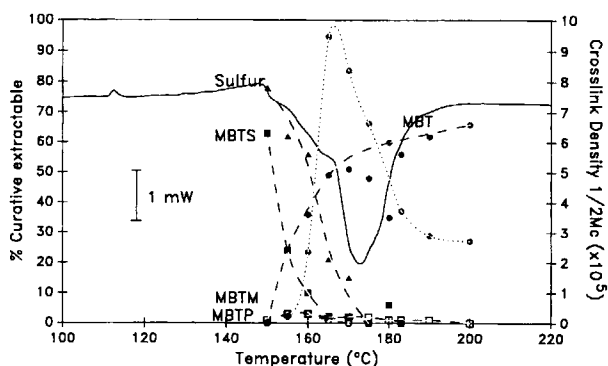

Figure 4   Analysis of the IR/MBTS/sulfur/ZnO vulcanization system. DSC curve, heating rate 2.5°C/min, M_i = 23.7954 mg, M_f = 23.6774 mg. (· · · ·) Crosslink density $\frac{1}{2} M_c$ (× 10⁵. (----) % Curative extractable.

Dogadkin et al.[2] suggested that crosslinking involved a free-radical process, benzothiazolyl radicals adding to a double bond. Carbon–carbon bond crosslinking was suggested although this study found no evidence of such bonds. Scheele,[7] too, proposed scission of the sulfur–sulfur bond in MBTS followed by a radical attack on the polymer and carbon–carbon crosslinking. The maximum crosslink density attained is very low and it is perhaps not surprising that some articles[2] record that MBTS does not lead to crosslinking in the absence of sulfur.

IR/MBTS/Sulfur

On heating MBTS in the presence of sulfur, considerably larger amounts of MBTPs are formed[8] and small amounts of these can now also be detected in the early stages of reaction in the rubber formulation (Fig. 3). As in the absence of rubber,[8] high sulfur loadings ensure that the amount of MBTM formed is low. Since the concentration of the more reactive MBTPs is higher than in the IR/MBTS system, mercaptobenzothiazole groups bind to the polymer more readily, approximately 50% of the MBTS being bound at 150°C compared to a similar amount at 180°C in IR/MBTS. This is consistent with the finding by Campbell and Wise[1] that the replacement of MBTS in a formulation by an equivalent amount of MBTT, the tetrasulfide of MBTP, reduced the cure delay time. Crosslinking is rapid above 155°C and is accompanied by the equally rapid release of MBT. This indicates an identical reaction mechanism to that proposed above. The absence of MBT prior to crosslinking, and its rapid formation once crosslinking starts, points to the additive rather than substitutive interaction of MBTPs with IR, crosslinking resulting from reaction of polysulfidic pendent groups with adjacent polymer chains as detailed above. As in the IR/MBTS system, the amount of MBT formed far exceeds the number of crosslinks, again pointing to intramolecular reactions. Most of the benzothiazole can be accounted for as MBT at higher temperatures, confirming that pendent groups were mainly polysulfidic or that monosulfidic groups were activated with sulfur as demonstrated above.

The DSC curve shows the occurrence of two exothermic events, the end of the first exotherm coinciding with the MBTS being used up. However, at this point, 43% of the sulfur remains while a high concentration of MBT has built up. It is suggested that the remaining sulfur is consumed via MBT-accelerated sulfur vulcanization that occurs rapidly[4] in this temperature region. Despite the second crosslinking process, the maximum crosslink density applies at the end of the first exotherm and thereafter declines, i.e., during the second exotherm crosslink, breaking reactions exceed the rate of crosslinking via the latter reaction.

Dogadkin et al.[2] claimed that MBT was the actual accelerator and was completely consumed during the reaction. The present study shows that MBT acceleration becomes important only once all the MBTS has been consumed. No carbon–carbon crosslinks were detected as has been proposed.[2]

The Effect of ZnO

As MBTS does not interact with ZnO,[11,12] the initial behavior of the system is not expected to differ from that in the absence of ZnO. Indeed, (a) the DSC vulcanization curve of the IR/MBTS/sulfur/ZnO system again clearly shows the presence of two exothermic events; (b) in the absence of sulfur, large amounts of MBTM are detected as the MBTS concentration decreases, while in the presence of sulfur, the MBTM concentration is lower and some MBTPs can be extracted; and (c) MBT is rapidly liberated once crosslinking starts. MBT and ZnO readily interact[13] and $Zn(mbt)_2$ will form in the rubber at this stage. The total amount of MBT liberated both in the absence and presence of sulfur is less than when there is no ZnO in either system (cf. Figs. 1 and 2; 3 and 4). In particular, in the sulfur system, only 50% MBT is extractable in the presence of ZnO compared to 75% in the absence of ZnO at the point where all of the MBTS has been consumed. [One may ask why all of the MBT is not trapped and the answer may lie in the formation of a layer of $Zn(mbt)_2$ at the surface of ZnO particles, preventing further reaction. During compounding, the MBT/ZnO reaction goes to completion,[13] but the high shearing forces that operate during compounding would disrupt such a layer of material.]

The main difference occasioned by ZnO is an increase in the crosslink density maximum which occurs at the point at which all of the MBTS has been utilized; for the MBTS systems, $\frac{1}{2} M_c = 0.06 \times 10^{-5}$ vs. 0.42×10^{-5} mol/mL, respectively, and for the MBTS/sulfur systems, $\frac{1}{2} M_c = 6.48 \times 10^{-5}$ vs. 9.48×10^{-5} mol/mL, respectively. The high crosslink density is achieved during the MBTS vulcanization reaction, i.e., in the period during which MBT is liberated and is trapped to form $Zn(mbt)_2$. It is the ZnO particle, not $Zn(mbt)_2$, that ensures the development of a high crosslink density; the $Zn(mbt)_2$/sulfur-accelerated reaction leads to a maximum crosslink density of only 5×10^{-5} mol/

mL.[13] It is suggested that both crosslinking and cyclization can occur via H abstraction by the N atom in the benzothiazole group. The mechanism whereby ZnO increases the crosslink density is by no means clear, but by forming $Zn(mbt)_2$, the ZnO may facilitate the removal of BtS groups, giving a persulfenyl radical on the polymer chain that could link to a similar radical on another chain, thereby reducing pendent group–chain cyclization reactions.

CONCLUSIONS

Polysulfidic complexes of MBTS form very readily on heating, particularly in the presence of elemental sulfur and it is shown that vulcanization is initiated by the addition of such MBTPs to the polymer chain. The absence of MBT in the product spectrum at this stage points to the formation of pendent groups via an additive rather than a substitutive process. Crosslinking results mainly from the abstraction by the benzothiazole group (N atom) of hydrogen on a neighboring chain. The high ratio of moles of MBT released to moles of crosslinks formed (> 10) points to parallel intramolecular reactions that will result in cyclic structures rather than crosslinks. MBT released in the process will also act as an accelerator, particularly in the latter stages when all of the MBTS has been consumed, but while some sulfur still remains. MBTS and ZnO do not interact and $Zn(mbt)_2$ is formed in the compound only once MBT is released. Higher crosslink densities, found in the presence of ZnO, are attributed to the oxide, aiding abstraction of the benzothiazole pendent group to give $Zn(mbt)_2$. It is ZnO, not $Zn(mbt)_2$, that is responsible for higher crosslink densities.

REFERENCES

1. R. H. Campbell and R. W. Wise, *Rubb. Chem. Tech.*, **37**, 635 (1964).
2. B. Dogadkin, V. Selyukova, Z. Tarasova, A. Dobromyslova, M. Feldshtein, and M. Kaplunov, *Rubb. Chem. Tech.*, **29**, 917 (1956).
3. I. A. Tutorskii, L. B. Ginsburg, and B. A. Dogadkin, *Rubb. Chem. Tech.*, **34**, 334 (1961).
4. M. C. Throdahl, *Rubb. Age*, **67**, 445 (1950).
5. O. A. Zeide and K. D. Petrov, *Kauchuk i Rezina*, 51 (1937).
6. B. C. Barton, *Ind. Eng. Chem.*, **42**, 671 (1950).
7. W. Scheele, *Rubb. Chem. Tech.*, **34**, 1306 (1961).
8. M. H. S. Gradwell, B. Morgan, and W. J. McGill, *J. Appl. Polym. Sci.*, **56**, 1581 (1995).
9. J. R. Shelton and E. T. McDonel, *Rubb. Chem. Tech.*, **33**, 342 (1960).
10. R. S. Kapur, J. L. Koenig, and J. R. Shelton, *Rubb. Chem. Tech.*, **47**, 911 (1974).
11. M. H. S. Gradwell and W. J. McGill, *J. Appl. Polym. Sci.*, **51**, 177 (1994).
12. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2651 (1991).
13. M. H. S. Gradwell and W. J. McGill, *J. Appl. Polym. Sci.*, **58**, 2185 (1995).
14. M. H. S. Gradwell and W. J. McGill, *J. Appl. Polym. Sci.*, **58**, 2193 (1995).
15. L. Bateman, C. G. Moore, M. Porter, and B. Saville, in *The Chemistry and Physics of Rubber-like Substances*, L. Bateman, Ed., Maclaren, London, 1963, Chap. 15.
16. J. J. D'Amico, S. T. Webster, R. H. Campbell, and C. E. Twine, *J. Org. Chem.*, **30**, 3618 (1965).
17. T. G. Levi, *Gazz. Chim. Ital.*, **61**, 383 (1931).
18. R. F. Naylor, *J. Chem. Soc.*, **4**, 2749 (1949).
19. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **44**, 587 (1992).
20. M. Geyser and W. J. McGill, *J. Appl. Polym. Sci.*, to appear.
21. A. V. Chapman and M. Porter, in *Natural Rubber Science and Technology*, A. Roberts, Ed., Oxford University Press, Oxford, 1988, Chap. 12.