

Elucidation of the Vulcanization Structures of Filled *cis*-1,4-Polybutadiene Rubber by Solid State Carbon-13 NMR Spectroscopy

Su-Dong Kim, Eun-Kyung Park*, and Juwhan Ryu[†]

Dept. of Polymer Science and Engineering, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon, Korea 305-764

*Small and Medium Business Administration, (Dunsan-dong) 1 dong, 139 Seonsaro, Seo-gu, Daejeon, Korea 302-701

(Received November 13, 2008, Revised & Accepted November 24, 2008)

고체상태 NMR을 이용한 *cis*-1,4-polybutadiene 충전고무의 가황가교 구조 규명

김수동·박은경*·류주환[†]

충남대학교 공과대학 바이오응용화학부, *중소기업청
(2008년 11월 13일 접수, 2008년 11월 24일 수정 및 채택)

ABSTRACT : Using solid state ¹³C NMR, polybutadiene rubber vulcanizates were qualitatively and quantitatively analyzed. In the filled conventional system of BR vulcanizate accelerated with TBBS, addition to the olefinic double bond and substitution in the α position to the double bond occurred simultaneously. Also the latter α substitution reaction was faster than the former addition reaction at initial reaction time. In addition, it was suggested that double bond-addition-polysulfide structures might be modified into 5-membered and 6-membered cyclic structures in overcure time. These chain modifications were correlated with the decrease in the chemical crosslink density in overcure time.

요약 : 고체상태 ¹³C NMR을 이용하여 폴리부타디엔 고무(BR) 가황체의 정성 및 정량분석을 행하였다. TBBS로 촉진된 기존의 충전 BR 가황체에서는 올레핀성 이중결합에의 부가반응과 이중결합 옆의 α 위치에서의 치환반응이 동시에 일어났다. 또한 반응 초기에는 이중결합 옆의 α 위치에서의 치환반응은 이중결합에의 부가반응보다 빠르게 진행되었다. 한편 과가류(overcure) 시간 동안 이중결합-부가 폴리설파이드 구조는 5각형 및 6각형 고리 구조로 변형되는 것으로 추정되었다. 이러한 사슬 변형은 과가류 시간에 발생하는 화학적 가교 밀도와 상관되었다.

Keywords : Solid state NMR, BR, vulcanization, TBBS acceleration

I. Introduction

Ever since the discovery of the vulcanization of rubber by Charles Goodyear in 1839, rubbers have been one of the important industrial polymeric

materials. The development and research of the advanced rubber materials is of ongoing interest and examples include nanocomposites, blends, application of new types of fillers, high-performance elastomers for a wide range of temperatures, recycling, and biotechnology.¹⁻⁸

Due to the intrinsic complexity of the structures

[†] 대표저자(e-mail : juwhan@cnu.ac.kr)

of vulcanized rubbers, a variety of techniques have been developed for their characterization. Among others, solid state NMR spectroscopy is one of the most powerful techniques, especially for the investigation of chemical microstructures on the molecular level. To enhance the properties of rubbers, it is essential that the degree of crosslink density and microstructure should be characterized. Recent methodology of solid state NMR is capable of providing information on the microstructure and the crosslink density of rubber vulcanizate.

The physical properties of butadiene rubber(BR) depend on their vulcanization structure. Therefore to enhance their properties, the qualitative and quantitative analyses of the vulcanization structures are necessary.

Solid state studies for the rubber vulcanization have traditionally relied on the characterization of the average mechanical properties of cured vulcanizates.⁹⁻¹¹ In this case, theoretical crosslinked network models must be considered to interpret the molecular basis of the performance properties assessed by such average mechanical properties. Unfortunately, the interpretive accuracy of such models depends circularly on the specific topological assumptions they make about the networks to be characterized.¹²

In contrast, solid state NMR inherently provides the potential to identify and quantify molecular network species in rubber vulcanizates as functions of formulating and processing variables. During recent several decades, the methods of solid state NMR have been advanced and used successfully in rubber studies.¹³⁻²² Now, the methods of solid state NMR are accepted as a powerful technique in rubber researches and developments.

Sulfur vulcanization of BR has been known for years,²³ but the exact mechanism viz. by either addition at or substitution α to the olefinic double bonds remained one of the major topics of interest in rubber chemistry.²⁴ However, Seyger et al. showed that vulcanization accelerated with *N*-cyclohexyl-2-benzothiazole sulfenamide(CBS) was mainly addition to double bond and that of BR accelerated with tet-

ramethyl thiuram disulfide(TMTD) was mainly substitution α to the olefinic double bonds by using model compounds and solid state NMR analyses.²⁵⁻²⁷

In this study, we examined the vulcanization structure of the filled high *cis*-polybutadiene rubber accelerated with *N*-t-butylbenzothiazole-2-sulfenamide(TBBS) as a function of vulcanization time using solid state NMR spectroscopy.

II . Experimental

High *cis*-BR was obtained from Kumho Petrochemical Co., Ltd. (97.3 % *cis*, 1.8 % *trans*, 0.6 % vinyl content, $M_n = 130,000$ and $M_w = 550,000$).

The recipes of the compounds used are given in Table 1. All samples were prepared in the form of cylindrical disks. They were cut from 1.5 mm thick sheets that had been cured in a hydraulic press under a nominal pressure of 14 MPa at 150 °C for various periods of time. Using rheometer, t_{10} , t_{50} , t_{90} , and overcure (60 min) were given as the cure times. After the vulcanization, unreacted compounds were extracted with cyclohexane using a soxhlet extractor for 12 hr. Residual imbibed cyclohexane was removed in a vacuum oven.

NMR experiments were performed using a Bruker DSX 400 spectrometer operating at 100.61 MHz for ¹³C. The ¹³C NMR spectra of dry vulcanizates were obtained for samples prepared by molding carefully with a recycle time of 4 s and a spin rate of 4 KHz. The pulse sequence of gated high power decoupling(GHPD) was used for the acquisition(Figure 1). Usually the accumulation of ~10,000 transients resulted in ¹³C NMR spectra with reasonable signal-to-noise ratios. To obtain good resolution of ¹³C NMR

Table 1. The Recipe for BR Vulcanizates.

	Composition (phr)
BR	100
HAF	60
ZnO	3
Stearic Acid	2
Sulfur	2.38
TBBS	0.75

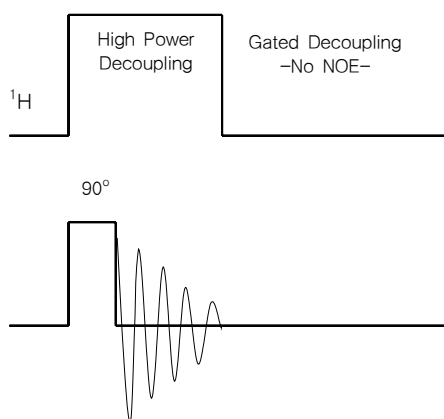


Figure 1. The GHPD pulse sequence for ^{13}C NMR high resolution spectroscopy.

spectra, the temperature was increased to 80 °C. To observe the variation of each peak, the quantification analysis of the peaks was performed using curve fitting method.

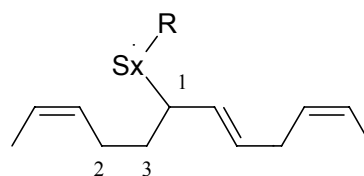
III. Results and Discussion

1. The Peak Assignments of NMR Spectra of BR Vulcanizates

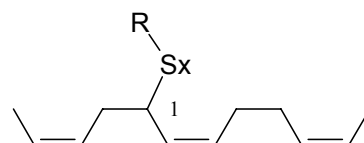
The peak assignments of NMR spectra are very important to the study of BR vulcanizates. The microstructure study of the BR vulcanizates with various variances can only be performed based on the correct peak assignments. Usually vulcanizate structures are predicted using model compounds. The microstructures of BR are assigned by using the calculated chemical shifts of model compounds. As auxiliary methods to confirm the peaks assignments, DEPT, H-H COSY, C-H COSY, and NOESY etc., have been used.²⁵⁻²⁷

The microstructures of the BR vulcanizate with accelerators of sulfenamide species and activator have been suggested as follows.^{12,27}

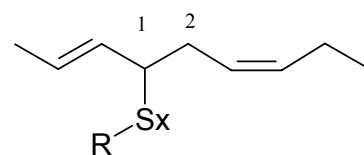
Seyger et al. showed that the vulcanization mechanism of BR accelerated with sulfenamide species mainly was addition to double bond resulting in the double bond addition (structure I, D-A). Also they suggested that the sulfurs added in double bond may



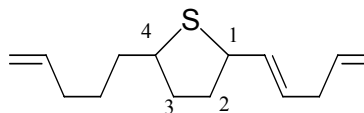
(I) D-A (Double bond addition)



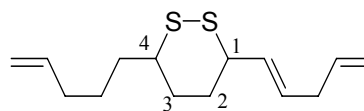
(II) C-S (Cis-alpha substitution)



(III) T-S (Trans-alpha substitution)



(IV) 5-M (5-membered rearrangement)



(V) 6-M (6-membered rearrangement)

undergo rearrangement to form 5-membered cyclic structure (structure IV, 5-M) and 6-membered cyclic structure (structure V, 6-M).²⁷

Because our experimental system is conventional system (Conv), substitution α to the olefinic double bonds cannot be excluded, which is usually accompanied by the double bond addition in unaccelerated BR vulcanizate. Koenig et al. expected cis-alpha substitution (structure II, C-S) and trans-alpha substitution (structure III, T-S) and have shown the existence of these structures in their study.¹²

^{13}C NMR spectrum of BR accelerated with TBBS

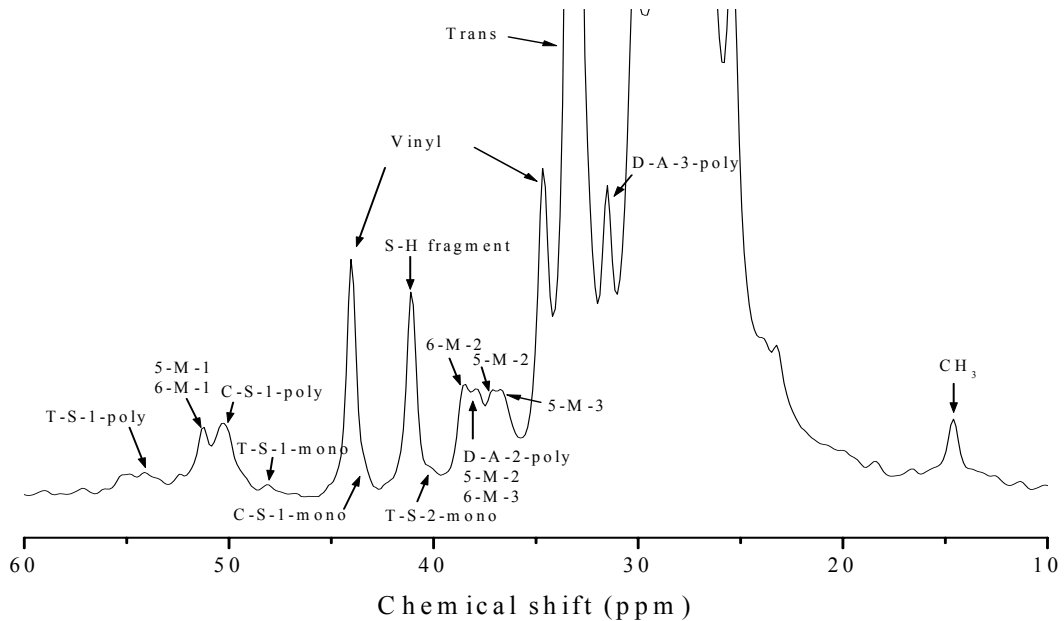


Figure 2. The ^{13}C NMR spectrum of overcured (60 min) BR accelerated with TBBS.

is shown in Figure 2. Although all the aliphatic carbon peaks of the expected structures do not appear in Figure 2 due to the intrinsic resolution limit of solid state NMR, the microstructures of the BR vulcanizate can be confirmed through comparing some peaks of the spectrum with previously published chemical shifts.

Table 2. The Peak Assignments of ^{13}C NMR Spectrum.

	Number	Chemical shift (ppm)
D-A-poly (Double bond addition)	2	37.8
	3	31.5
C-S (Cis-alpha substitution)	1-Mono	43.3
	1-Di/Poly	50.1
T-S (Trans-alpha substitution)	2-Mono	40.2
	1-Di/Poly	54.1
5-M (5-membered-rearrangement)	1	51.2
	2	36.9
	3	36.6
6-M (6-membered-rearrangement)	1	51.2
	2	38.4
	3	37.8

The chemical shifts of each structure were determined and the result is summarized in Table 2. The crosslinking structure originated from the double bond addition (D-A-poly) can be confirmed at δ 31.5 and δ 37.8 ppm. Cyclic compounds (5-M and 6-M) can be confirmed at δ 36.6, δ 36.9, δ 38.4, and δ 51.2 ppm. C-S-mono, C-S-di/poly, T-S-mono, and T-S-di/poly can also be confirmed at δ 43.3, δ 50.1, δ 40.2, and δ 54.1 ppm, respectively.

2. Quantitative Analysis as a Function of Cure Time

The ^{13}C NMR spectra of the BR vulcanizates are shown in Figure 3. It is well known that the crosslink density greatly influences the physical properties of rubbers.⁹ Thus, the measurement of the crosslink density is essential for the study of the physical properties of rubbers. Generally, there are two methods to measure the crosslink density. One is the equilibrium-swelling method using thermodynamic statistical crosslinking theory. This can directly cor-

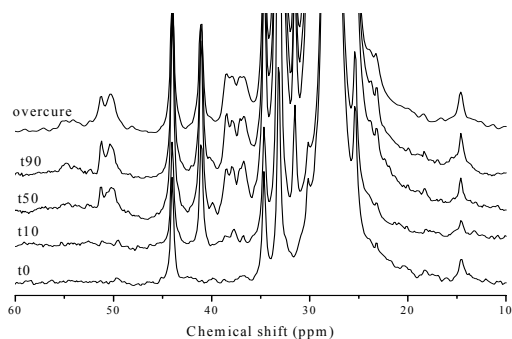


Figure 3. The ^{13}C NMR spectra of BR vulcanizates accelerated with TBBS for the indicated times.

relate the physical properties of rubbers. Therefore the crosslink density measured by the equilibrium-swelling method is called physical crosslink density. The other is the measurement of chemical crosslink density using solid state NMR. The microstructures of rubber can be qualitatively and quantitatively analyzed and the crosslink density can be calculated by measuring the density of microstructures. However, the sulfide structures cannot be discerned whether they are crosslink structures or dangling structures, and whether they are disulfides or polysulfides due to the low resolution of solid state NMR.

In the case of NMR, the chemical crosslink den-

sities are calculated by the following equations.²⁸

$$2[S]_X = \frac{I(S_X)}{I_0} \frac{\rho_r}{M_0} \quad (1)$$

$$2[S]_{total} = \sum 2[S]_X \quad (2)$$

where

$2[S]_X$: microstructure density of each structure (mol/cm^3)

$2[S]_{total}$: total crosslink density (mol/cm^3)

$I(S_X)$: peak integral of each crosslink structure

I_0 : average intensity of the backbone carbon

ρ_r : density of BR (g/cm^3)

M_0 : molar mass of the butadiene unit (g/mol)

With the BR vulcanizates of t_{10} , t_{50} , t_{90} , and overcure, we performed the quantitative analysis for the assigned peaks and calculated microstructure density and chemical crosslink densities using equations (1) and (2). Also we measured the physical crosslink densities using the previously reported equilibrium-swelling method.¹² The results are summarized in Table 3.

Except the overcure state, it is observed that the microstructure densities of all species increased in our experimental system. There is a study that the percent concentrations of the crosslinked species can

Table 3. The Curve Fitting Results for the Microstructures of the BR Vulcanizates as a Function of Cure Time.

	Unit: ($10^{-4}\text{mol}/\text{cm}^3$)							
	t_{10}		t_{50}		t_{90}		overcure	
	% area	Microstructure density	% area	Microstructure density	% area	Microstructure density	% Area	Microstructure density
D-A-poly (31.5 ppm)	7.3	0.33	26.7	2.24	25.2	3.18	16	2.07
T-S-mono (40.2 ppm)	13	0.59	6.8	0.60	12	1.51	18.3	2.37
C-S-mono (43.3 ppm)	25.7	1.18	21.8	1.84	24.2	3.05	20.7	2.67
C-S-poly (50.1 ppm)	14.8	0.68	11.5	0.96	10.5	1.32	9.7	1.25
T-S-poly (54.1 ppm)	10.9	0.5	7.5	0.63	8.1	1.02	10.8	1.39
5-M, 6-M (51.2 ppm)	6	0.2	6.5	0.41	4.4	0.44	7.6	0.74
S-H (41.2 ppm)	22.4	0.73	19.3	1.2	15.6	1.58	16.8	1.64
Chemical Corsslink density	3.28		6.27		10.1		9.75	
Physical Crosslink density	0.21		0.93		1.09		1.11	

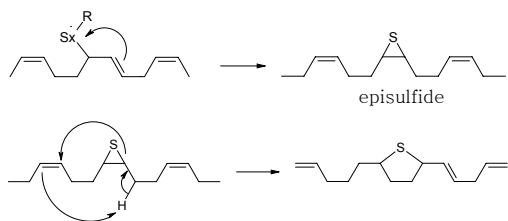


Figure 4. The rearrangement mechanism after the double bond addition reaction for cyclic sulfide formation.

provide a rough indication for the structural changes.¹²

In the initial cure time of t_{10} , it is observed that the amount of crosslink species resulting from the α substitution is larger than that from the addition. Thus it was considered that the α substitution reaction is faster than the addition reaction in t_{10} . Also it is observed that the D-A-poly structure decreases and 5-M and 6-M cyclic structures increase in overcure time. These results suggest that the D-A-poly structures may be first converted into episulfide species and then modified next into 5-M and 6-M cyclic structures in overcure time due to the cyclic rearrangement reactions after the addition reaction as shown in Figure 4.

Comparing the chemical densities and the physical densities, it is shown that the chemical densities are greater than the physical densities even though we did not include the cyclic structures in the calculation of the chemical crosslink densities. Sulfur-vulcanized BR networks must possess a significant proportion of mechanically ineffective dangling mono/poly crosslink structures. Because the sulfide structures cannot be discerned whether they are crosslink structures or dangling structures in the solid state NMR analysis of the rubber vulcanizates, it is considered that the dangling structures contributed more to result in the larger chemical crosslink densities than the physical crosslink densities.

IV. Conclusions

Solid state NMR spectroscopy has been used to obtain valuable information on microstructures of

BR. It has been applied to many studies on rubber vulcanizates. In this study, we analyzed the filled conventional system of BR vulcanizates accelerated with TBBS. It was confirmed that the addition reaction at the olefinic double bond and the substitution reaction at the α position to the double bond occurred simultaneously. The α substitution reaction was faster than the addition reaction to double bond in initial reaction time. Also it was suggested that the D-A-poly structures might be modified into the 5-M and 6-M cyclic structures in overcure time.

References

1. T. Toshihiro, "Recent trends of polybutadiene and polyisoprene", *J. Soc. Rubber Ind., Japan*, **78**(2), 42-45 (2005)
2. S. Ostad-Movahed, A. Ansarifar, and M. Song, "Using modulated-temperature differential scanning calorimetry to study interphases in blends of styrene-butadiene and polybutadiene rubbers filled with a silanized silica nanofiller", *J. Appl. Polym. Sci.*, **111**(3), 1644-1652 (2009).
3. A. Thitithammawong, C. Nakason, K. Sahakaro, and J. W. M. Noordermeer, "Multifunctional peroxide as alternative crosslink agents for dynamically vulcanized epoxidized natural rubber/polypropylene blends", *J. Appl. Polym. Sci.*, **111**(2), 819-825 (2009).
4. P. Prasopnatra, P. Saeoui, and C. Sirisinha, "Rheological properties of recycled chlorinated polyethylene/natural rubber blends vulcanized by sulfur", *J. Appl. Polym. Sci.*, **111**(2), 1051-1056 (2009).
5. T. Kuila, S. K. Srivastava, and A. K. Bhowmick, "Rubber/LDH nanocomposites by solution blending", *J. Appl. Polym. Sci.*, **111**(2), 635-641 (2009).
6. J. B. van Beilen and Y. Poirier, "Establishment of new crops for the production of natural rubber", *Trends Biotechnol.*, **25**(11), 522-529 (2007).
7. R. Bhatt, D. Shah, K. C. Patel, and U. Tivedi, "PHA-rubber blends: synthesis, characterization and biodegradation", *Bioresour. Technol.*, **99**(11), 4615-4620 (2008)
8. J. T. Sakdapipanich, "Structural characterization of natural rubber based on recent evidence from

- selective enzymatic treatments”, *J. Biosci. Bioeng.*, **103**(4), 287-292 (2007)
9. N. J. Morrison and M. Porter, “Temperature effects on the stability of intermediates and crosslinks in sulfur vulcanization”, *Rubber Chem. Technol.*, **57**(1), 63-85 (1984).
 10. B. Saville and A. A. Watson, “Structural characterization of sulphur-vulcanized rubber networks”, *Rubber Chem. Technol.*, **40**(1), 100-148 (1967).
 11. M. Nasir and G. K. Teh, “The effects of various types of crosslinks on the physical properties of natural rubber”, *Eur. Polym. J.*, **24**(8), 733-736 (1988).
 12. S. R. Smith and J. L. Koenig, “Solid-state carbon-13 NMR studies of vulcanized elastomers. IX. TMTD-vulcanized *cis*-1,4-polybutadiene at 75.5 MHz”, *Rubber Chem. Technol.*, **65**(1), 176-200 (1992).
 13. A. Yoshika, K. Komuro, A. Ueda, H. Watanabe, S. Akita, T. Masuda, and A. Nakajima, “Structure and physical properties of high-vinyl polybutadiene rubbers and their blends”, *Pure & Appl. Chem.*, **58**(12), 1697-1706 (1986).
 14. A. M. Zaper and K. L. Koenig, “Solid-state ¹³C NMR studied of vulcanized elastomers, 4. Sulfur-vulcanized polybutadiene”, *Die Makromol. Chemie*, **189**(6), 1239-1251 (1988).
 15. J. L. Koenig, “Spectroscopic characterization of the molecular structure of elastomeric networks”, *Rubber Chem. Technol.*, **73**(3), 385-404 (2000).
 16. H. Menge, S. Hotopf, and H. Schneider, “Partially deuterated poly(butadiene) Part II. Deuteron NMR investigation of strain-induced segment anisotropy”, *Polymer*, **41**(11), 4189-4201 (2000).
 17. J. Sakadapipanich, T. Kowitkeerawut, K. Seiichi, and Y. Tanaka, “Structural characterization of highly *cis*-1,4-polybutadiene: A comparing study in swollen and solid state using NMR technique”, *Polym. Bulletin*, **46**(6), 479-485 (2001).
 18. V. M. Litvinov, M. van Duin, and Geleen, “Real-time ¹H NMR relaxation study of EPDM vulcanization”, *KGK Kautschuk Gummi Kunststoffe*, **55**(9), 460 (2002).
 19. R. Winsters, W. Heinen, M. A. L. Verbruggen, J. Lugtenburg, M. Van Duin, and H. J. M. De Groot, “Solid-state ¹³C NMR study of accelerated-sulfur-vulcanized ¹³C-labeled ENB-EPDM”, *Macromolecule*, **35**(5), 1958-1966 (2002).
 20. S. Kariyo and S. Stapf, “NMR relaxation dispersion of vulcanized natural rubber”, *Sol. St. Nucl. Magn. Reson.*, **25**(1-3), 64-71 (2004).
 21. J. Ukawa, S. Kawahara, and J. Sakai, “Structural characterization of vulcanized natural rubber by latex state ¹³C NMR spectroscopy”, *J. Polym. Sci. Part B: Polym. Phys.*, **45**(9), 1003-1009 (2007).
 22. J. Rault, J. Marchal, P. Judeinstein, and P. A. Albouy, “Chain orientation in natural rubber, Part II: 2H-NMR study”, *Eur. Phys. J. E, Soft Matter*, **21**(3), 243-261 (2007).
 23. L. Bateman, ed., “*The Chemistry and Physics of Rubber-like Substances*”, Maclaren, London, 1963.
 24. Skinner, T. D., “The CBS-accelerated sulfuration of natural rubber and *cis*-1,4-polybutadiene”, *Rubber Chem. Technol.*, 1971, **45**(1), 182-192.
 25. R. M. Seyger, R. Hulst, and A. Bantjes, “Vulcanization of Butadiene Rubber by Means of Cyclic Disulfides. 1. A 2D NMR Study on the Cross-Link Structure of a BR Model Compound Vulcanizate”, *Macromolecule*, 1999, **32**(22), 7504-7508.
 26. R. Hulst, R. M. Seyger, J. P. M. van Duynhoven, L. van der Does, J. W. M. Noordermeer, and A. Bantjes, “Vulcanization of butadiene rubber by means of cyclic disulfides. 2. A 2D solid state HRMAS NMR study on cross-link structures in BR vulcanizates”, *Macromolecule*, **32**(22), 7509-7520 (1999).
 27. R. Hulst, R. M. Seyger, and A. Bantjes, A., “Vulcanization of butadiene rubber by means of cyclic disulfides. 3. A 2D solid state HRMAS NMR study on accelerated sulfur vulcanizates of BR rubber”, *Macromolecule*, 1999, **32**(22), 7521-7529.
 28. M. Mori and J. L. Koenig, “Solid-state ¹³C-NMR and equilibrium-swelling studies of filled, TBBS-accelerated sulfur vulcanization of natural rubber”, *J. Appl. poly. Sci.*, 1998, **70**(7), 1391-1399.