

Dual Function Curative for NR

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Synopsis

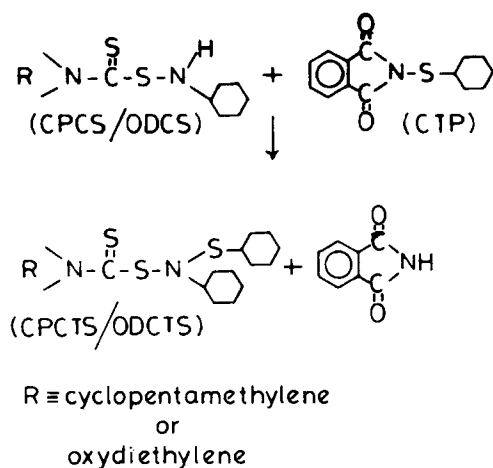
Two derivatives of thiocarbamyl sulfenamide containing thiocyclohexyl moiety on sulfenamide nitrogen atom have been synthesized and evaluated for their action as accelerator cum retarder in NR gum stocks.

INTRODUCTION

The scorchy behavior of thiocarbamyl sulfenamide has been moderated¹ by incorporating *N*-cyclohexyl thiophthalimide (CTP) which would delay the process. The performance of this retarder is not adequate and is very much dependent upon the nature of amine moiety on the carbamate *N*-atom. Moreover, CTP generates phthalimide, an extraneous material, that sometimes causes blooming on the vulcanizates. In a recent investigation² it has been shown that phthalimide might reduce the modulus and tensile strength of NR vulcanizates during aging. In the present investigation an attempt has been made to formulate a compound that would exhibit the accelerating as well as the retarding activity. This compound can be used effectively as a rubber additive that would eliminate the undesirable effect of a side product generated from the parent compound. From the structure of CTP it is seen that cyclohexyl thiomoiety is attached to nitrogen to incorporate an S—N bond that is reactive towards accelerators,^{1,3,4} especially MBT. This S—N bond can be introduced in a suitable thiocarbamyl sulfenamide whose curing efficiency is similar to thiuram ultra accelerators, through the NH functionality; as a result the retarding as well as accelerating activity of the resultant compound could be observed. With this in mind, *N*-cyclopentamethylenethiocarbamyl-*N'*-cyclohexyl sulfenamide (CPCS) and *N*-oxydiethylenethiocarbamyl-*N'*-cyclohexyl sulfenamide (ODCS) were selected as representative thiocarbamyl sulfenamide accelerators that have been chemically modified as shown in Scheme 1:

EXPERIMENTAL

The accelerators and retarders employed in the study are shown in Table I. The vulcanizing ingredients (zinc oxide, stearic acid, sulfur, accelerator, and retarder) were incorporated into NR on a 203 × 104 mm lab mill in accordance with the recipe as shown in Table II. The stocks were cured under pressure at 140°C, and the vulcanizates were kept for 24 h at ambient temperature before the measurement of modulus at 200% elongation and



Scheme 1. Formation of CPCTS/ODCTS from CPCS/ODCS-CTP reaction

TABLE I
List of Compounds Used

Chemical name	Abbreviation	Structure
Cyclohexyl thiomorpholine ^{1,5}	CM	
Cyclohexyl thiopiperidine ^{1,5}	CP	
<i>N</i> -cyclopentamethylene thiocarbamyl- <i>N'</i> -cyclohexyl sulfenamide ⁶	CPCS	
<i>N</i> -cyclopentamethylene thiocarbamyl- <i>N'</i> -(cyclohexyl thiocyclohexyl) sulfenamide	CPCTS	
<i>N</i> -cyclopentamethylene thiocarbamyl cyclohexyl disulfide ¹	CPTCD	
Bis(cyclopentamethylene) thiuram disulfide ^{1,7,8}	CPTD	
Bis(cyclopentamethylene) thiuram monosulfide ^{1,7,9}	CPTM	
<i>N</i> -cyclopentamethylene thiocarbamyl- <i>N'</i> -cyclopentameth- ylene sulfenamide ⁶	CTCS	

TABLE I
Continued

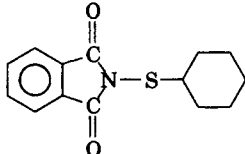
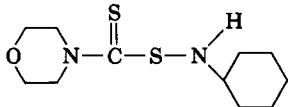
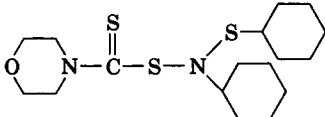
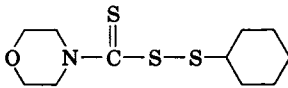
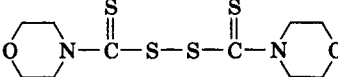
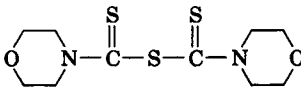
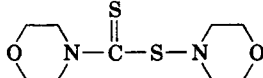
Chemical name	Abbreviation	Structure
<i>N</i> -cyclohexyl thiophthalimide	CTP	
<i>N</i> -oxydiethylenethiocarbamyl- <i>N'</i> -cyclohexyl sulfenamide ⁶	ODCS	
<i>N</i> -oxydiethylenethiocarbamyl- <i>N'</i> -(cyclohexyl, thiocyclohexyl) sulfenamide	ODCTS	
<i>N</i> -oxydiethylenethiocarbamyl cyclohexyl disulfide ¹	OTCD	
Bis(oxydiethylene) thiuram disulfide ^{1,7,8}	OTD	
Bis(oxydiethylene) thiuram monosulfide ⁹	OTM	
<i>N</i> -oxydiethylenethiocarbamyl- <i>N'</i> -oxydiethylene sulfenamide	OTOS	

TABLE II
Stock Formulations

Ingredient stock no.	1	2	3	4	5	6
RMA 1X (g)	100	100	100	100	100	100
Zinc oxide (g)	5	5	5	5	5	5
Stearic acid (g)	2	2	2	2	2	2
Sulfur (g)	0.5	0.5	0.5	0.5	0.5	0.5
CPCS (g)	2.322	2.322	—	—	—	—
ODCS (g)	—	—	2.340	2.340	—	—
CP (g)	—	0.398	—	—	—	—
CM (g)	—	—	—	0.402	—	—
CPCTS (g)	—	—	—	—	3.348	—
ODCTS (g)	—	—	—	—	—	3.366

TABLE III
Physical Data of Stocks Obtained at 140°C

Mix no.	Maximum torque R_{∞} (N m)	Scorch time t_2 (min)	Optimum cure time t_{90} (min)	200% modulus (MPa)	Tensile strength (MPa)
1	4.4	5.0	26.0	0.84	16.67
2	3.7	7.0	28.0	0.70	14.91
3	4.2	7.0	27.0	0.81	14.47
4	3.6	12.5	29.0	0.72	13.36
5	4.1	9.0	32.0	0.80	16.61
6	3.9	19.0	33.0	0.79	14.81

tensile strength according to ASTM designation D 412-51 T using dumbbell-shaped test pieces. The modulus and tensile strength of the vulcanizates and the cure data obtained on a Monsanto rheometer (R-100) are provided in Table III.

Various compounds formed in the reaction of rubber additives heated at 140°C were identified using HPLC technique.^{1,10,11} A definite amount of vulcanizates (grossly undercured stocks) containing the rubber additives was extracted with boiling acetone for 1 h. Acetone was then removed under vacuum and 5 cm³ of acetonitrile–water (70 : 30 v/v) was added, which served the eluent for the HPLC system. Chromatograms were then obtained by injecting 2 mm³ of the clear solution onto the HPLC column. The reaction products obtained were identified using a 25 cm waters μ -c₁₈ Bondapack reverse phase chromatography column, by retention time as well as co-injection of authentic samples. A varian UV detector operating at 254 nm was used.

**Preparation of *N*-Cyclopentamethylene
Thiocarbamyl-*N'*-(Cyclohexyl, Thiocyclohexyl) Sulfenamide
(CPCTS) and *N*-Oxydiethylene Thiocarbamyl-*N'*-(Cyclohexyl,
Thiocyclohexyl) Sulfenamide (ODCTS)**

A mixture containing 5.22 g (0.02 mol) of CTP and 0.02 mol of appropriate sulfenamide in 50 cm³ of isopropyl alcohol was heated at reflux (82–83°C) for 10 h. The solution thus obtained was kept stirring at ambient temperature for 24 h when phthalimide precipitated out, which was removed by filtration. To the filtrate, 70 cm³ of water containing 4.8 g (0.03 mol) of NaOH was added and stirring continued for 30 min. The reaction mixture extracted with 60 cm³ of diethyl ether, separated, washed with water until washing were neutral, and then dried over anhydrous Na₂SO₄. The ether was removed in vacuum and the solid thus obtained were found to be pure based on the following analyses.

CPCTS. mp = 53°C (recrystallized from ethanol). Found 58.01% C, 8.16% H, 7.15% N, and 25.76% S; C₁₈H₃₂N₂S₃ by calculation contains 58.06% C,

8.60% H, 7.52% N, and 25.80% S; NMR: δ (CCl_4), 0.80–2.30 (m, 26 H, methylene protons), 3.50–3.90 (m, 6 H, $\text{N}-\text{CH}_2-$, $-\text{S}-\text{CH}$, and $\text{N}-\text{CH}$ merged).

ODCTS. mp = 114°C (recrystallized from ethanol). Found 54.14% C, 8.16% H, 7.39% N, and 25.51% S; $\text{C}_{17}\text{H}_{30}\text{N}_2\text{OS}_3$ by calculation contains 54.54% C, 8.02% H, 7.48% N, and 25.66% S; NMR: δ (CCl_4), 0.95–2.11 (m, 20 H, methylene protons), 3.28–4.11 (m, 10 H, $\text{N}-\text{CH}_2-$, $-\text{O}-\text{CH}_2-$ and $-\text{SCH}$ merged).

^1H -NMR spectrum at 60 MHz was taken in a Varian T-60 A NMR spectrometer.

RESULTS AND DISCUSSION

The choice of CPCS and ODSCS as the base accelerator has been guided by the fact that under vulcanizing conditions it gives rise to active thiuram compounds that are more or less scorchy.¹ The effect of CP or CM on this scorchy accelerator has been included in this study in order to compare the data with that of modified thiocarbonyl sulfenamide. Six mixes according to the recipes given in table I were prepared, and the curing behavior of these compounds is shown in Figures 1 and 2. It can be seen from the rheographs

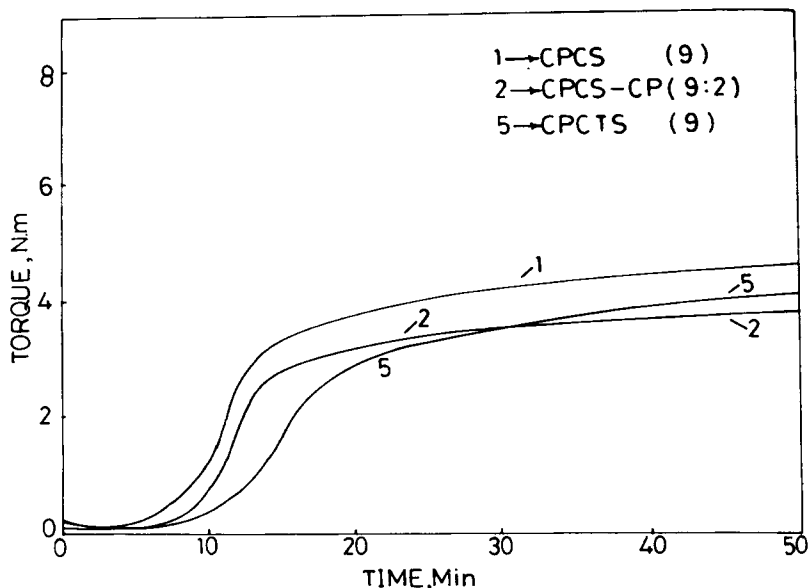


Fig. 1. Rheographs of NR gum stocks cured at 140°C: (1) CPCS (9); (2) CPCS-CP (9:2); (5) CPCTS (9).

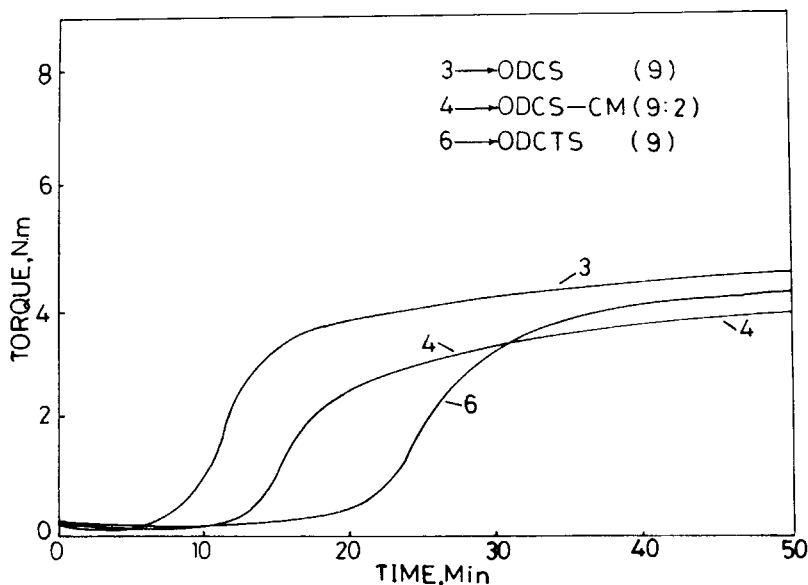


Fig. 2. Rheographs of NR gum stocks cured at 140°C: (3) ODCS (9); (4) ODCS-CM (9:2); (6) ODCTS (9).

that CP or CM has a retarding effect upon CPCS or ODCS, respectively. It also diminishes the cure rate and maximum torque somewhat. The cure characteristics of CPCTS or ODCTS are also shown in Figures 1 and 2 (curves 5 and 6). The results are indicative of the interaction of CP or CM with the accelerator system. It is evident from the rheograph that similar type of reaction are occurring when CPCTS or ODCTS is dispersed in rubber and heated to 140°C in the early stage of vulcanization.

To gain insight into the reactions occurring in these systems, we performed HPLC studies. CPCS or ODCS was first allowed to react with CP or CM at 140°C in the presence of rubber. The results are depicted in Figures 3(a) and 3(b), respectively. It is evident from the chromatogram that CP, CPTM, CTCS, CPTD, CPCS and CPTCD [see Fig. 3(a)] and CM, OTM, OTOS, OTD, ODCS, and OTCPD [see Fig. 3(b)] are generated in the medium. The same reaction products are obtained when the modified thiocarbamyl sulfenamide, viz., CPCTS or ODCTS, is dispersed in rubber under vulcanizing conditions, and the results are depicted in the chromatogram [Fig. 4(a) and 4(b)]. The following reaction scheme based on the free radical decomposition^{1,12} of the CPCTS or ODCTS in actual vulcanizing conditions provide a probable route for the generation of various compounds:

The existence of CPTD, CPTM, CPTCD, CP and CPCS in the reaction medium indirectly lends support to these reaction.

Accelerating Activity of CPCTS and ODCTS

Accelerating activity of CPCTS and ODCTS has been established by rheometric studies and tensile properties of the vulcanizates. Cure characteristics (Fig. 1, curve 5, and Fig. 2, curve 6) and tensile properties of the stocks (Table II, mixes 5 and 6) indicate that both CPCTS and ODCTS do act as

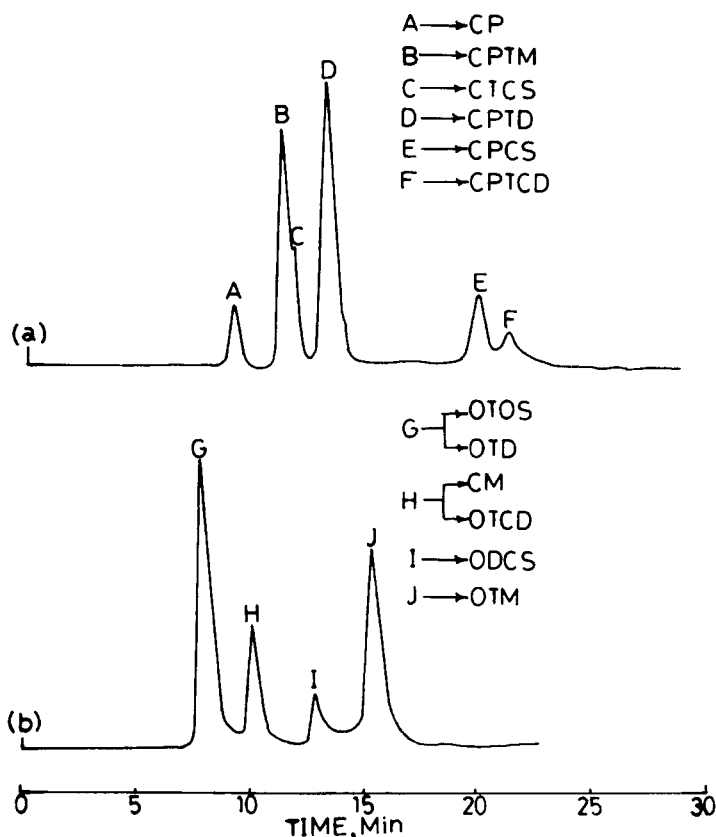


Fig. 3. High performance liquid chromatogram of the extract obtained from 0.370 g of NR vulcanizate cured at 140°C for 2 min. (a) Stock 2: (A) CP; (B) CPTM; (C) CTCS; (D) CPTD; (E) CPCS; (F) CPTCD. (b) Stock 4: (G) OTOS, OTD; (H) CM, OTCD; (I) ODSCS; (J) OTM.

accelerator in the vulcanization of NR gum stocks. The efficiency of CPCTS, however, is superior to that of ODCTS. This is because of the fact that CPCTS produce CPTD [chromatogram 4(a)] and ODCTS generated OTD [chromatogram 4(b)] in the early stage of vulcanization of NR, of which the vulcanizing behavior of CPTD is superior to that of OTD as reported earlier.¹

Scorch Delay Properties of CPCTS and ODCTS

Comparison of the retardation characteristics of stocks 5 and 6 (Table II) shows that both CPCTS and ODCTS increase the scorch time, which is even better than that offered by CP or CM (2 mmol) in combination with CPCS or ODSCS (9 mmol), respectively (stocks 2 and 4, Table II). It is evident from the chromatogram [Figs. 4(a) and (b)] that CPCTS and ODCTS generate CP and CM, respectively, which are supposed to behave as an effective retarder for thiocarbamyl sulfenamide.¹ The delay action is due to the presence of thiocyclohexyl group in thiocarbamyl sulfenamide similar to that of CTP, which delays the promotion of reaction of sulfenamide with sulfur by dithiocarbamic acid. The thiocyclohexyl group captures the amine moiety of the acid formed

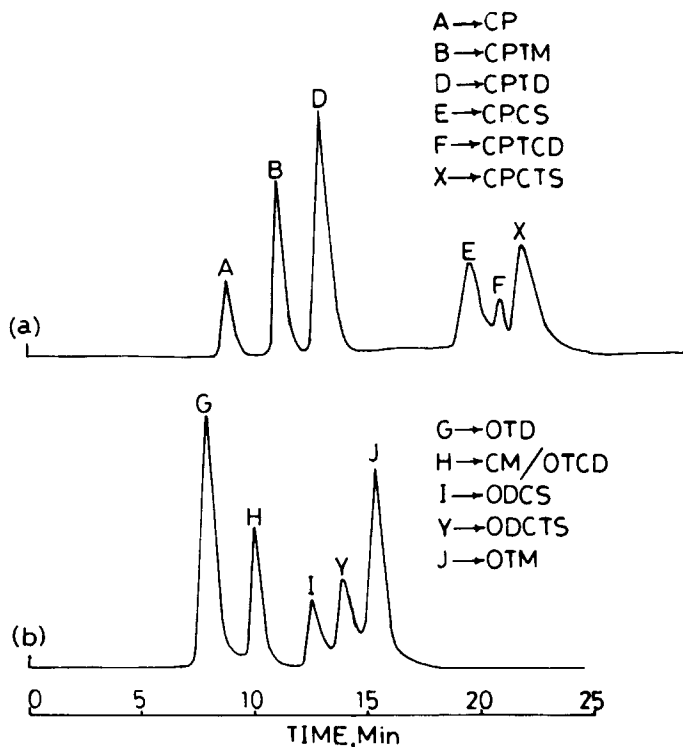


Fig. 4. High performance liquid chromatogram of the extract obtained from 0.370 g of NR vulcanizate cured at 140°C for 2 min. (a) Stock 5; (A) CP; (B) CPTM; (D) CPTD; (E) CPCS; (F) CPTCD; (X) CPCTS. (b) Stock 6; (G) OTD; (H) CM/OTCD; (I) ODCS; (Y) ODCTS; (J) OTM.

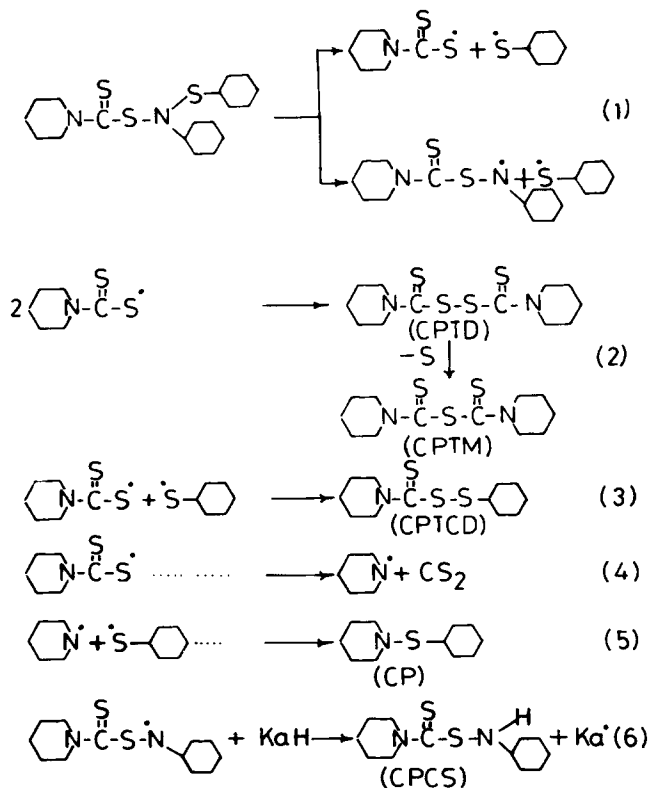
from thiocarbamyl sulfenamide forming CM or CP, as the case may be. The increase in scorch time of the stocks 5 and 6 compared to 2 and 4, respectively, may be explained as in the former case; some time is required to produce CP or CM whereas in the latter they are added extraneously.

The physical properties of the mixes in terms of modulus and tensile strength has been demonstrated through relevant data presented in Table III. It is seen that the modulus and tensile values are not affected; rather an improvement is noticed when the sulfenamide has been modified by introducing thiocyclohexyl group at NH functionality [compare the data of mixes 2 and 4 with that of 5 and 6, respectively; Table III]. On the other hand, as observed by us,¹ CP or CM hampers the modulus and tensile values of the vulcanizates containing thiocarbamyl sulfenamide [compare the data of mixes 1 and 3 with that of 2 and 4 respectively, Table III].

It is apparent from the results and discussion that CPCTS or ODCTS play the dual role of a retarder and an accelerator in the vulcanization of NR.

CONCLUSION

It may be said that it is possible to combine retardation and accelerator activities in a suitable thiocarbamyl sulfenamide having NH functionalities at sulfenamide nitrogen atom by suitable chemical modification, and that both the activities can be retained with little mutual influence.



$\text{KaH} \equiv \text{RUBBER}$

Scheme 2. Formation of various products from CPCTS-NR reaction.

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References

1. R. N. Datta, P. K. Das, and D. K. Basu, *Rubber Chem. Technol.*, **59**, 525 (1986).
2. P. K. Das, R. N. Datta, and D. K. Basu, *Rubber Chem. Technol.*, to appear.
3. R. I. Leib, A. B. Sullivan, and C. D. Trivette, Jr., *Rubber Chem. Technol.*, **43**, 1188 (1970).
4. P. N. Son, *Rubber Chem. Technol.*, **46**, 999 (1973).
5. J. J. D'Amico, E. Morita, A. B. Sullivan, K. Boustany, K. T. Potts, J. Kane, and D. McKeough, *Rubber Chem. Technol.*, **46**, 1299 (1973).
6. G. E. P. Smith, G. Alliger, E. L. Carr, and K. C. Young, *J. Org. Chem.*, **14**, 935 (1949).
7. R. N. Datta, M. M. Das, D. K. Basu, and A. K. Chaudhuri, *Rubber Chem. Technol.*, **57**, 879 (1984).
8. E. L. Carr, G. E. P. Smith, Jr., and G. Alliger, *J. Org. Chem.*, **14**, 921 (1949).
9. R. Henry and W. M. Dehn, *J. Am. Chem. Soc.*, **72**, 2806 (1950).
10. R. N. Datta and D. K. Basu, *Rubber Chem. Technol.*, **58**, 27 (1986).
11. R. N. Datta, P. K. Das, and D. K. Basu, *J. Appl. Polym. Sci.*, **32**, 5849 (1986).
12. W. Scheele, *Rubber Chem. Technol.*, **34**, 1306 (1961).

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